Surface-engineered low-enriched Uranium-Molybdenum fuel for research reactors.

In- and out-of-pile studies for the conversion of research reactors from using high-enriched to low-enriched nuclear fuels.

by
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Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning.

Albert Einstein
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# Chapter 1 Introduction

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1 Research Reactors and their fuels

Research reactors (RR) comprise a wide range of civil and commercial nuclear reactors which are generally not used for power generation. The primary purpose of a RR is to provide a neutron source not only for research but also for the production of radioisotopes, and other radiation services. They are small relative to power reactors whose primary function is to produce heat to make electricity. Typically, a RR produces power in the range between 10 MW\(_{th}\) and 100 MW\(_{th}\) while up to 3000 MW\(_{th}\) (or 1000MW\(_e\)) is generally produced in a nuclear power plant.

Research reactors are simpler than power reactors and operate at lower temperatures. They need far less fuel, and far less fission products build up as the fuel is used. Compared to the tons of fuel enriched to 3 to 5 % \(^{235}\text{U}\) used in a power reactor, only a few kg of uranium is needed in a RR but in order to obtain a high neutron flux the fuel for the latter one is higher enriched (up to 93 % \(^{235}\text{U}\)) and is replaced more often. RR also have a very high power density in the core, which requires special design features. Like power reactors, the core needs cooling, though only the higher-powered test reactors need forced cooling. Usually a moderator is required to slow down the neutrons and enhance fission. As neutron production is their main function, most research reactors also need a reflector to reduce neutron loss from the core.

1.1 History [1]

![Figure 1 The world’s first nuclear reactor: Chicago Pile no 1 (CP-1)](image)

The Chicago Pile-1 (Figure 1), built at the university of Chicago was the world’s first nuclear research reactor. CP-1 was built as part of the Manhattan project, a US initiated research and development program to produce the first atomic bomb. The reactor, assembled under the supervisions of Enrico Fermi and Leó Szilárd, consisted of uranium pellets (neutron
source) and graphite blocks (moderator), while cadmium-coated rods controlled the neutron activity in the pile. It should be noted that CP-1 had no radiation shielding or cooling system of any kind. CP-1 became critical for the first time in 1942.

One year later, in 1943, the X-10 Graphite Reactor at Oak Ridge National Laboratory in Oak Ridge, Tennessee went into operation. The X-10 pile was the first reactor designed and built for continuous operation. The reactor was mainly used to produce larger quantities (grams) of plutonium by irradiating uranium. The X-10 reactor consisted of a huge block of graphite pierced by channels in which rows of cylindrical uranium slugs formed long rods. Cooling air circulated through the channels on all sides of the slugs. After the Second World War ended, the X-10 graphite reactor became the first facility in the world to produce radioactive isotopes for peacetime use. The X-10 Graphite Reactor was shut down in 1963 after twenty years of use, but a similar design to the X-10 reactor is still in operation today, namely the Belgian BR1 reactor in Mol, Belgium.

Prior to the termination of World War II, work was initiated at Oak Ridge National Laboratory to develop and produce a cheap, reliable, thin-plate fuel component for service in a high neutron flux reactor. This effort culminated in the successful startup, and sustained operation thereafter, of the Materials Testing Reactor (MTR) at a 30-megawatt power level on March 31, 1952. This date was a milestone in reactor development for it not only clearly demonstrated the feasibility of constructing a high-flux research reactor, but also proved that the basic principles employed in the design and manufacture of aluminum plate-type fuel elements were sound [2]. The fuel elements are made of an assembly of plates. Each plate contains fuel in the form of an enriched uranium-aluminum alloy that is clad on all sides with aluminum. These composite plates are spaced apart to allow water to flow freely between them, the water serving as both coolant and moderator. The MTR at the National Reactor Testing Station near Idaho Falls, Idaho, was the first reactor to employ aluminum plate-type fuel elements [3].

In 1947, Canada developed the powerful 20-megawatt National Research Experimental (NRX) nuclear research reactor at the Chalk River facility. It was designed mostly for science and innovation. Starting the early 1950’s, NRX was used to produce isotopes and at several beam ports, experiments could be conducted. Currently Canada with its NRU research reactor built in 1957 to replace NRX, is the world’s largest producer of radioisotopes.

Since 1943, over 670 research and test reactors have been built worldwide, most of them in the USA (227) and in the former Soviet Union (97). Today (d.d. 2012), Russia has the most research reactors (62), followed by USA (54), Japan (18), France (15), Germany (14) and China (13). Even small and developing countries have research reactors. About 20 more reactors are planned or are under construction, and 361 have been shut down or decommissioned [4].

Although a large variety of designs exist, most research reactors have a pool type design where the core, consisting of the fuel assemblies, control rods and empty channels for
experiments, is sitting in a pool of water. Water in this case is the coolant as well as the moderator while graphite or Beryllium acts as neutron reflectors. Cooling may be by natural convection of the pool water, although this is augmented for operation at higher power by pumping pool water through the core. Tank type reactors are of similar design but with the core contained in an aluminum tank. The cooling water is pumped through the core, but the pressure within the tank is only moderately elevated. Another widespread design is the TRIGA reactor, which uses aluminum cladded uranium zirconium hydride (UZrH) based fuel elements stored in a pool of water and usually graphite or beryllium is used as reflector.

1.2 Research reactors in Belgium

The BR1 (Figure 2) was the first Belgian reactor and became critical for the first time in May 1956. It is an air-cooled reactor with graphite as moderator and a thermal power of 4 MW. The design of BR1 is comparable to the X-10 pile built in the 1940’s in Oak Ridge. Until after the start-up of BR2 in 1963, BR1 was also used for the production of radioisotopes for medical applications. The reactor worked continuously, 24 hours a day, 7 days a week.

The reactor now only works on request of the experimenters, for at most 8 hours a day, at a maximum power of 700 kW. Even after 50 years of continuous service, the reactor still is not retired and continues to operate on its original fuel. Thanks to its flexibility, low exploitation and maintenance cost and easy access to the experimental channels, BR1 is a very useful instrument for industry, research centres and universities. The radiation channels of the reactor are often used for different purposes:

- Neutron Activation Analysis; a very accurate and precise analytical method for the determination of the composition of all kinds of materials, even at trace levels;
- Activation of trace elements for the detection of leaks in pipelines of different chemical processes, the analysis of the chemical persistence and for flow measuring;
- Irradiation of electronic components that are used in space and nuclear industry;
- Calibration of neutron and gamma-ray detectors in the neutron or gamma-ray reference fields present in the large cavity in the vertical thermal column.

The neutron field of BR1 is very well characterized and thermalized. These properties make BR1 a very useful tool to produce high resistivity (>400 Ωcm) Neutron Transmutation Doped (NTD) – Si [5].

The BR2 reactor (Figure 3) became operational in January 1963. With its 100 MWth high-neutron flux (n/s.cm²) it is one of the most powerful research reactors in the world.

The central part of the BR2 consists of a beryllium matrix composed of 79 hexagonal channels containing the nuclear fuel elements, the control rods and various experiments and plugs. In the center, the core has a vertical 200 mm diameter channel, with all the other channels inclined to form a hyperboloid arrangement around it. This hyperboloid of revolution combines compactness with easy access at the top and bottom covers, allowing complex irradiation devices to be inserted and withdrawn.

![Figure 3 Cross section (left) and top cover (right) view of the BR2 reactor.](image)

The reactor can be operated at the power level of 50 to 100 MW, currently about 120 full power days per year. The maximum neutron flux is $1.2 \times 10^{15}$ cm$^{-2}$s$^{-1}$ ($E_n<0.5$ eV) and $8.4 \times 10^{14}$ cm$^{-2}$s$^{-1}$ ($E_n>1.0$ MeV) [6].

The reactor BR2 has more than 100 irradiation positions, including a large number of 84 mm test holes/channels in the Be-matrix – traps for fast neutron fluxes in the axis of fuel elements, 4 peripheral 200 mm channels for large irradiation devices and a 200 mm central trap for high thermal neutron flux [6].

The BR2 reactor is a reactor with multiple applications:
- Material research : prediction of safe lifetime of structural reactor materials for fusion and fission
- Nuclear fuel research : testing of nuclear fuels for various reactor types
• Production of doped silicon: irradiation of NTD-silicon for the semiconductor industry
• Production of radioisotopes: BR2 produces about 16% of the world’s annual Mo-99/Tc-99m for medical use. More than 50 radioisotopes are produced for medical and industrial applications.

1.3 Fuel for research reactors [7,8,9]

In the 1950’s and early 1960’s, only Low-Enriched-Uranium (LEU, <20% ²³⁵U) was exported by the U.S. for use in research reactors. However, gradually more research reactors faced more demanding experiments (materials testing, isotope production), increasing the need for high neutron fluxes or power density. Fuel elements with higher ²³⁵U loadings became necessary to meet these requirements. Higher loadings can either be achieved by development of fuels and core designs with higher uranium density or by increasing the uranium enrichment. Of these two choices the latter one prevailed and by the 1960’s Highly-Enriched-Uranium (HEU, ~93% ²³⁵U enriched) became readily available and was widely used in research reactors, including those reactors where LEU would have sufficed.

Many research reactors around the world use MTR type fuel elements, which are formed by assembling a number of fuel plates. Initially, the core of a fuel plate was a uranium-aluminum alloy (U-Al) containing 18 wt% of highly enriched uranium (HEU) (>90 wt% ²³⁵U) in Al. In the 70’s, with the concern about nuclear weapons non-proliferation, the research reactors began to use fuels containing low-enriched uranium (LEU) (<20 wt% ²³⁵U). However, in order to maintain the reactivity and lifetime of the converted reactor cores, it was necessary to increase the amount of uranium in each fuel plate. This meant that for the U-Al alloy, the uranium concentration had to be increased to 45 wt% to compensate the decrease in enrichment. Fuel plates containing U-Al alloy up to 30 wt% of uranium were easily fabricated but difficulties arose in the fabrication of fuel plates with a U-Al alloy containing 45 wt% of uranium, because of the fragility and tendency for segregation of this alloy. An alternative to overcome this problem was the use of dispersion fuels. In that case the core of the fuel plate is a dispersion of uranium compounds in aluminum and as such could incorporate larger quantities of low-enriched uranium [10].

Dispersion fuels in general, consist of fuel-bearing particles dispersed in a metallic, ceramic or graphite medium. The basic idea of a dispersion fuel is to isolate the fuel particles so that a substantial volume of the matrix remains undamaged by the fission products that are ejected out of the fuel kernel. Fission products have a large kinetic energy creating defects in the matrix and as such could compromise the mechanical stability of the fuel plate. Therefore, in dispersion fuels, the fuel particles are contained and/or restrained, allowing much higher burn-ups than would be possible in bulk fuel; the fission products are contained and good heat transfer paths to the cladding are maintained.

Uranium aluminide-aluminum (UAlₓ/Al) dispersion fuels were being used in many moderate- and high-power reactors around the world. These fuels were initially developed for the
Advanced Test Reactor (ATR) in 1962, and were subsequently used in the Materials Test Reactor (MTR) and Experimental Test Reactor (ETR) in the U.S. and in many European reactors including the Belgian Reactor-2 (BR-2) and the High Flux Reactor (HFR Grenoble). The uranium aluminide is fabricated from a melting and casting operation and as a result usually contained a mixture of UAl₄, UAl₃ and UAl₂ (a typical composition is around 63% UAl₃, 31% UAl₄ and 6% UAl₂). Such a composition is referred to as UAlₓ. To produce a fuel plate, the UAlₓ fuel is ground and dispersed in a pure Al powder matrix. This mixture, commonly referred to as meat and forming the core of the fuel plate, is compacted and assembled in a frame that is placed between two cladding plates. The final dimensions of the fuel plate are obtained by hot and cold rolling (a more detailed description of the fuel plate fabrication can be found in the next chapter).

At the time of the development of dispersion fuels (1960's), HEU (93 wt% ²³⁵U) was still available and especially the high power research reactors continued to make use of it. The highest loadings, i.e. the amount of U per cm³ meat, are used in the BR2 (~1.3 g U/cm³) and ATR (~1.6 g U/cm³).

## 2 The RERTR program

We are, we are, we are, we are the RERTR
We can convert Reactors, be they near, or be they far
From HEU to LEU, or enrichments from the Czar
We are, we are, we are, we are the RERTR

(From the RERTR song by “D&P” 1996)

Around 1977, with approximately half of the research reactors using HEU, concerns were raised about their nuclear proliferation potential. It was considered that (unirradiated) HEU could be diverted the fuel plate production facility, during transport or from storage and be used for non-peaceful purposes. These concerns have led to the launch in 1978 of the Reduced Enrichment Research and Test Reactor program (RERTR).

The RERTR program has as a mission “To minimize and, to the extent possible, eliminate the use of HEU in civil nuclear applications by working to convert research reactors and radioisotope production processes to the use of LEU fuel and targets throughout the world.”

To convert existing RR’s to the use of low enriched fuel, the RERTR program had to take into account that this was only possible if the safety margins and reliability of the new fuel would not be lower than that of the existing design based on HEU and that major modifications of the reactor core were not tolerable. In addition, only limited loss of reactor performance (flux per unit power) and marginal increase of operational cost can be accepted.

A simple replacement of the HEU by LEU is thus not possible, as this would reduce core reactivity; decrease the ²³⁵U burn up capability and as such lead to an increased operational...
cost. To compensate the reduced enrichment by enlarging the core would result in a decrease in flux per unit power.

One of the options to replace HEU by LEU fuel was to increase the amount of fuel in a fuel element. This can be achieved either by increasing the volume occupied by the fuel or to increase the amount of fuel packed into the available volume. The first option might require redesigning of the fuel element as this option can only be realized by

- decreasing the thickness of the cladding and increasing the meat volume. However, the thickness of the cladding cannot be reduced below a certain limit as this is needed for containment of fission products and assure good heat conductivity.
- keeping the minimum clad thickness, increasing the meat volume and therefore decreasing the spacing in-between fuel plates. This would however cause insufficient cooling of the plates and possibly create a pressure drop across the core.
- increasing the thickness of the meat/cladding, keeping the spacing of the cooling channel but reducing the number of fuel plates: the reduction of the number of plates is limited by the minimum heat transfer surface needed.

Increasing the amount of uranium packed in an available volume (or increase the loading) has almost no influence on the thermal-hydraulic properties of the core and therefore does not require redesigning of the fuel element. However, the roll bonding technique limits the concentration of the dispersed phase to about 40 - 50 vol %. Too high loadings result in a loss in mechanical integrity of the fuel plate caused by problems such as dogboning (thickening of the fuel meat at the extremities of the plate), minimum clad thickness and/or stray fuel particles.

The implications of the goals set by the RERTR program for the fuel development were thus two-fold:

- increase the U loading in the used fuels to the highest technological possible level. For UAl\textsubscript{x}/Al this meant a limit of 2.3 gU/cm\textsuperscript{3}
- develop new fuels with high intrinsic U densities.

As far as the HEU-LEU conversion was concerned, all those RR’s that required uranium densities lower than the technological limit were converted. For the other research reactors, needing a higher uranium loading, the RERTR program and other foreign country programs aimed at the development and quantification of high density LEU fuels.

2.1 High density LEU fuels.

High density of uranium in dispersion fuel can only be attained by using a dispersant with a high intrinsic uranium density. Figure 4 shows the potential of various uranium compounds. In the 1980's the fuel development was mainly focused on the development of the uranium silicides, U\textsubscript{3}Si and U\textsubscript{3}Si\textsubscript{2} as prime candidates and U\textsubscript{6}Fe as attractive alternative [11].

The irradiation performance of fuel plates is determined by excessive plate swelling, usually induced by unstable behavior of the fuel (formation of interaction layers and/or huge fission gas bubbles). The excessive swelling could finally lead to plate failure.
First irradiation experiments on U$_6$Fe, U$_3$Si, U$_3$Si$_2$ and UAl$_3$ showed that only UAl$_3$ and U$_3$Si$_2$ remain stable up to high fission densities while for U$_6$Fe and U$_3$Si$^1$ break-away swelling of the plates was observed at medium and low fission densities [12].

![Graph](image.png)

Figure 4 U-density in the fuel meat as function of the volume fraction occupied by the dispersant. The theoretical densities of the phases and dispersion are used.

U$_3$Si$_2$ dispersion fuel was further evaluated and it was concluded that plate type fuels suitable and acceptable for use in research and test reactors could be fabricated with U$_3$Si$_2$/Al dispersion compacts with uranium loadings up to 4.8 g/cm$^3$. The development and qualification (NUREG-1313 [13]) by the U.S.Nuclear Regulatory Commission of U$_3$Si$_2$-Al dispersion fuel led to the conversion of nearly 90% of the RR’s by the end of the 1980’s. The design of new LEU reactors, even anno 2012 (RJH), are still largely based on this fuel.

Even though the European fuel plate manufacturer CERCA (Compagnie pour l’Étude et la Réalisation de Combustibles Atomiques, currently a full subsidiary of AREVA) announced in 1993 that it had developed an advanced fabrication process which allowed the loading of U$_3$Si$_2$-Al fuel to be increased to 6.0 g U/cm$^3$ [14] and for UN-Al up to 7 gU/cm$^3$ [15], efforts to search for a better replacement continued as there were still reactors that could not convert to U$_3$Si$_2$-based fuel without loss in performance. Those reactors are in Europe: BR2 (Belgium), RHF (France), FRM II (Germany), Orphee (France), the US high performance research reactors: MURR, HIFR, NBSR, ATR and MISTR and the Russian reactors : ARGUS, OR, IR-8, IRT-MEPHI, IRT-T and MIR. The French Jules Horowitz reactor (RJH) is currently under construction and was initially designed to run on high density fuel but this fuel development will not be finished in time so RJH will start up on U$_3$Si$_2$ fuel with a slightly enlarged core.

$^1$ Only low temperature (<200 °C) irradiation of U$_3$Si (plate type) will lead to breakaway swelling (fuel turns amorphous). In high temperature conditions (~400 °C) with larger constraint (pin type), as is in the NRU (Canada) and HANARO (Korea) reactors, U$_3$Si shows more stable behavior (fuel stays crystalline).
These high flux reactors cannot convert with the existing qualified, commercially available \( \text{U}_3\text{Si}_2 \) fuel with uranium loadings up to 4.8 g/cm\(^3\). Each fission of \(^{235}\text{U}\) produces 2-3 fast neutrons. Therefore if the power of the reactor is fixed, the number of fissions and the number of fast neutrons produced are known. Hence if the geometry of the reactor does not change when converting to LEU fuel, the fast flux will remain the same. Fast neutrons can be thermalized (essentially by water) or captured (essentially by \(^{238}\text{U}\)). Going from HEU to LEU will greatly increase the quantity of \(^{238}\text{U}\) in the core and hence the number of captures. On the other hand, the capture of fast neutrons in \(^{238}\text{U}\) produces Pu that later produces fission neutrons that will contribute to the thermal flux. Converting to LEU while keeping the core geometry and power the same, will result in a slight decrease of the thermal flux in various irradiation positions. The local geometry can however be optimized to minimize this decrease in thermal flux [16]. Furthermore, even with an equal initial quantity of \(^{235}\text{U}\), the initial reactivity with LEU fuel will be lower, dramatically reducing the cycle length. This is the main reason that makes the conversion from HEU to LEU difficult for many reactors. However by increasing the initial quantity of \(^{235}\text{U}\), the reactivity increases and hence a longer cycle is reached. For the ORPHEE reactor in France, it is calculated that conversion from HEU to silicide LEU with a loading of 4.8 g/cm\(^3\) decreases the cycle length from 100 to 53 days. A linear law exists between fuel density and cycle length meaning that to obtain an equal cycle length, a fuel density of at least 8.5 g/cm\(^3\) is required [16].

High power reactors therefore require high density fuels able to withstand high to very high heat flux (W/cm\(^2\)) or fission rate (f/s), high burn-up (fission density f/cm\(^3\)) and high to very high coolant flows. Since it was not practical to fabricate the current benchmark fuel type, \( \text{U}_3\text{Si}_2 \), on a commercial scale at densities above 6.0 g/cm\(^3\), a new fuel type was needed. Compounds with a sufficient uranium density such as \( \text{U}_6\text{Mn} \) and \( \text{U}_6\text{Fe} \) were tested and found to exhibit unsuitable material behavior during irradiation. The only remaining candidate fuels were pure uranium and uranium with small alloying additions (Mo, Zr, Ti, ..).

Pure uranium, in the \(\alpha\)-phase, has poor irradiation characteristics (see chapter 2), but alloys designed to keep uranium in the metastable \(\gamma\)-phase were judged to have promise as fuel material.

Molybdenum for instance, exhibits a high degree of solid solubility in \(\gamma\)-uranium. By quenching the U(Mo) alloy from the \(\gamma\)-phase, a metastable \(\gamma\)-state will be retained at room temperature. U(Mo) alloys were thus considered as one of the most promising uranium alloys to be used as dispersion fuel due to the good irradiation performance of its cubic \(\gamma\)-phase

### 2.2 Fuel development and qualification

One of the main prerequisites is that new fuels supplied for research reactor core conversion should be qualified. Fuel performance qualification is limited to tests performed to demonstrate that the new product, in the configuration to be used as a driver fuel in one or
more reactors, meets the specified requirements. The qualification irradiations for fuel developed and to be qualified for a certain generic class of reactors, should be conducted under the most stringent conditions (e.g. maximum heat flux) applicable to that class of reactors. Usually, the qualification test fuel assembly (FA) is prototypic of fuel assemblies used in at least one of the higher performance reactors of the same class. It may be irradiated in the reactor in which it is meant to be used, or better yet, in a test reactor capable of creating conditions exceeding those reachable by the target reactor. An essential requirement is that the FA and irradiation conditions be prototypic enough to convince the regulatory body in charge to issue a license for use of the fuel in the proposed reactor [17].

Several steps are recommended in the fuel qualification process:

- step 1: focus on research and development (testing activities leading to the selection of a preferred fuel type),
- step 2: focus on fuel performance qualification to demonstrate that the selected fuel meets specified performance requirements,
- step 3: focus on qualification of the fuel manufacturer [17].

This thesis will describe the first step in the qualification process: the research and the development of a U(Mo) based new dispersion fuel.

The development of U(Mo) fuels with very high densities was initiated more than ten years ago [18]. In 1997 two irradiation test vehicles were inserted into the Advanced Test Reactor (ATR) in Idaho. The two experiments, designated RERTR-1 and RERTR-2, were used as screening experiments to determine which of the LEU fuels could be deemed promising at the start of the advanced fuels effort and were worthy of more detailed study. The first two RERTR experiments were performed using microplates (76 mm x 22 mm x 1.3mm) and were designed to be low power (max heat flux at BOL$^2$ 50-70 W/cm$^2$) and low temperature (max BOL clad temperature 65-70 °C) irradiations, with an intermediate fuel loading (4 g U/cm$^3$). The main conclusion after post irradiation analysis of these first two tests was that uranium alloys with a molybdenum content between 6 and 10% by weight showed excellent irradiation behavior at low temperatures [19]. Following the examination of the RERTR-1 & 2 experiments, it was decided to perform a more aggressive irradiation. For the RERTR-3 experiment nanoplates (41 mm x 10 mm x 1.5 mm) were irradiated, testing the fuel types under conditions of highest fissile uranium densities (8.5 g/cm$^3$), highest power (max heat flux at BOL 400 W/cm$^2$) and highest fuel temperatures found in today’s highest power research reactors (max BOL clad temperature 150 °C) [20]. Post irradiation examination revealed a greater than anticipated fuel-matrix interaction. The interaction rate was found to be inversely proportional to the molybdenum content of the fuel. Due to the extent of the reaction, the aluminum in the matrix was quickly depleted. The low thermal conductivity of

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$^2$ BOL = Beginning of life; term related to a fuel plate or fuel assembly and the time of inserting it in the reactor core.
the reaction product raised the fuel centerline temperatures higher than anticipated. Despite these higher temperatures, the fuel performance was satisfactory. The formation of the aluminide interaction product appeared to be the only aspect of fuel behavior that was significantly affected by temperature. The irradiation behavior of the U-Mo fuel itself was athermal over the temperature range tested [21].

Following the aggressive RERTR -3 tests, an additional test was planned to expose fuel to high burn-up at nominal temperatures. Based on the positive results of the first three tests, the two further tests, RERTR-4 & 5, were designed with larger, so-called mini plates that are more prototypic of full-size test reactor fuel plates and allow for more accurate post irradiation measurements. RERTR-4 & 5 were planned to test the candidate fuels at nominal research reactor conditions with fuel loading in the intermediate and high uranium loading (6 and 8 g U/cm³). RERTR-4 was discharged after a peak fuel burn-up of 80 at.% ²³⁵U, while RERTR-5 after the peak burn-up had reached 50 at.%²³⁵U. It was initially concluded that U-Mo/Al dispersion fuel with uranium loadings of up 8 g/cm³ performed very well under irradiation [22], but more recently it was noticed that even in those experiments coarse porosity had appeared between the matrix and the interaction phase when the fuel-Al interaction had consumed a major part of the Al matrix [23,24].

In Europe, also several screening test were performed. The program initiated by CEA (France) mainly focused on the effect of heat flux on the irradiation behavior of full-sized plates [21]. The values tested have been ~140 W/cm² for IRIS-1 experiment, ~240 W/cm² for IRIS-2, and ~340 W/cm² for FUTURE. The objective was to reach a maximum local burn-up of 70% in each of them. The first experiment, IRIS-1, was designed with ground U(Mo) powder (opposed to atomized powder in the other experiments) and low temperature (75 °C). The extensive program of post irradiation examinations has confirmed the very good behavior of the high uranium loading U7wt%Mo and U9wt%Mo plates up to 240 full power days and peak burn-up of 67.5% [6]. The IRIS-2 and FUTURE experiments were then started in parallel.

3 From HEU UAx to LEU U(Mo) in 4 experiments.

The BR2 reactor still uses HEU. However, since the dispersed U(Mo) fuel system with a density of ~ 8 - 9 gUtot/cc got into the qualification process, the US-Belgian collaboration on conversion intensified [25].

- a common conversion feasibility study was initiated together with Argonne National Lab (ANL)
- common efforts for the qualification of high density UMo fuel were being set-up,
- draft conversion schedule has been developed,
- recently collaboration with other European stakeholders was started to execute a qualification program of the dispersed UMo fuel system at high heat-fluxes up to high burn-up (LEONIDAS, HERACLES).
In this thesis, the studies conducted at SCK•CEN to support the conversion of the BR2 core from HEU to LEU U(Mo) dispersion fuel are described in 4 irradiation experiments FUTURE, BR1, E-FUTURE and SELENIUM. A brief introduction to these experiments is given in this chapter, while the next chapters provide the more detailed results.

3.1 The FUTURE experiment:
The French Program for U(Mo) fuel qualification, launched in 1999, was a close collaboration between CERCA, CEA, FRAMATOME (ANP), TECHNICATOME and COGEMA and made important contributions to the development of U(Mo) dispersion fuel. In 2003, two LEU fuel plates consisting of U7wt%Mo atomized powder dispersed in an aluminum matrix, were irradiated in the FUTURE irradiation rig of the BR2 reactor. The plates were submitted to a maximum heat flux of 353 W/cm², while the surface cladding temperature was kept below 130°C. After 40 full power days, visual examination of the fuel plates, coupled with similar indications coming from parallel US and Russian irradiation experiments, revealed an increase of the plate thickness. In view of this observation, the irradiation campaign was prematurely stopped and the fuel plates were retrieved from the reactor, having at their end-of-life a maximum burn-up of 32.8% $^{235}$U. An extensive post-irradiation campaign revealed that the U(Mo) fuel particles have interacted with the Al matrix, resulting in a thick amorphous interaction layer. At the interface of the interaction layer and the matrix, crescent shaped voids were observed. It is believed that the swelling of the fuel plate is the combined result of the formation of an amorphous U–Mo–Al interaction layer that in combination with thermo-mechanical stresses in the flat fuel plate, weakened the meat and lead to the formation of voids.

3.2 BR1 experiment:
The interaction of uranium with aluminum in nuclear fuel is a known problem. The ORNL graphite reactor X-10 [26] and the BR1 reactor, have been designed to use natural uranium fuel rods, clad with aluminum. The composition of the fuel rods is a uranium slug in an aluminum can, which was sealed off (by means of arc welding) with a cap. The first U slugs for the X-10 reactor were simply canned by forcing the slug in the can. However, the interaction between the uranium and aluminum, as well as air pockets in the cap weld caused failure of several of the rods. This has led to the idea of using diffusion barriers and bond aids during the production of the fuel rods. The barriers were intended to inhibit the interdiffusion of uranium and aluminum at temperatures around 200 °C, whereas bonding layers were needed to enhance the heat flow across the interface. Adequate bonding and impediment of the U–Al interaction could be achieved at the same time by using an aluminum-silicon alloy.

The fuel rods of the BR1 research reactor at SCK•CEN, are almost identical to those used in the X-10 reactor. The BR1 reactor still contains its original fuel rods. After more than 50 years irradiation at low temperature, some of the fuel rods were examined to analyze the diffusion barriers and bonding layers.
The microstructure of the fuel, bonding and anti-diffusion layer and cladding revealed that the AlSi bonding layer does provide a tight bond between fuel and cladding but that it is a thin USi layer on the U slug that acts as effective anti-diffusion layer and not the intended U(Al,Si)$_3$ layer.

It was concluded that the application of silicide layers on a U surface is an effective means to counteract the interaction of the metallic uranium with an aluminum cladding under low-flux, low-temperature irradiation conditions. This conclusion supported other observations made at that time.

### 3.3 E-FUTURE experiment:

It was repeatedly shown that U(Mo) exhibits unacceptable pillowing behavior in its application as a classical (i.e. dispersed in a pure Al matrix), flat dispersion fuel plate. Ever since, a significant amount of effort and research has been directed towards stabilizing the U(Mo) in-pile behavior in dispersion fuel plates by adding Si to the Al matrix.

The LEONIDAS program, a European initiative, started by SCK•CEN, ILL, CEA and AREVA-CERCA, initiated the qualification of the U(Mo)-Al(Si) dispersion fuel for high power reactors. The first experiment of the program, called E-FUTURE I, was performed to select the Si concentration and the fuel plate heat treatment parameters for further qualification. It consisted of the irradiation of 4 distinct (4% and 6% Si, 2 different heat treatments) full size, flat fuel plates in the BR2 reactor (470 W/cm$^2$ peak BOL power, ~70% peak burn-up). After the irradiation, the E-FUTURE plates were examined non-destructively and found to have pillowed in the high burn-up positions. Destructive analyses of the E-FUTURE plates confirm stable behavior up to a burn-up of 60%$^{235}$U, but at higher burn-up, the formation of thick interaction layers (not homogenous in thickness) and of voids mostly in-between fuel kernels or adjacent to the kernel surface are observed. The positive effect of a higher Si amount added to the matrix and the higher annealing temperature was however derived unambiguously.

Further analysis showed that in a matrix consisting of a mixture of Al and Si powders, the large Si particles were not being efficiently transported to the fuel kernels as the formation of a Si rich diffusion layer (SiRDL) with inhomogeneous layer thickness was observed as well as a remainder of large Si particles after irradiation.

The E-FUTURE II experiment is based on the irradiation of fuel plates containing even higher Si content and on the difference between adding Si to the matrix as a mixture or as an AlSi alloy. Out-of-pile studies have shown that the use of an AlSi alloy gives a better spatial dispersion and finer size distribution of the Si precipitates in the matrix. Such a matrix microstructure should lead to an enhancement of the Si effect since the Si availability is expected to be more efficient during the fabrication but also during irradiation by fission induced diffusion.

Unfortunately, the E-FUTURE II plates showed excessive deformation. Further PIE is needed to reveal the underlying cause of this.
3.4 SELENIUM experiment

To minimize the amount of Si to be added to the matrix and avoid having to apply special heat treatments to the fuel plates during fabrication, it would be advantageous to put the Si at the position where it is needed, that is on the surface of the fuel kernel. A way to accomplish this is to coat U(Mo) powder with a pure silicon layer by means of physical vapor deposition. On the other hand, application of a diffusion barrier to avoid all U(Mo)-Al interaction is an alternative route to prevent IL formation and can be accomplished by coating. In 2008, SCK•CEN started the SELENIUM project "Surface Engineering of Low ENriched Uranium-Molybdenum" with the main goal of applying coatings to spherical U(Mo) particles.

In 2011, two fuel plates, one with Si coated and one with ZrN coated U(Mo) fuel particles, were manufactured using the standard fuel plate production route. In April 2012, these fuel plates were loaded in the BR2 reactor for three cycles at irradiation conditions comparable to the E-FUTURE experiment (470 W/cm² peak BOL power, ~70% peak burn-up).

The non-destructive post-irradiation examinations showed that typical swelling has occurred and no pillowing has been observed on either plate. The fuel swelling evolves linearly with the fission density but at high burn-up, an accelerated swelling behavior is seen. Post irradiation examinations have been performed and confirm this microstructure.
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Chapter 2 Uranium-Molybdenum as a nuclear fuel

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1 Uranium and Uranium – Molybdenum alloy

Uranium exists in three polymorphic forms (Figure 5):

- orthorhombic α phase: stable up to 668 °C
- tetragonal β phase: stable between 668 and 776 °C
- bcc γ phase: stable above 776 °C

Pure uranium and various alloys of uranium that exist in the orthorhombic α-phase are poor performers under irradiation due to anisotropic growth that induces grain-boundary tearing and resultant breakaway swelling [1]. The high temperature γ phase is more resistant to thermal cycling and irradiation damage because of the isotropic nature of this phase.

The composition and temperature range over which the α, β and γ phase remain stable can be altered by alloying of uranium. Several transition metals, more in particular the 4d and 5d elements in Group IV through VIII of the periodic table, form a solid solution with γ-U. The stabilizing power of these elements increases with their atomic number since more d electrons will participate in bonding due to hybridization with s and p orbital electrons. However, their solubility will decrease as the size difference with the U atom increases. Increase of bond strength with increasing atomic number promotes formation of an intermetallic rather than a solid solution. The first two elements in the 4d series, Zr and Nb, form solid solutions with γU, but U-Zr cannot be retained in γ phase while U-Nb can be retained in this phase but only at high Nb concentrations. The elements at the other end of
the block, Pd and Pt have only limited solid solubility in U and will form a stable intermetallic compound with U [2].

Molybdenum is the best compromise because γ-U with Mo in solid solution possesses acceptable irradiation stability, mechanical properties and corrosion resistance [3,4]. Unfortunately, Mo has a non-negligible parasitic absorption cross-section for neutrons (2.6 b). U-Mo alloys (U(Mo)) containing at least 2.94 wt% or 7 at% Mo (Figure 5) retain the γ structure upon quenching. Although the stability of the U(Mo) γ phase will increase with the amount of Mo, the maximum concentration of Mo in U(Mo) to be used as LEU fuel should be limited to 10 wt% Mo as otherwise the required high U density criterion is not met (see chapter 1). On the other hand, to allow for sufficient time to fabricate the U(Mo) fuel plate, a process during which U in the plate is submitted to temperatures up to 450 – 500 °C, a minimum addition of approximately 5 wt% (20at%) is needed as can be deduced from the time-temperature-transformation (TTT) diagram [5,2] in Figure 6. Below that concentration the decomposition of the γ-U to α-U and U₂Mo phase occurs readily.

![TTT diagram indicating the starting points of the decomposition of γ stabilized U5wt%Mo (12 at%Mo), U8wt%Mo (18 at% Mo), U10wt%Mo (22 at% Mo) and U12 wt%Mo (25 at%Mo) (from [2]).](image)

The rate at which the quenched γ-U(Mo) phase will decompose in a homogeneous alloy is strongly dependent upon the isothermal treatment temperature, being more pronounced when the alloy is near the eutectoid temperature (550 °C) [1,2]. The α-U phase forms continuously by a cellular matrix decomposition reaction as a function of time, nucleating primarily at sub-grain boundaries and leading to precipitation at the grain boundaries [3]. For the 7 wt% Mo alloy, decomposition of γ-U(Mo) into α-U(Mo) is relatively rapid as defined by the TTT diagram, with the kinetics becoming much more sluggish with increased wt% Mo [6].

To study these U(Mo) alloys, small coupons of U with varying Mo content were prepared in an arc furnace at SCK•CEN. The weighted amounts of uranium and molybdenum were put under a slightly overpressure Ar atmosphere and melted. To obtain a homogeneous
microstructure of the alloy, the coupons were re-melted several times. The microstructure of the polished samples was investigated using scanning electron microscopy (SEM) and electronprobe microanalysis (EPMA).

![Figure 7: U rich segregation boundaries can be observed on the backscattered electron images of respectively U6wt%Mo, U8wt%Mo, U10wt%Mo and U12wt%Mo. The samples were prepared in an arc furnace and re-melted 4 times.](image)

As in most refractory metals, compositional segregation occurred due to differences in melting temperature $T_{m \text{Mo}}: 2896 \text{ K} (2623 \text{ °C})$ and $T_{m \text{U}}: 1405 \text{ K} (1132 \text{ °C})$ (Figure 7). Elemental distribution X-ray maps obtained with EPMA (Figure 8) confirm the segregation of Mo on the grain boundaries and furthermore show the formation of a dendritic structure with increasing Mo content, indicating increased difficulties in homogenization.
The precipitates observed throughout the matrix (black spots in the Mo X-ray maps of Figure 8) are identified as UC particles, due to C impurities in the starting material.

To cure the observed compositional segregation, the samples were submitted to thermal treatment (annealing at 250 °C for 72 hours), to obtain a homogeneous alloy (Figure 9).

The lattice parameters of the prepared and heat treated alloys were measured using X-ray diffraction (XRD) (Figure 10). As expected, an increase in the Mo content of the alloy decreases the lattice parameter because the atomic radius of Mo (145 pm) is smaller than uranium (175 pm). Also included in Figure 10 are lattice parameter values reported in
literature [7,8]. A linear regression line through the lattice parameters acquired from the samples measured at SCK•CEN yields \( a = 3.493 - 0.007813 \times \text{wt}\%\text{Mo Å} \). This is in good comparison with the values measured by Burkes et al. [7] on depleted U(Mo) foil alloys. They find a linear relation of \( a = 3.4812 - 0.0066 \times \text{wt}\%\text{Mo Å} \). The deviation from the equation found by Park et al. [8] is somewhat larger, \( a = 3.5270 - 0.0119 \times \text{wt}\%\text{Mo Å} \), though the individual measurement points still fall within the 1σ error. Possible discrepancies should be attributed to the differences in actual Mo composition compared to the nominal composition and to the differences in measurement and calculation techniques.

The measurements by Park were performed with neutron diffraction on atomized U(Mo) powder. As will be shown in the next section, the microstructure of atomized U(Mo) powder differs substantially from cast U(Mo).

![Lattice parameters of the U-Mo alloys with γ-structure as a function of Mo content.](image)

**Figure 10** Lattice parameters of the U-Mo alloys with γ-structure as a function of Mo content.

## 2 Fabrication of atomized and ground U(Mo) powder.

For the fabrication of dispersion fuel plates, a powder of the uranium compound is required. Currently U(Mo) powder can be produced by machining and grinding of the alloy (ground fuel) or by centrifugal atomization (atomized fuel).

### 2.1 Ground U(Mo) powder

Ground powder can be fabricated by comminuting (pulverizing) cast coupons using standard techniques such as hammer milling, ball milling or jaw crushers. The mill is installed in a glove box and is operated under an inert atmosphere. U–Mo alloy is ductile, which poses difficulties for comminution. To improve workability of the alloy, a small amount of oxygen is admitted to the glove box during the comminution process. A built-in rotary classifier system allows the finely powdered product to leave the grinding chamber, but the oversized particles from the initial grinding stage are continuously returned to the mill for further grinding. The resulting powder therefore has an irregular shape and contains oxygen (Figure
11) which comes from the extended time needed to obtain the desired particle size [9]. The comminuted powders consist of homogeneously distributed equiaxially shaped grains. In addition, they are heavily cold-worked and thus contain a high concentration of dislocations. During hot-rolling and subsequent irradiation of the fuel plates, this dislocation structure will undergo recrystallization (polygonization). The boundaries of the final subgrain structure provide nucleation sites for gas bubbles. Comminuted powders are made from well-homogenized cast alloy rods, and will therefore not contain the ‘cored’ cellular structure typical of the rapidly solidified alloy.

Figure 11 Al, O, U and Mo X-ray maps showing the formation of UOx layers in the fresh ground fuel kernel.

2.2 U(Mo) atomized powder

Atomization is a well-known process to manufacture metal powders. Various atomization processes exist, but not all of them are suitable to produce U(Mo) powders. Korea Atomic Energy Research Institute (KAERI) has developed a proprietary atomization route for U(Mo) (United States Patent 5978432). The rotating disk atomization process comprises melting, atomization and collecting. The melting chamber contains a crucible with a nozzle in which the uranium lumps and molybdenum buttons are induction melted.
The molten metal is fed through an orifice onto a rotating disk in an argon atmosphere (Figure 12). The diameter of the atomizing chamber is large (2.5 m) to allow for sufficient solidification before the atomized melt droplets reach the chamber wall [10].

The observed cell structure of the atomized U(Mo) particles (Figure 13) is usually found in rapidly cooled alloys that have a substantial liquid-solidus gap. When the liquid U(Mo) drop cools down and meets the solidus lines, it will solidify forming what is commonly referred to as cells. Normally as cooling continues, the solidification proceeds but the solid phase will contain a decreasing amount of molybdenum. During the cooling down of the melt in the atomization process, the remaining liquid phase will not slowly move to the equilibrium state but it will solidify abruptly, creating thick Mo-deficient U(Mo) layers around the formed cells. Compositional analysis (EDX) reveal that irrespectively of the alloy composition, the Mo
content at the cell boundaries is about 2 to 3 at% lower than that at the inside of the cell [4,11,12].

The atomized powder is collected in a container at the bottom of the funnel shaped chamber. Powder size distribution is classified by sieve analysis.

Compared to ground fuel, the spherical atomized U(Mo) powder has a lower surface-to-volume ratio, which lowers the surface available for formation of interaction products between the fuel particles and Al matrix.

3 Fuel plate production

To produce a fuel plate, the meat powder (mixture of pure Al and the fuel particles) is compacted and assembled in a frame which is placed between two cladding plates (Figure 14).

The frame and cladding are usually made of commercial aluminum alloy (Al 60661, AG3NE, AlFeNi). The complete set of compact, frame and cladding is fixed by welding at the edges but the corners are left open. In a next step the assembly is inserted in a furnace at a temperature of ± 425 - 500 °C (depending on the type of cladding) for approximately one hour. Hot rolling is performed in several passes according to a well-established rolling schedule. This schedule defines the thickness reduction per pass in order to control the final dimensions of the fuel meat. Between each pass, the assemblies are reheated for several minutes.

After hot rolling, the plates are submitted to a QA program:

- X-ray radiography: A high exposure radiograph is taken to measure the dimensions/shape of the meat, its position within the plate and to identify stray particles (fuel particles outside the meat zone). On a second lower exposure radiograph, the homogeneity of the uranium distribution is checked.
- Archive microscopic examinations: to verify cladding thickness (to protect the fuel meat from corrosion effects a minimum clad thickness is required), grain size/shape, microscopic defects, and debond regions. If the cladding fails, the core is exposed
and the reactor environment is contaminated with high activity radioactive material. For this reason, the thickness of the cladding on the finished fuel plate is one of the most important specifications for plate type fuel.

- **Ultrasound**: To detect the non-bond regions an immersion ultrasonic technique has been developed
- **Bend test**: to examine cladding integrity
- **Blister test**: to test the resistance of the plate to the formation of blisters (a blister results from inadequate bonding between meat and cladding). During this test the plate is submitted to higher temperatures (450 – 500 °C) for approximately 2 hours.
- **The porosity is measured by means of immersion**

Fuel plates passing the blister test are sheared based on the recorded x-ray radiography, to meet the specified dimensions.

The final geometry of the fuel plate can be either flat or curved (Figure 15).

Several thin fuel plates are arranged and mechanically fixed by swaging or welding in rectangular boxes or assembled in such a way that they form a cylindrical tube. A standard fuel element is also equipped with at one end a nozzle and at the opposite end a handling pin.

Due to its specific design, a standard BR2 fuel assemblies (Figure 16) consist of six concentric cylindrical tubes, each tube being an assembly of three equal curved segments made of rolled plates which are mechanically fixed by the roll swaging technique into three solid grooved radial stiffeners. One standard BR2 fuel assembly contains 400 g $^{235}$U in the form of highly enriched (93% $^{235}$U) $\text{UAl}_x$, with a loading of about 1.30 g U/cm³ meat (Figure 18).
4 Experimental fuel plates for BR2

The experimental fuel plates fabricated to be irradiated at BR2 are typically flat and have dimensions similar to the curved plates used in the standard BR2 fuel assembly.

An experimental flat fuel plate is typically 970 mm long, 57 mm wide and has a thickness of approximately 1.27 mm (Figure 17). The meat, containing the dispersed fuel, is located in the central part of the plate and has following dimensions: nominal length ~762 mm, width ~45 mm. The nominal thickness of the meat is approximately 510 µm.

The technological limit for the use of Al/dispersions is 45-50 % by volume of fissile material dispersed, since enough Al matrix should be present to provide for sufficient heat conductivity. Around 2001 atomized U7wt%Mo was made available by KAERI for testing and qualification. This meant that for an experimental LEU U(7wt%Mo) plate a loading of 8 g U/cm³ was required (Figure 18) which can be obtained by dispersing approximately 140 g U in ~20 g Al. Of this total amount of uranium and with an enrichment of 19.75%, ~27.65 g is fissile $^{235}$U.
Figure 18 U-density in the fuel meat as function of the volume fraction occupied by the dispersant. The loading required for the BR2 reactor are indicated by black dots.

A special irradiation device for experimental high density flat fuel plates, was designed at SCK•CEN. In the FUTURE (FUel Test Utility for REsearch Reactor) device, two experimental plates can be positioned. After loading of the plates in the basket, the device is inserted in one of the irradiation channels of BR2 (Figure 19b). An evolution of this device, known as the E-FUTURE basket can hold up to four plates (Figure 19a).

Figure 19 The E-FUTURE basket can contain up to 4 fuel plates (a). The schematic overview shows FUTURE basket with two U(Mo) fuel plates (blue boxes) and dosimeter (red circles) (b).
References


Chapter 3 Properties of irradiated fuel

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1 Irradiation of U(Mo) fuel

As already introduced in Chapter 1, the core purpose of a Research Reactor is the production of neutrons to feed experiments. To generate neutrons, the reactor relies on fission occurring in its driver fuel containing fissile materials. When the fissile nuclei in this driver fuel (mostly $^{235}$U, but certainly for LEU based fuels also a non-negligible part of $^{239}$Pu) undergo fission, the result is the production of fission products (FP), neutrons (n) and Energy (E). When the fissile nucleus is split into (typically) 2 fission fragments, 2-3 fast neutrons (Figure 20) and about 200 MeV of energy is released.

![Figure 20 Schematic overview of the neutron capture by a $^{235}$U nucleus](image)

In this chapter, the results of a fission event and its consequences (see Figure 21) on reactor materials will be introduced. Most attention will be given to the U(Mo) fuel plate behavior and the evolution of its properties with the accumulation of more and more fissions (burn-up). This evolution, particularly the swelling of the plate, will be the main issue in the fuel qualification process, as it will have to stay within a clearly defined set of safety limits. It will be a function of the way in which the fuel is operated (e.g. the power it is required to generate).

A fundamental understanding of the fuel behavior is needed to implement this knowledge in a fuel performance prediction code (e.g. DART-THERMAL [1], MAIA [2]).

1.1 Neutron production

For each fission event, typically 2-3 neutrons are produced. The released fast neutrons have an energy ranging from 2 MeV to a maximum of 14 MeV. These neutrons are subsequently thermalized by the moderator (water) in the reactor and maintain the chain reaction, as they will interact with other fissile nuclides to generate new fissions.

A fraction of the neutrons is lost because they interact with non-fissile nuclides or they do not lead to fission. This can happen when a neutron is captured by a $^{235}$U nucleus and leads to formation of $^{236}$U or when it is captured by a $^{238}$U nucleus (particularly in LEU fuel), leading to formation of $^{239}$U, which by 2 beta decays forms $^{239}$Pu, which is fissile again. These 2
reactions will have to be taken into account when burn-ups, typically expressed in $%^{235}\text{U}$ burned in a fuel, are converted to fission densities, which is the physical amount of fissions that have occurred per unit of volume (see chapter 4). Some of the neutrons interact with nuclides from structural materials, get absorbed in the control rods (transmutation) or by experiments. In some cases, radioactive nuclides are formed and the process is coined activation.

Figure 21: Summary of the most important phenomena occurring as a consequence of a fission event. The most relevant phenomena for the subject of this thesis are those resulting from the fission products, as these are the phenomena that alter the fuel and cause its microstructure and properties to evolve with the accumulation of fissions (burn-up).

As the fast neutrons traverse the materials in the reactor, they also generate displacement cascades by collisions with the atoms in the materials. The contribution of fast neutrons to the damage of the fuel is small compared with the damage caused by the heavy fission products in a thermal reactor (see below). Consequently, the contribution of fast neutrons to the damage generated in the fuel is neglected. The damage they generate in structural
materials, particularly the vessel of the reactor, is cumulative and eventually leads to changes in the mechanical properties (e.g. neutron embrittlement) of materials. As these effects are not in the scope of this thesis, we will not go into details on this.

1.2 Energy production

For each fission event, roughly 200 MeV of energy is released. Fission products are released with a kinetic energy of about 167 MeV, while the balance of the energy is carried out by fast neutrons (2 – 14 MeV), gamma rays (prompt and delayed), beta particles and neutrinos. Roughly 190 MeV of that energy is deposited in the fuel itself, causing it to heat up. To prevent overheating of the plate, it needs to be cooled by the reactor primary cooling systems, through which the heat is evacuated. For most Research Reactors, the heat is dissipated to a secondary circuit and then to an ultimate heat sink (e.g. cooling tower). The amount of energy deposited by the plate per second divided by the active plate surface gives the average heat flux at which the plate is operated, which is therefore expressed in W/cm². As the amount of fissions generated in the plate varies with the position, the average power generated by the plate is different from the local maximum power. For BR2, the typical maximum local heat flux allowed on a plate is 470 W/cm² (see below).

Using the conversion 1 MeV = 1.6 10⁻⁶ erg = 1.6x10⁻⁶ x 10⁻⁷ W.s, one can calculate that 3.12 x 10¹⁰ fissions per second (fission rate) will generate 1 W of power or that fissioning of 1.2 x 10⁻¹¹ gram of ²³⁵U per second gives 1W of power. The average power generated by a fuel plate having a cooling surface $S$ of the fuel plate at a heat flux $Q_s$ is [3]:

$$P_{fis}^{dep} = Q_s \times 2S \quad \text{Eq. 1}$$

With typical dimensions of 76 x 4.5 cm for the cooling surface (i.e. the surface covering the meat) of an experimental fuel plate (see chapter 2), the deposited power in the plate at an average heat flux of 350 W/cm² equals 2.4 x 10⁵ W. In those irradiation conditions, for a U7wt%Mo/Al dispersion fuel plate with a loading of 8 gU/cm³ and a typical meat thickness of 510 µm, the deposited power in a fuel kernel having a diameter of 70 µm at a heat flux of 470 W/cm³ is 3.4x10⁻³ W. Taken in account that 3.12 x 10¹⁰ fissions per second will generate 1 W of power, 10⁶ fissions per second will occur in one fuel kernel. This means that per % of ²³⁵U used (fission or capture), a total of ~4-5x10¹⁴ fissions will take place in one fuel kernel.

In dispersion fuel plates, the energy released in the fuel kernels is dissipated by the Al matrix to the Al alloy cladding. The cooling of the plates during irradiation is ensured by pumping water (downwards) through the narrow gaps left in between the plates. The speed of the coolant depends on the generated heat flux (W/cm²). The narrow cooling gaps are exactly the reason why fuel plate swelling needs to be kept under control, as reduction of the cooling gaps reduces cooling efficiency, which can eventually cause the plate to overheat and fail. In the worst case, loss-of-flow (LOF) occurs, which can cause melting of the plate [4,5], but usually the plate will have failed well before that, causing fission products to be
released in the primary coolant, where they are detected. When their concentration exceeds safety limits, the reactor will be stopped.

During steady-state operation, the heat removal at BR2 must maintain the cladding and fuel temperatures well below the blistering\(^3\) threshold temperature. This is achieved by assuming sufficient margins to Onset of Nucleate Boiling (ONB). The BR2 maximum nominal heat flux is defined as the heat flux at which ONB occurs.\(^6\)

Historically, the maximum heat flux was determined to be 603 W/cm\(^2\). Based on loss-of-flow/loss-of-pressure tests performed in 1963, the authorized maximum heat flux was set to 430 W/cm\(^2\) for BR2 routine operation in order to maintain fuel integrity after such an event. As the cooling water flows downward through the BR2 core, a reversal of the coolant flow is required when the primary pumps stop and natural convection is established. This flow reversal condition limits the maximum heat flux. Currently, a permanent deviation up to 470 W/cm\(^2\) is authorized\(^6\). Therefore, for qualification of plates containing new fuels, the average heat flux is typically set to 350 W/cm\(^2\), but locally a maximum flux of 470 W/cm\(^2\) should be obtained.

As seen from Figure 22, a minimum flow of approximately 7.3 m/s is needed to allow the maximum heat flux of 470 W/cm\(^2\). Usually, for the cooling of the fuel plates a nominal flow of 10.4 m/s is taken to maintain a margin with respect to the minimum value.

![Figure 22 Calculated heat flux as function of the average coolant speed (from \(^6\))](image)

The neutron flux in a compact reactor core typical for a Research reactor is not constant. It varies with the position in the reactor. For any given position in the central plane of the reactor, the flux varies with the height (elevation), which means also the power in the plates

\(^3\) Blisters are produced when the cladding detaches from the meat as a result of the trapped fission gases contained in the meat.
and the heat distribution is variable. To obtain knowledge on the shape of the neutron flux (and heat distribution) over the fuel plates in the FUTURE device, the basket was equipped with dosimeters and loaded into one of the BR2 channels (Figure 23).

A benchmark calculation (MCNP$^4$) of the conventional thermal neutron fluxes was performed and the results were compared to the dosimeter results. The distribution of the thermal neutron flux shows a typical roughly cosine profile (Figure 23) and a good comparison is seen between the measurements and calculation.

![Figure 23](image)

Figure 23 Left: The schematic overview shows FUTURE basket with two U(Mo) fuel plates (blue boxes) and dosimeter (red circles). Right: Distribution of the conventional thermal neutron flux in dosimeters located in the center of the Al holder (extracted from [3]).

As the energy generated in the plate causes it to heat up, the thermal energy will be transported to the coolant, generating a temperature distribution over the plate thickness depending on the thermal properties of the materials. The resulting fuel temperature during normal operating regime of the reactor will be around 130 °C while the temperature on the outer surface of the cladding remains below 90 °C. As this fuel is mostly metallic, temperature gradients will not be very large, but the heating of a fuel plate surface in contact with cooling water will cause corrosion of the cladding.

Aluminum alloys undergo oxidation, even at room temperature, if oxygen is available. They produce a protective oxide (Al$_2$O$_3$) of which the growth rate saturates in a short time. The protective oxide, however, degrades in water over time by the formation of various oxide-hydrates at the outer surface, leaving only a thin protective Al$_2$O$_3$ layer on the aluminum surface [7]. The most frequently found oxide-hydrates are boehmite (Al$_2$O$_3$.H$_2$O) and bayerite (Al$_2$O$_3$.3H$_2$O) [8]. In the BR2 reactor, these (hydr)oxide layers generally grow to a thickness of 30-40 µm before spallation starts to occur. The formation of the oxides in itself generates a swelling effect, while the spallation thins the fuel plate.

---

$^4$ MCNP (Monte Carlo N-Particle extended) is a software package for simulating nuclear processes developed at Los Alamos National Laboratory.
Formation of oxides on the cladding can affect the fuel performance as the thermal conductivity of the oxide (~30W/mK) is lower than that of aluminum (~200W/mK) [7]. Maximum local fuel and cladding temperatures are ~250°C and ~140°C respectively, mainly because of this thermal barrier.

Scanning electron microscopy (Figure 24a) results on the oxide layer on a typical AlFeNi cladding, show cracking of the layer and locally even complete detachment from the cladding. This is interpreted as the result of dehydration of the layer (evaporation of the lattice water) during the drying of the fuel element in the hot cell. The SEM images also show that the cladding contains numerous precipitates, which are identified by reference to the literature [9,10] and X-ray mapping with EPMA, as AlFeNi particles.

Due to the high density contrast between the AlFeNi particles and the Al, the backscattered electron image (Figure 24b) clearly shows that the precipitates can also be found in the oxide layer but only in the part of the layer close to the cladding. Closer to the outer surface of the oxide layer, no precipitates are found. The SEM image on the unpolished outer cladding surface (Figure 25) clearly shows the cracking of the oxide layer probably due to dehydration.

Figure 24(a) Secondary electron image showing cracks in the oxide layer. (b) The backscattered electron image of the oxide layer reveals white particles, which are identified as AlFeNi precipitates typical for this type of cladding (from [8]).

Figure 25 Secondary electron image of the outer fuel plate surface. The cracked pattern observed is a result of dehydration of the oxide layer.
1.3 Fission fragment production

Fission leads to the production of fission fragments, basically it is the transmutation of fissile nuclei into other nuclei which themselves may be radioactive. As such, they are the origin of the decay heat generated by nuclear fuel after its use in the reactor (which can be sufficient to cause melting of fuels, as known from the Fukushima event). They also form the radioactive waste remaining after the fuel is spent.

![Fission Product Yields](image)

**Figure 26** Fission product yields by mass for thermal neutron fission of U-235.

The fragments produced by fission differ from event to event. The mass distribution of the fission products is represented by a fission yield curve, in which the percentage of the different products is plotted against mass number (Figure 26). Yields vary from $10^{-5}$ % to about 6 % and the range is so large that a logarithmic scale is used for the ordinate of the yield curve. The maximum yields lie near mass numbers of 95 and 139. The most prominent fission products are isotopes of Cs, Nd, Xe, Ba, I, Ru, Sr, Mo, Zr, Kr, Ce, etc...

The fission process is highly asymmetric and the energy of the fission products is inversely proportional to their mass numbers. As previously stated, every nuclear fission releases ~200MeV of energy, which is transported mainly by the kinetic energy of the outgoing fragments (80%). Typical energies for the fission fragments are ~80-100 MeV for the heavy fragment and ~60-70 MeV for the lighter fragment. This amount of kinetic energy given to the fission fragments is dissipated in the fuel material itself, causing:

- Atom displacement damage: displacement of atoms from their normal position in the structure of the irradiated material. The displaced atoms may leave lattice vacancies and end up in interstitial locations or cause interchange of dissimilar atoms in the lattice structure. When multiple atom displacements occur at the interface between two or more different materials, the ion driven mobility of the atoms causes interdiffusion and ion mixing occurs.
• Ionization: the removal of electrons from atoms in the material by e.g. fission fragments results in the formation of ion pairs in the path of the particles. Eventually, most of the kinetic energy of the fission products is transformed into lattice vibration (heat), but a fraction is stored as potential energy, e.g. under the form of defects. The crystal structure of the irradiated material may be modified through all these energetic interactions. Changes in the microstructure of the materials can be expected, ultimately leading to changes in basic mechanical properties such as hardness, ductility, creep properties, etc.

In the next sections, the damage caused by the displacement cascades occurring in the fuel materials will be described in more detail. A better knowledge of this damage is needed to understand the irradiation behavior of U(Mo) fuel.

An ion loses its kinetic energy when traversing condensed matter by either elastic or inelastic collisions. The stopping power can be defined as the sum of the elastic component or nuclear stopping power \((dE/dx)_n\) and the inelastic or the electronic stopping \((dE/dx)_e\) power

\[
\frac{dE}{dx} = \left(\frac{dE}{dx}\right)_n + \left(\frac{dE}{dx}\right)_e = S_n + S_e
\]

The processes involved in the interaction between the swift heavy ion\(^5\) and the target material mainly depend on the kinetic energy of the ion and the charges of the incident ions and atoms of the irradiated material. Overall, we can say that at low energies \((E < 0.01\) MeV/u) the energy loss is dominated by nuclear stopping power \((S_n)\). Interaction with target nuclei dominates and leads to large angular scattering of the projectiles. Hence, the memory of the incident beam direction is rapidly lost and material alterations, which result from displacement cascades, are rather isotropic.

At high energies of the incident ion, \((E > 0.1\) MeV/u), energy loss is dominated by the electronic stopping power \((S_e)\). Interaction with target electrons leads to excitation or ionization of the target atoms and kinetic energy of the ejected target electrons. These electronic processes lead to an almost continuous energy loss, retaining the incident beam direction. This interaction is important at ion energies > 0.1 MeV/amu and primarily generates a hot electron gas around the straight ion trajectory.

The nuclear and electronic energy loss can be calculated using the TRIM (Transport of Ions in Mater) program [11]. The released fission products are highly charged and can be presented as ionized ions accelerated to their corresponding kinetic energies. In Figure 27 the \(S_e\) and \(S_n\) for Xenon ions having energies ranging between 10 keV and 100 GeV traversing a U(Mo) specimen, are shown.

\(^5\) Swift heavy ion irradiations can be used to simulate the damage from spontaneous fission events in solids.
Fission fragments, having energies in the MeV range, are slowed down mainly by electronic stopping, and move almost in a straight path. When the ion has slowed down sufficiently, the collisions with nuclei (the nuclear stopping) become more and more probable, finally dominating the slowing down (Figure 28). The typical range for a fission fragment to slow down is ~12 µm in a low density material such as Al, while for U(Mo) only ~5µm is needed to slow the Xe ion down.

![Figure 27 Nuclear, electronic, and total energy loss for xenon ions in U(Mo), versus particle energy.](image)

In the electronic slowing-down regime ($S_e \gg S_n$), most of the energy of the incident ions is transferred to the host electrons, resulting in a high electronic ionization (ionic spike) and / or a high temperature increase of the electronic subsystem (thermal spike).

![80 MeV Xe in Al and U(Mo)](image)

![Figure 28 Stopping range of an 80 MeV Xe ion (fission fragment) in pure Al and U7wt%Mo.](image)
The incident MeV energy is transferred to the electronic subsystem of the material and the excited electrons attain thermodynamic equilibrium in $10^{-15}$ s via electron–electron interactions. This energy is subsequently released to the lattice atoms through electron–phonon (e–p) coupling in $10^{-13}$ to $10^{-10}$ s causing defects and atomic displacements. Depending on the strength of the electron-phonon (e–p) coupling factor $g$, matter along the incident ion path may melt and the mixing at interfaces is attributed to interdiffusion in the molten ion tracks [12]. When the energy deposited on the atoms exceeds the energy necessary to melt (defined as the energy to reach the melting temperature plus the enthalpy of fusion), the irradiated materials are said to be sensitive to the electronic energy loss process [13]. Several experiments [14] show that the materials with strong e-p coupling show this sensitivity. Both Al and U exhibit a weak electron–phonon (e–p) coupling ($g = \text{respectively } 8.14 \times 10^{11}$ and $12.4 \times 10^{11}$ W/cm$^3$K [14]). In that respect it is suggested that Al and U are relatively insensitive to electronic stopping power. For $S_e$ insensitive materials no interdiffusion in the hot liquid state is expected and intermixing at interfaces results from ballistic effects.

During the nuclear collision portion of the slowing down process, target atoms are permanently displaced from their lattice sites and relocated several lattice sites away. When this process takes place at the boundary separating two different materials, interface mixing occurs. The transportation of atoms through repeated single collision events between the incident ions and target atoms is known as recoil mixing. In addition to recoil mixing, another ballistic phenomenon is possible during irradiation; enhanced atomic mixing can occur when multiple displacements of target atoms result from a single incident ion. In the multiple displacement process, an initially displaced target atom (primary recoil) continues the knock-on-atom processes, producing secondary recoil atom displacements which in turn displace additional atoms. The multiple displacement sequence of collision events is commonly referred to as a collision cascade or displacement spike. Atomic mixing resulting from a series of uncorrelated low-energy atomic displacements is referred to as cascade mixing. At the low irradiation temperatures generally found in Research Reactor fuels, this cascade mixing process will be an important phenomenon leading to microstructural changes.

![Figure 29 Displacements in the target versus kinetic energy of the incident ion as calculated with the TRIM-code.](image-url)
A 1 MeV ion may affect approximately $10^4$ atoms (Figure 29), making up one of these spikes. Since displacements take place mainly in the last few micrometers of each heavy ion trace, it is not surprising that the number of displacements above a given threshold does not vary much with the kinetic energy of the incident ion (Figure 29). As the formation of the displacement cascade comes to an end, all the moving displaced atoms reach a point where they have insufficient energy to cause further displacement. Remaining energy transfers will be at sub-threshold levels and the energy will be shared between neighboring atoms and dissipated as lattice vibrations or heat. This period of lattice heating is referred to as the thermal phase of the collision cascade and may exist for several picoseconds before being quenched to ambient temperature.

In Table 1 the total spike temperature $T_t$ is defined as the sum of the calculated spike temperature $\Delta T_s$ and the minimum irradiation temperature $T_0$ (350K), used in determining the experimental activation energy [15]. Comparison of $\Delta T_s$ to the melting temperature $T_m$ of the lowest melting compound, eutectic or element in the ion mixing experiment, shows that for the U/Al system bombarded with Xe ions ($E=400$ keV) the spike temperature alone exceeds the threshold needed to induce melting [16,15]. For all the systems the spike temperature exceeds the $\alpha$ to $\gamma$ U transition temperature (see chapter 2) indicating that irradiation will stabilize the $\gamma$ phase.

<table>
<thead>
<tr>
<th>ion</th>
<th>Ion energy (keV)</th>
<th>$S_n$ [11] (eV/nm)</th>
<th>$\Delta H_{mix}^{\text{liq}}$ [17] (kJ/mol)</th>
<th>$\Delta T_s$ [16] (K)</th>
<th>$T_t$ (K)</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Al</td>
<td>Xe</td>
<td>400</td>
<td>37</td>
<td>-63</td>
<td>720</td>
<td>1440</td>
</tr>
<tr>
<td>U-Al</td>
<td>Ar</td>
<td>400</td>
<td>5.5</td>
<td>-63</td>
<td>720</td>
<td>1470</td>
</tr>
<tr>
<td>U-Si</td>
<td>Ar</td>
<td>400</td>
<td>6</td>
<td>-74</td>
<td>720</td>
<td>1440</td>
</tr>
</tbody>
</table>

Table 1 The nuclear stopping energy of various ions in U bilayer systems is calculated from TRIM. The heat of mixing for the systems is given as well as the total spike temperature $T_t$, which is the sum of the calculated spike temperature $\Delta T_s$ and the irradiation temperature $T_0$ (350 K).

2 Microstructural changes

Concerning the qualification of the safe and reliable operation of a fuel design as driver fuel for a reactor, the central question is the evolution of its properties. Particularly for fuel plates, the narrow width of the cooling gaps between plates in an element means that the increase in the thickness of a plate (swelling) is particularly important for qualification. The origins of the observed swelling of a fuel plate can be found in its microstructure and its evolution with burn-up accumulation. The most important cause of changes in the microstructure of a Research Reactor fuel, since it is run at low temperature, lies in the high flux ($\sim 10^8$ ion pairs per second per kernel) of internal ion bombardment and implantation by fission fragments constantly occurring in the fuel.
As seen previously, when a high energy particle (such as a fission fragment) strikes an atom in the lattice, kinetic energy is transferred from the incoming atom to the lattice atom. The amount of energy transferred can be affected by the energy of the incoming particle, angle of interaction between the atoms, and charge of the particles. When enough energy is transferred to an atom to eject the atom from its lattice site into the interstices of the lattice, a Frenkel defect pair (a vacancy and interstitial atom) is formed. Other defects may include grain boundaries, voids and dislocation loops, precipitates, and gas stabilized bubbles [18].

The defects present in the material are governed by the irradiation conditions such as dose rate, dose, particle type, and operating temperature. The dose rate determines how quickly defects form, the total dose in the material reflects the total number of defects produced in the material and the incoming particle type has a major effect on the damage cascade created in the material [18].

The operating temperature has varying effects on the microstructure [18]:

- Low temperature can lead to increased defect concentrations as well as amorphization due to a lack of diffusion capability in the material.
- High temperatures lead to increased diffusion and allow defects to diffuse to sinks much more readily, which can lead to dislocation loop formation or void formation in the material.
- Very high temperatures will quickly anneal any radiation damage created.

With vacancies and interstitials being produced in the material continuously during irradiation, defects seek to form the lowest energy configuration possible. This can lead to recombination, loss to sinks, and, most importantly for irradiation studies, combining with other interstitials or vacancies to form clusters of defects. The most commonly studied defects in irradiated materials are dislocation loops. These defects lead to increased radiation hardening in the material, which affects the material’s mechanical properties, such as yield strength and ductility [18]. For fuel materials, in addition to these irradiation effects, also the chemistry of the fuel is continuously changing as fission products are incorporated in the material.

When U-Mo/Al dispersion fuel is irradiated, several radiation-induced microstructural changes occur and they influence the fuel performance. The main changes are:

- Chemical changes by incorporation of fission products (FP): Fission products are present in the fuel as solid and gaseous atoms. The solid and gaseous fission products affect fuel properties such as melting temperature, thermal conductivity, and cause swelling [19].
- The formation of a fuel-matrix interaction layer (IL): The growth of an IL in dispersion fuels has become a major fuel performance issue. The IL layer is formed between the matrix and fuel kernels in dispersion fuel.
affected by combinations of physical and irradiation parameters, which include:
what phases formed, additives in the matrix and fuel kernel, burn-up, and
operating temperature [18].

- a result of the intermixing effect generated by the FP ions.
- Amorphization: occurs when a material loses all crystalline structure and becomes random or only consisting of short-range order. Amorphization can occur when irradiations are conducted at low temperatures. At low temperatures, the diffusion of point defects is low and they cannot recombine or reach sinks easily. The defect concentration continues to increase in the material until all of the ordered crystalline structure is consumed, leaving only a short ordering of crystalline structure. Amorphization in metal systems is often referred to as metallic glass formation [18].
- Restructuring: Irradiation-induced grain refinement (often also referred to as irradiation-induced recrystallization) is a general phenomenon that has been observed to occur in a variety of nuclear fuel types, e.g. UO₂, U₃O₈ and U(Mo). The restructuring process results in sub-micron sized grains that accelerate fission-gas swelling due to the combination of short diffusion distances, increased grain-boundary area per unit volume, and greater intergranular bubble growth rates as compared to that in the grain interior [20].
- Swelling: fuel swelling in dispersion fuel is a combined effect resulting from the accumulation of fission product elements and fuel microstructural changes which include the formation of an interaction layer and irradiation-enhanced sintering of fabrication voids. Fission-product-induced swelling can be divided into two parts: one that is induced by solid fission products and the other by fission gas bubbles. The solid fission product induced swelling is caused by volume difference between a split uranium atom by fission and the produced solid fission products that reside in the U–Mo lattice. Fission gas bubble swelling is dependent upon factors such as fuel composition, fuel type, fabrication process and fission rate [21].

Throughout the remainder of this chapter a more detailed description of the microstructural changes is given.

2.1 Interaction layer formation

The formation of interaction layers at the interfaces of the U-Mo particles and Al matrix during irradiation is one of the challenging issues in the development of dispersion fuel. It has been found that the formation of such an IL has a substantial impact on the fuel plate behavior. Various out of pile studies have been conducted to investigate the possible phases formed [22,23].

2.1.1 Formation mechanism of interaction layers

This section is based on following publications: [11-19]
The interaction layer formation requires interdiffusion of the U(Mo) fuel and the matrix. This interdiffusion may be simulated out-of-pile by thermal activation. For the diffusion experiments performed in this thesis, U(Mo) kernels were mixed with pure Al powder and pressed into pellets using a manual hydraulic press [24]. Subsequently, annealing tests of the dispersion fuel model samples were carried out in vacuum sealed quartz tubes. The annealing temperatures were chosen to simulate to some degree the thermal component of the in-pile diffusion (340°C), the fabrication behavior (450°C) and the enhanced diffusion due to fission product recoils (550°C). From Figure 30, it can be concluded that only at temperatures as high as 550 °C, a substantial interaction between the fuel and Al occurs.

As the operating temperatures in research reactors are low, it is likely that the formation of the interaction layer in-pile is not resulting from thermally driven diffusion. This is confirmed by the post irradiation examination of a low enriched U(Mo)/AlSi dispersion fuel plate (from the E-FUTURE I experiment, chapter 6) irradiated up to an average burn-up of 65 % $^{235}$U.

![Figure 30](image1.png)

*Figure 30 Electron microprobe combined X-ray mappings (Al blue, U red and Mo green) show the interaction between a U(Mo) particle and the surrounding Al matrix at different annealing temperatures/times.*

The X-ray distribution map obtained with electronprobe micro-analysis (EPMA) in Figure 31 show clearly the presence of a stray depleted U(Mo) kernel identified thanks to the higher U Mα intensity (no burn-up of U) and absence of fission gas (Xe X-ray map). Compared to adjacent enriched particles at the interface of the depleted U(Mo) kernel with the Al matrix, no IL formed on the stray depleted U(Mo) particle (Figure 31 encircled in red).

![Figure 31](image2.png)

*Figure 31 U, Xe and Al X-ray map of a stray depleted U(Mo) particle (DU) in fuel plate U7MC6301 of the E-FUTURE I experiment.*
It should be concluded that the formation of an interaction layer in-pile is mainly resulting from intermixing of the fuel and matrix as the interface is bombarded by fission products.

Figure 32 Schematic representation of the formation of an interaction layer by radiation induced intermixing.

The fuel-matrix intermixing is in essence a ballistic process. Roughly a few thousand fission fragments pass through each µm² of kernel surface each second at moderate to high power, leading to a total fluence of the order of $10^{10}$ ions/µm² of kernel surface at maximum burn-up. The knock-on atoms (U, Mo, Al and coating material) will be displaced and intermixed (Figure 32). This intermixing will take place over only a few 100 nm, but as the burn-up increases, atoms will be displaced multiple times and eventually interaction layers of some 10 µm can be produced.

TRIM simulations [11] were done using a randomly oriented (0-90°) influx of fission fragments, assuming Mo and Xe ions with random energies ranging from 75-85 MeV, originating randomly from 0-5 µm deep in the U(Mo). Per fission event in the simulation, a few hundred atoms are displaced (directly by the incident ion or indirectly by the knock-on atoms), but less than 0.1% of the recoil atoms gain an energy of >1MeV and are displaced over larger distances.

Figure 33 The distribution of final recoil positions obtained by TRIM calculation of pure Al-U(Mo) system. The shaded area represents the layer in which there is a direct contact between Al and U(Mo).
Taking into account only the ballistic aspects of the ion mixing, Figure 33 shows the distribution of final recoil positions in a simulation of ion bombardment of respectively a pure U(Mo)/Al interface after 20000 ions. It is clearly seen that ion (or fission fragment) induced intermixing causes the creation of an interaction layer of up to 1 µm. TRIM does not simulate multiple recoils, so displaced atoms are not displaced again in the simulation. In pile, such multiple recoils will certainly occur, which can cause the interaction layer to grow further. Furthermore, the uranium incorporated in the IL will also undergo fission, leading to a new source of ion tracks.

2.1.2 Growth kinetics of the interaction layer

This section is largely based on following publications : [25]

Interdiffusion is the rate controlling process in the growth of an interaction layer in out-of-pile tests performed at high temperatures. Fick’s law of diffusion is given by \( J = -\frac{d\Delta C}{dx} \) with \( J \) the Al flux, \( D \) the Al diffusion coefficient and \( C \) the concentration of Al in the IL. The Al flux can also be expressed as \( J = \left( \frac{\rho}{M} \right) \frac{\partial x}{\partial t} \) where \( \rho \) and \( M \) are respectively the density and the molecular mass of the IL compound. Equating these two equations and integrating gives [25]:

\[
Y^2 = k \cdot t \quad \text{Eq. 3}
\]

with \( Y \) the thickness of the IL, \( k = \left( \frac{2M}{\rho} \right) \Delta C D \) the IL growth coefficient, \( \Delta C \) the absolute value of the Al concentration gradient across the IL. Assuming that the reaction product is invariant \( \left( \frac{2M}{\rho} \right) \Delta C \approx \text{constant} \) and expressing \( D \) as an Arrhenius type equation, the growth of the IL can be calculated using [25]:

\[
Y^2 = A \cdot t \cdot e \left( -\frac{Q}{RT} \right) \quad \text{Eq. 4}
\]

with \( Y \) the thickness of the IL (cm), \( A \) a pre-exponential constant, \( t \) the time (s) , \( T \) the absolute temperature (k), \( R \) the gas constant (8.31 J/mol.K) and \( Q \) the activation energy for interdiffusion (J/mol).

However, the fuel temperature of in-pile tests is much lower (<200 °C) than in out-of-pile tests which are usually performed at temperatures as high as 500 - 600 °C. Simple extrapolations to the low temperature regime of the IL growth correlations for out-of-pile tests yield orders of magnitude smaller IL thickness values. This implies that thermally activated diffusion must be augmented by fission enhanced diffusion during irradiation. As discussed in 2.1.1, in the displacement spikes the slowing down of fission fragments involves a process of rapid heating and quenching. In a more conductive medium such as a metallic fuel, dissipation of the thermal displacement spike to the surrounding medium and the restoration of local thermal homogenization will take place in a very short time. Consequently, the contribution to diffusion enhancement by thermal activation of a fission
event is less important than that from the generation and annihilation of defects that directly influence interdiffusion. The defect generation rate is proportional to the fission rate. Taking this into account, the growth rate of the IL formed in-pile can be calculated by modifying Eq. 5 by including a fission rate dependent term [25]

$$Y^2 = A \cdot \dot{\gamma}^x t \cdot e \left( -\frac{Q}{RT} \right)$$  \hspace{1cm} \text{Eq. 5}

with $Y$ the thickness of the IL, $A$ a pre-exponential constant, $\dot{\gamma}$ the fission rate, $x$ the exponent of the fission rate dependence, $t$ the time, $Q$ the activation energy for irradiation test which is related to the mobility of the vacancies, $R$ the gas constant and $T$ the temperature.

The pre-exponential constant $A$ and the activation energy $Q$, can be obtained by comparing the calculated interaction layer thicknesses and the results of the post irradiation examination (PIE). The activation energy is a function of the irradiation temperature as, amongst other factors, the composition of the IL is temperature dependent [26]. The activation energies for the in-pile data are about an order of magnitude smaller than those for the out-of-pile data because out-of-pile diffusion is more temperature dependent than in-pile diffusion. In-pile diffusion relies on vacancy migration that occurs at lower energies than the atom activation in out-of-pile diffusion [25].

![Figure 34 Calculated layer growth resulting from the interaction between U(Mo) and Al during irradiation at 120 °C, 150 °C, 180 °C and 200 °C.](image)

The interaction layer growth correlation employed in the DART- THERMAL fuel performance code [1] is developed by using mini-plate data and can be applied to U(Mo)/Al dispersion fuels irradiated at temperatures between 90 – 200 °C

$$Y^2 = 2.6 \times 10^{-16} \cdot \dot{\gamma}^{0.5} \cdot t \cdot \exp \left( -\frac{Q}{RT} \right)$$  \hspace{1cm} \text{Eq. 6}

In Figure 34 the growth of the IL formed in U(Mo)/Al dispersion fuel irradiated for 40 days is calculated using Eq. 6.
2.1.3 Observed interaction layers

2.1.3.1 UAlₓ/Al interaction
UAlₓ dispersion fuel, which has a typical composition around 63% UAl₃, 31% UAl₄ and 6% UAl₂ also reacts with the Al matrix during irradiation, even at low temperature [27] (Figure 36). UAl₂ and UAl₃ react with matrix Al according to the peritectoid reactions UAl₂+Al→UAl₃ and UAl₃+Al→UAl₄. Because there is no higher compound in terms of Al content than UAl₄, only UAl₄ stays stable with Al.

![Phase diagram for the Al-U system.](image)

Local X-ray analysis (EPMA) enriched UAlₓ fuel irradiated to a burn-up of 21% ²³⁵U, showed that the formed IL was metallic glas of composition U₀.₉Al₄ [4].

![Backscattered electron image of the IL resulting from interaction between UAlₓ fuel particles and the Al matrix.](image)
2.1.3.2 U-Si/Al interaction

\( U_3Si_2 \), \( U_3Si \), and USi react with Al (Figure 37) to form a single intermetallic compound, \( U(Al, Si)_3 \). The solubility of Al in \( U_3Si_2 \), \( U_3Si \), and USi is very small (<<1 at.%). \( U(Al, Si)_3 \) has a composition intermediate between \( UAl_3 \) and \( USi_3 \), both of which are mutually soluble [28]. The composition of the U–Si–Al interaction layer formed during an irradiation experiment is often described as \( U(Al, Si)_3 \) in reference to the out-of-pile experiments [29]. The composition of the interaction layer formed in \( U_3Si_2 \) plates irradiated up to an average burn up of 54% \(^{235}\)U (peak burn-ups of 87% \(^{235}\)U), was measured to be \( U_x(Al, Si)_y \) with \( y \sim 4.6 \) [8]. It should be kept in mind that also the U in the IL undergoes fission and the IL composition therefore will continuously evolve as more burn-up is accumulated.

![Figure 37 Backscattered electron image of the IL resulting from the interaction between the \( U_3Si_2 \) fuel particle and the Al matrix [8].](image)

2.1.3.3 U(Mo)/Al interaction

The ternary sections of the U–Mo–Al phase diagram (Figure 38) were assessed at room temperature on air-quenched samples heat-treated at 800 °C [30]. From the binary diagrams, it can be seen that at 800 °C the stable compounds \( UAl_2 \), \( UAl_3 \), \( Mo_3Al \), \( Mo_3Al_8 \) and \( Mo_4Al_{17} \) (in Figure 38 indicated by red dots) are formed. The solubility of Al in Mo is found to extend up to 12 at.% Al. The mutual solubility of Mo and Al in U extends up to 38 at.%Mo and 3%Al, forming a ternary field. The substitution of Al by Mo atoms in the cubic (MgCu\(_2\)) type binary \( UAl_2 \) leads to an extended solid solution \( UAl_{2-x}Mo_x \) up to \( x=0.5 \), but such substitution in \( UAl_3 \) is nearly negligible, being of the order of 1 at.%. Consequently, the substitution of Mo atoms to Al sites in the ternary extension of binary phases should lead to an \( U(Al_{2-x}Mo_x) \)-type notation, rather than the \( (U, Mo)Al_x \) commonly written in papers. We will nevertheless maintain this notation in this thesis as it is generally used throughout the field.
The formation of ternary compounds $\text{UMo}_2\text{Al}_{20}$ and $\text{U}_6\text{Mo}_4\text{Al}_{43}$ was also confirmed. However, the synthesis of ternary alloys with the stoichiometric composition $6:4:43$ shows a three-phase equilibrium $\text{UAl}_3 - \text{U}_6\text{Mo}_4\text{Al}_{43} - \text{UMo}_2\text{Al}_{20}$. X-ray diffraction and more clearly microprobe analysis revealed that these ternary intermetallic are typically non-stoichiometric, and show significant homogeneity ranges; $\text{U}_6\text{Mo}_{4+x}\text{Al}_{43-x}$ with $0 < x < 3$ and $\text{UMo}_{2-x}\text{Al}_{20+x}$ with $-0.3 < x < 0.75$ at 800 °C.

The red line in Figure 38 represents the intermixing path between the U7Mo fuel and the Al matrix. It crosses successively the tie-lines $\text{UAl}_3 - \text{UMo}_{2-x}\text{Al}_{20+x}$, $\text{UAl}_3 - \text{U}_6\text{Mo}_{4+x}\text{Al}_{43-x}$, and $\text{UAI}_{2-x}\text{Mo}_x - \text{U}_6\text{Mo}_{4+x}\text{Al}_{43-x}$. According to this path the (thermally activated) formed interaction layers at an $\text{U(Mo)}/\text{Al}$ interface at 800 °C would consist of:

\begin{center}
\begin{tabular}{c|c|c|c|c}
 & Al & Al+UAI$_3$+UMo$_{2-x}$Al$_{20+x}$ & UAI$_3$+UMo$_{2-x}$Al$_{20+x}$+U$_6$Mo$_{4+x}$Al$_{43-x}$ & U(Mo) \\
\end{tabular}
\end{center}

Ultimately, if a sufficient amount of Al is available, the U(Mo) fuel particles could be totally consumed to form the UAI$_{2-x}$Mo$_x$ phase, which itself is expected to be stable thermally and under irradiation [30]. The Al/U+Mo ratio of the first interaction layer (closest to the Al
matrix) ranges between 3 and 9, while for the layer close to the fuel the ratio Al/U+Mo ranges between 3 and 5.

As will be seen in the next chapter, the interaction layers formed in the in-pile tests have an average Al/U+Mo ratio ranging between 3.3 and 5 (Figure 39). It is very unlikely that a thermodynamic equilibrium will be reached in-pile. Again, continuous evolution of the stoichiometry can be expected as U is consumed by fission, ion mixing continues while the temperatures vary with the generated power (often declining with burn-up) and oxide formation (increasing unless with spalling). Furthermore, the in-pile IL is amorphous and differs markedly from the thermally generated ones.

![Backscattered electron image of the IL resulting from the interaction between the U(Mo) fuel particle and the Al matrix](image)

**Figure 39** Backscattered electron image of the IL resulting from the interaction between the U(Mo) fuel particle and the Al matrix [31].

2.2 Amorphization

*This section is largely based on following publications: [47-55]*

A large amount of radiation damage destroys the long- and short-range order in a crystal [32]. But the irradiation conditions determine whether and when a compound amorphizes or not. Hence, amorphization susceptibility is not simply a material property but depends also on the irradiation conditions [33]. A large number of uranium compounds and alloys have been found to become amorphous and exhibit glass-like behavior when exposed to irradiation.

Amorphization is easier at low temperatures, due to the absence of dynamic annealing. As the irradiation temperature is increased, different annealing stages corresponding to the activation energies of different defects are reached. These annealing stages make amorphization progressively more difficult until at the critical temperature \( T_c \), the annealing rate is larger than the damage rate and amorphization is no longer possible. The annealing mechanism activated at \( T_c \) does not allow the amorphous phase to reach the glass transition temperature \( T_g \) \( (T_g > T_c) \) [33]. Amorphization is thus a low temperature...
phenomenon as amorphized materials recrystallize at $T_g$. Above that temperature the material shows crystalline irradiation behavior. The glass transition temperature $T_g$ is always lower than the melting temperature, $(T_m)$, of the crystalline state of the material, if one exists. For uranium bearing compounds with a low melting point (Table 2), the glass transition temperature will also be low. For those compounds ($\text{U}_3\text{Si}$, $\text{U}_6\text{Fe}$, $\text{UA}_4$, .. ) amorphization during low temperature irradiation can occur readily.

<table>
<thead>
<tr>
<th>Uranium bearing compound</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2$</td>
<td>2875</td>
</tr>
<tr>
<td>$\text{U}_3\text{Si}_2$</td>
<td>1655</td>
</tr>
<tr>
<td>$\text{UA}_2$</td>
<td>1590</td>
</tr>
<tr>
<td>$\text{USi}_3$</td>
<td>1510</td>
</tr>
<tr>
<td>$\text{UA}_3$</td>
<td>1350</td>
</tr>
<tr>
<td>$\text{U}_9\text{Mo}$</td>
<td>1160</td>
</tr>
<tr>
<td>$\text{U}_3\text{Si}$</td>
<td>930</td>
</tr>
<tr>
<td>$\text{U}_6\text{Fe}$</td>
<td>815</td>
</tr>
<tr>
<td>$\text{UA}_4$</td>
<td>731</td>
</tr>
<tr>
<td>$\text{U}_6\text{Mn}$</td>
<td>725</td>
</tr>
</tbody>
</table>

Table 2 Melting points of uranium bearing compounds [34,35]

Gibbs free energy of formation of a compound ($\Delta G=\Delta H-T\Delta S$) is the measure of the stability of a compound or the spontaneity of a reaction or transformation. Although non-equilibrium conditions prevail during irradiation, thermodynamic analysis is still a reliable method to predict the real situations. Since enthalpy is the dominant part of Gibbs free energy, knowing enthalpy of formation of a compound provides an approximate measure of how stable the compound is relative to other comparable compounds.

Miedema’s model [36] analytically assesses the enthalpy change during mixing of two elements by using an empirical correlation. The correlation for the formation enthalpy of an AB binary is given by

$$\Delta H_f = c_A f_B^A \frac{2AV_A^{2/3}}{(n_{ws A}^{-1/3} + n_{ws B}^{-1/3})} \left\{ -P(\Delta \varphi)^2 + Q(\Delta n_{ws}^{1/3})^2 - R \right\}$$  \hspace{1cm} \text{Eq. 7}

where $\Delta H_f$ is given in kJ/mol of atoms, $c_A$ the concentration of A, $f_B^A$ is the degree to which A atoms are in contact with B atoms, $V$ is the atomic volume, $n_{ws}$ is the electron density, $\varphi$ is the electronic charge and $P$, $Q$ and $R$ are constants fitted to experimental data.

Miedema’s model can also be used to determine the glass forming range of a particular alloy system. An amorphous phase can be formed if the enthalpy of formation of the amorphous phase is less than that of the solid solution phase. The enthalpy of formation of a solid solution comprises of three components; chemical, elastic and structural contributions.
\[
\Delta H_{ss} = \Delta H^\text{chem} + \Delta H^\text{elas} + \Delta H^\text{struct}
\]  
\(\text{Eq. 8}\)

\(\Delta H^\text{chem}, \Delta H^\text{elas} \) and \(\Delta H^\text{struct}\) are the chemical, elastic and structural contributions of enthalpy respectively. The chemical contribution of enthalpy is represented as:

\[
\Delta H^c = X_A X_B \left[ X_A \Delta h^\text{Sol}_{B \text{ in } A} + X_B \Delta h^\text{Sol}_{A \text{ in } B} \right]
\]  
\(\text{Eq. 9}\)

where \(X_A\) and \(X_B\) are the mole fraction of the A and B atoms respectively, and \(\Delta h^\text{Sol}\) is the enthalpy of solution for one element into another at infinite dilution.

The elastic contribution of enthalpy is directly related to lattice mismatch energy and it is calculated based on the atomic size difference between solute and the solvent atoms:

\[
\Delta H^e = X_A X_B \left[ X_A \Delta h^e_{B \text{ in } A} + X_B \Delta h^e_{A \text{ in } B} \right]
\]  
\(\text{Eq. 10}\)

\(\Delta h^e\) is calculated from

\[
\Delta h^e_{i \text{ in } j} = \frac{2\mu_j (V_i - V_j)^2}{V_j (3 + 4\mu_j K_i)}
\]  
\(\text{Eq. 11}\)

with \(\mu_j\) the shear modulus of the solvent, \(V_i\) and \(V_j\) are the molar volumes of the solute and solvent respectively and \(K_i\) is the compressibility of the solute.

The structural contribution to enthalpy, which arises from the valence and crystal structure of the solute and the solvent atoms, is said to have a very minor contribution and is neglected.

In the case of an amorphous phase, the elastic contributions are not important because there is no periodic structure, and so the atoms are not constrained to fit in a certain volume. The enthalpy of the amorphous phase formation is based on the chemical contribution of the enthalpy and the enthalpy of melting of the individual components and is obtained by the following equation:

\[
\Delta H_{\text{amorph}} = \Delta H^c + \alpha (X_A T_{m,A} + X_B T_{m,B})
\]  
\(\text{Eq. 12}\)

with \(\Delta H^c\) the chemical term (taken equal to the chemical term of the solid solution), \(X_i\) the mol fraction of elements A and B, \(\alpha\) a constant obtained by fitting = 3.5 J/mol atoms [37] and \(T_{m,i}\) the melting temperature of the ith component.

For all calculations hereafter, the Miedema calculator designed by R.F. Zang et al. is used [38,39].

The shape of the enthalpy composition curves for solid solution and amorphous phases for U with different elements can give a clue as to how the alloy behaves at low temperature where entropy contribution will be low and free energy of the alloy is mostly dominated by
the enthalpy. Systems with a negative $\Delta H$ show spontaneous intermixing whereas in the positive $\Delta H$ systems the non-equilibrium alloys have to survive a thermodynamic driving force for phase decomposition.

2.2.1 U-Si and U-Al system

As is clear from Figure 40, the measured enthalpies of the crystalline U–Si alloy are more than a factor of two smaller than the Miedema-calculated quantities. As such, the calculated formation enthalpy for an amorphous liquid U–Si and U-Al alloys is over predicted. This discrepancy could be due, in part, to the application of the Miedema semi empirical method, which is in principle only valid at 0 K, to higher temperatures. In addition, the presence of Si–Si bonds pushes the limits of applicability of the Miedema method which is primarily intended for metals [40]. The key assumption here is that although the Miedema estimate is not quantitative, the method provides a reasonable estimate of the shape of the formation enthalpy vs. composition curve.

The more negative enthalpy of formation for the U-Si systems indicates that these compounds are more readily formed compared to the U-Al alloys.

U–Si and U-Al compounds are amorphous during irradiation because the glass transition temperature for U-compounds is much higher than typical fuel operation temperatures (~120 °C).

![Figure 40 Enthalpies of formation of U–Si and U–Al alloys. The solid lines are the predictions calculated using the Miedema model [38,39,40], while the symbols are measured data points that can be found in literature [41,42].](image)

All uranium aluminides and silicides undergo amorphization, depending on the fission rate and temperature. Therefore, the reaction products of these fuels with Al are also subject to amorphization. The lower the irradiation temperature and the higher the fission rate, the more the tendency of amorphization. Among the three, UAl$_4$ is the easiest and UAl$_2$ is the hardest for amorphization, while for the silicides U$_3$Si amorphizes more readily than U$_3$Si$_2$. 

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2.2.2 U-Mo and U-Zr system

In general the tendency for the formation of amorphous alloys has been largely seen in systems that exhibit negative heat of mixing ($\Delta H$). However, there are many elements that do not form alloys at room temperature and pressure due the absence of a driving force. These are the “immiscible systems,” in which the two constituent elements show little or no mutual solubility up to very high temperatures, even in the liquid state. They are characterized by a large positive $\Delta H$ in both the liquid and solid states. There are other systems, that have a positive $\Delta H$ but its magnitude is not as large to prevent the elements from mixing. This is due to the entropic contribution to the free energy of mixing at high temperatures. But at lower temperatures, such as room temperature, the positive $\Delta H$ dominates, leading to phase separation, where the constituent elements become immiscible, exhibiting very small mutual solid solubility and no intermediate phases [43].

![Figure 41 Enthalpies of formation of U-Mo and U-Zr alloys. The solid lines are the predictions calculated using the Miedema model [38,39,40].](image)

The enthalpy of formation for the U-Mo and U-Zr system of the crystalline (Figure 41), amorphous phase and the solid solution are higher than zero for all compositions, thus suggesting that they are thermodynamically unstable. The convex upward enthalpy of solid solution in both systems also indicates a tendency of phase separation at low temperature over long period of time leading to the formation of solid solutions of different compositions or intermetallic phases.

2.2.3 U-Fe and U-Mn system

For the U-Mn systems (Figure 42), the energy of formation of both the amorphous phase and the crystalline solid solution are higher than zero for all compositions. So there is no chemical driving force to form either an amorphous state or a crystalline solid solution from the elemental components.
Figure 42 Enthalpies of formation of U–Fe and U–Mn alloys. The solid lines are the predictions calculated using the Miedema model [38,39,40], while the symbols are measured data points that can be found in literature [32].

The energy of formation of the amorphous phase (Figure 3), for U₆Fe and U₆Mn is lower than that of the crystalline solid solution, i.e. during irradiation the amorphous phase is energetically preferred over the solid solution.

2.2.4 Amorphization in real fuel systems

As was shown in 2.1.1 the formation of an interaction layer in-pile is mainly resulting from bombarding the fuel/matrix interface with fission fragments creating thermal spikes. The heat produced in such a spike can be high enough to increase the local lattice temperature above the melting point of the material [44]. The diffusivities of metals in a liquid state are factors of 100 to 1000 times larger than diffusivities in a solid state. The latent heat is diffused through the crystal lattice quickly enough to freeze the molten volume without allowing crystallization. Consequently, the formed intermixing layer can become amorphous and has a glass-like behavior.

As described in 2.2.1, all three uranium aluminides undergo amorphization, depending on the fission rate and temperature. Therefore, the reaction products of uranium with Al are also subject to amorphization.

Figure 43 Both the featureless nature of the dark field image and the diffuse ring in the diffraction pattern show that the core of the UAlₓ fuel kernel and interaction layer are amorphous [45].
TEM investigation evidenced that high enriched UA_{x} fuel (90 % 235U enriched UA_{x} fuel dispersed in an Al matrix), irradiated to a burn-up of 21 % 235U, was amorphous after irradiation [45] (Figure 43).

The U–Si intermetallics (U₃Si and U₃Si₂) also become amorphous during irradiation, and TEM by J. Gan [46] showed that the reaction product between the fuel and matrix, U₃Si₂/Al, also undergoes amorphization.

The U(Mo) alloy is one of the rare metallic fuels that does not amorphize during irradiation up to fission densities found in LEU fuels. However it was shown that the reaction product between the fuel and the matrix, (U, Mo)Alₓ, becomes amorphous [47,48]. Not only the interaction layer, but also the layer between the cells of the U(Mo) atomized particles shows this amorphous nature (Figure 44).

2.3 Fission products

Fission products in nuclear fuel can be classified into categories based on their chemical state. The elements Kr, Xe, Br, I are volatile products but most other fission products are in solid form. Some of these solid fission products will remain in solid solution during operation while others will form metallic or oxide precipitates (only in ceramic oxide fuels).

The most abundant gases created from fission are the noble gases Kr and Xe (approximately 1/3 of all fissions). These gases, being largely insoluble in all materials, tend to precipitate into small gas bubbles and have a large impact on the microstructure and the swelling.

It is generally accepted [21] that bubbles nucleate in the wake of fission spikes because many bubbles are found in randomly oriented straight lines. According to Turnbull [49] the fission fragment creates a large amount of vacancies that agglomerate and form a cavity. This cavity can trap very quickly a few gas atoms, creating the initial bubble. TEM observations on UO₂ samples irradiated to a low dose of 10²² fissions/cm³ at 1000 °C show bubbles lying in a straight line, indicated that it was the fission fragment that spontaneously nucleated the bubbles in this aligned configuration [49]. During irradiation a significant amount of gas is building up continuously and thus gas bubbles, even when somewhat
rearranged by fission spikes, still form the best nuclei on which other gas atoms can precipitate [50]. The equilibrium condition is dynamic, since bubbles (particularly nanobubbles) are constantly destroyed by fission spikes, but we will not elaborate further on this here.

Transmission electron microscopy (TEM) of irradiated metallic U(Mo) fuel (Figure 45a) revealed also nanosized gas bubbles but located on an ordered superlattice. Formation of such gas bubble superlattice has also been observed in many metals after implantation with He gas [51,52,53] at temperatures below 0.2 \( T_m \) where \( T_m \) is the melting temperature (in K) of the metal. Electron diffraction from these He irradiated metals exhibit diffraction spot splitting with satellite spots around the matrix reflections. A similar observation was made, for the first time by Van den Berghe et al. [48], also on irradiated U(Mo) (Figure 45b).

![Figure 45](image)

**Figure 45** Bright field image of the bubble superlattice found in the U(Mo) particles. This image was taken at slightly underfocus conditions to reveal the bubble structure more clearly. b) Corresponding diffraction pattern, where the inset shows an enlarged image of the reflection indicated by the square. Diffraction spot splitting with satellite spots around the matrix reflection can be clearly seen.

Figure 46 shows a gas-filled bubble of radius \( r \) embedded in a solid medium that is subject to uniform hydrostatic stress \( \sigma \). The pressure \( p \) inside the bubble is given by the Laplace equation

\[
P = \frac{2\gamma}{r} + \sigma \quad \text{Eq. 13}
\]

with \( \gamma \) the surface tension. At equilibrium, the gas pressure acting to expand the bubble is just balanced by the hydrostatic stress in the solid and the surface-tension forces that tend to contract the bubble.

Bubbles grow by adding gas atoms to the bubble which increases the pressure. The compression around the bubble attracts vacancies which make the bubble grow. As such \( R \) increases and the pressure \( P \) drops and eventually equilibrium is reestablished.
According to Olander [21], sometimes the equilibrium relation Eq. 13 is not valid. Nanobubbles formed in fissile material may be able to accumulate fission gas atoms more rapidly than the bubble can expand to satisfy Eq. 13. Although vacancies and interstitial are produced plentiful in irradiated fissile materials, if the flow of vacancies to the bubble is not large enough to provide the volume increase needed to compensate for the increasing number of gas atoms collected by the bubble, an excess pressure can develop.

When a pressure excess (or deficit) develops in the bubble, there will be stress gradients in the vicinity of the bubble. Any imbalance between the interface and bulk stresses can be relieved by vacancy flow for small bubbles; large bubbles can attain mechanical equilibrium with the surrounding solid by plastic deformation.

![Figure 46 Gas-filled bubble in mechanical equilibrium with a solid under hydrostatic stress.](image)

The formation of fission gas bubbles and solid fission product precipitates having different atomic volumes from the fissioned uranium atoms, will contribute to the swelling of the fuel plate.

### 2.4 Swelling of U(Mo)

#### 2.4.1 Fission product induced swelling

*This section is largely based on following publication:* [22]

As is the case for any type of fuel element, acceptable irradiation behavior of dispersion fuel means

- dimensional stability of the fuel plate to high fissile burn-up under expected operating conditions so that no significant changes in reactivity and coolant flow result
- the absence of cladding failure to preclude fission product release to the environment

Dimensional changes usually manifest themselves as increases in fuel plate thickness (Figure 47). The cladding volume will be almost completely unaffected by irradiation so the changes occurring should be attributed to changes in the fuel/meat thickness.
Meat swelling in U(Mo)/Al dispersion fuel is a combined effect resulting from the accumulation of fission product elements (solid and gaseous) and fuel microstructural changes which include the formation of an interaction layer and irradiation-enhanced sintering of fabrication voids (porosity).

For dispersion fuel this swelling can be relatively large because of the high burn-up achieved and the fact that a fuel is chosen that retains the fission products well and no plenum (open volume) is present in the fuel plate design.

The total swelling of the fuel plate can be represented by

\[
\left( \frac{\Delta V}{V_0} \right)_{\text{total}} = \left( \frac{\Delta V}{V_0} \right)_g + \left( \frac{\Delta V}{V_0} \right)_s + \left( \frac{\Delta V}{V_0} \right)_{RP}
\]

with \( \left( \frac{\Delta V}{V_0} \right)_g \) the gaseous fission products, \( \left( \frac{\Delta V}{V_0} \right)_s \) the swelling resulting from the solid fission products and \( \left( \frac{\Delta V}{V_0} \right)_{RP} \) the swelling resulting from the formation of an interaction layer.

During the fabrication process, voids and microcracks are left in the dispersion fuel meat. These porosities help to accommodate fission products and to buffer volume increase during reactor operation. Once the as-fabricated pores are at least partially sintered shut, the fuel meat starts to swell [1]. For fuel plates with atomized fuel particles, the delay in swelling accommodated by fabrication porosity is generally negligible. This is not the case for ground fuel where fabrication porosity is much more prominent.

2.4.1.1 Fission gas swelling

The swelling resulting from gaseous fission products is affected by many parameters including burn-up, temperature, fission yield, etc. [18]. At low burn-up the fission gas atoms diffuse and nucleate and a nanobubble lattice is formed inside the fuel grains. With increasing fission density, the gas bubbles will grow and contribute significantly to the fuel swelling.
According to Olander [21] the volume increase resulting from the formation of \( N' \) bubbles of radius \( R \) per unit of solid fuel is

\[
\frac{\Delta V}{V_0} = \left( \frac{4\pi r^3}{3} \right) N' \tag{Eq. 15}
\]

Measurements of bubble densities during PIE determines \( N \), the number of bubbles per unit of total volume (solid + bubbles). The relation between \( N' \) (the number of bubbles per unit solid) is

\[
N' = \frac{N}{1 - \left( \frac{4\pi r^3}{3} \right) N} \tag{Eq. 16}
\]

Assuming that the fractional swelling is small and all bubbles have the same radius, a simplified and general fractional swelling due to fission gas bubbles can be defined as

\[
\frac{\Delta V}{V_0} = \left( \frac{4\pi r^3}{3} \right) N \tag{Eq. 17}
\]

Upon recrystallization, the nanobubble lattice inside the fuel grains gets destroyed and the overpressurized bubbles are released and coalesce into larger intergranular bubbles resulting in an increased swelling behavior.

Using the ideal gas law and Eq. 13 (ignoring the hydrostatic stress), the number of gas atoms stored in a nanobubble can described as

\[
n = \frac{p.V}{RT} = \frac{8\pi}{3} \cdot \gamma \cdot r^2 \tag{Eq. 18}
\]

As the total number of gas atoms in all fission gas bubbles \( n.N \) equals a constant and using eq.18 it can be stated that the number of bubbles \( N \sim \frac{1}{r^2} \). The total swelling resulting from fission gas atoms is thus proportional to the radius of the bubble the gas is in :

\[
\frac{\Delta V}{V_0} \sim \left( \frac{4\pi r^3}{3} \right) \frac{1}{r^2} \sim r \tag{Eq. 19}
\]

This means that for an equal amount of fission gas atoms, the swelling is larger in case these atoms are incorporated in large bubbles than when trapped in nanobubbles.

### 2.4.1.2 Solid fission product swelling

The volume change due to solid fission products that precipitate is related to the partial volume of the solid fission product. The partial volume of these compounds can be larger than the host material's partial volume leading to a net swelling [18]. A common method to estimate solid fission product swelling as a result of irradiation is by using Anselin’s calculation [54]. Olander [21] summarized it as follows:
 \[
\left( \frac{\Delta V}{V} \right)_s = \left( \sum_{solid\,fp} Y_i \frac{v_i}{v_U} - 1 \right) \beta \]

Eq. 20

with \( v_i \) and \( v_U \) respectively the partial volume of a solid product \( i \) and of uranium; \( Y_i \) the elemental yield of a solid FP for \(^{235}\text{U}\) irradiated 1 year in a fast neutron spectrum and cooled 15 days; and \( \beta \) the fractional burn-up.

Little is known on the chemical state of the solid fission products in irradiated U(Mo) fuel and in current modeling the contribution of solid fission product to the overall plate swelling is assumed to be a constant linear evolution with increasing burn-up.

However if we would calculated the partial volume and swelling resulting from the most common (yield > 1%) solid fission products formed in dispersion U(Mo) fuel (Table 3), it is found that the increase in total volume due to non-soluble fission products amounts to approximately 1% of the fuel volume per percent burn-up. On the other hand, elemental X-ray distribution maps recorded with electronprobe microanalysis (EPMA) show that Zr and Mo stay in solid solution with U(Mo) up to very high burn-up. Taking also in account that Zr has a high solubility limit in U, the fuel swelling caused by solid FP would show an increase of 0.64% per atom percent burn-up. This is comparable to the calculation performed by Liu et al [55] showing that the solid swelling \( \frac{\Delta V}{V} \) \(_{solid} \) = 0.5% \( \beta \), with \( \beta \) the burn-up.

<table>
<thead>
<tr>
<th>Fission product</th>
<th>Yield ( Y_i ) (%)[54]</th>
<th>Partial volume ( v_i )</th>
<th>( \frac{Y_i}{v_i} )</th>
<th>( \frac{v_i}{v_U} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>24.0</td>
<td>15.58</td>
<td>0.178</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>6.2</td>
<td>14.31</td>
<td>0.042</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>14.9</td>
<td>13.57</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>3.5</td>
<td>13.75</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>1.7</td>
<td>14.72</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
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<td>33.87</td>
<td>0.291</td>
<td>0.291</td>
</tr>
<tr>
<td>Zr</td>
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<td>22.28</td>
<td>0.307</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>6.3</td>
<td>63.55</td>
<td>0.191</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>4.4</td>
<td>33.0</td>
<td>0.069</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>14.4</td>
<td>34.0</td>
<td>0.234</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>8.6</td>
<td>56.19</td>
<td>0.231</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>18.8</td>
<td>35.0</td>
<td>0.314</td>
<td></td>
</tr>
<tr>
<td>( \sum )</td>
<td></td>
<td></td>
<td>1.989</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 The fuel swelling due to solid fission products using partial volumes.

It would also be possible that all solid fission products remain within the matrix during normal operating conditions, which for metallic fuel is most likely. In that case the swelling rate of the fuel would be defined by an increase in the lattice constant of the fuel crystal. The X-ray diffraction measurements on U-7.4 wt% Mo samples irradiated up to a burn-up of \( \sim 45 \% \) \(^{235}\text{U}\) and \( \sim 67 \% \) \(^{235}\text{U}\), show an increase of the \( \gamma\text{U} \) lattice parameter of respectively 0.37% and 0.39%. Such an increase of the U lattice parameter results in a swelling increase
of the unit cell volume by 1.16% at a burn-up of ~67% $^{235}$U. However, a continuous generation of radiation induced defects (interstitial loops) induces an internal stress in the material which also leads to strain in the form of lattice displacement.

The observed fuel swelling is most probably due to a combination of the swelling caused by the partial volume of the solid FP precipitates and the increase in $\gamma U$ unit cell volume initiated by soluble fission products.

2.4.2 Swelling related to the formation of interaction layers

There might be another type of swelling, which is related to the formation of the layer around the kernels resulting from the interaction of the fuel with the surrounding matrix during irradiation. If the density of this IL is not the same as the average of the reaction constitutes this would contribute to the overall swelling. In such a case can the increase in volume resulting from the depletion of high density U(Mo) fuel and accumulation of low density reaction product be calculated as:

$$\left(\frac{\Delta V}{V_0}\right)_{RP} = \frac{M_{RP}}{\rho_{RP}} \frac{\rho_{RP}}{\rho_{fuel}} - 1$$

where $V_{RP}$ is the volume of the interaction layer; $M_{RP}$ the molecular weight of the interaction layer which equals $M_{fuel} + xM_{matrix}$ with $M_{fuel}$ and $M_{matrix}$ the molar weights of the fuel and matrix, $x$ the the Al stoichiometry in $(U_{a}Mo_{1-a})Al_x$. $\rho_{RP}$, $\rho_{fuel}$, $\rho_{matrix}$ are respectively the densities of the interaction layer, fuel and matrix. As mentioned in 2.1.3.3, the interaction between U(Mo) fuel particles and the Al matrix results in the formation of an U(Mo)Al$_x$ with $x$ between 3.3 and 5. Assuming that the IL is homogenously composed of U(Mo)Al$_3$, which has a density of 6.8 g/cm$^3$ [57], the volume increase resulting from the formation of such an IL would be 3.6% according to Eq. 21. For the formation of a U(Mo)Al$_4$ IL, with a density of 5.7 g/cm$^3$ [57] the swelling would be 4.6%.

However, as the IL is amorphous, it can also be assumed that the interaction layer has no influence on the swelling. This would mean that the volume fraction of the IL consists of a proportional volume U(Mo) and Al. For the formation of a U(Mo)Al$_3$ layer and taking the atomic volumes (atomic weight over density, i.e Al=10 mol/cm$^3$ and U(Mo)= 12.9 mol/cm$^3$), this would mean that approximately 80% of the volume from the IL originates from the matrix and 20% from the fuel. Using these assumptions, the swelling of the fuel ($FSw$) and matrix ($MSw$) can be calculated from the volume fractions and meat thickness relative to the initial values:

$$FSw = \frac{(Vol\%_{m,F} \times T_m) - [(Vol\%_{i,F} \times T_i) - (Vol\%_{m,IL} \times T_m \times 0.2)]}{(Vol\%_{i,F} \times T_i)}$$  Eq. 22

$$MSw = \frac{(Vol\%_{m,M} \times T_m) - [(Vol\%_{i,M} \times T_i) - (Vol\%_{m,IL} \times T_m \times 0.8)]}{(Vol\%_{i,M} \times T_i)}$$  Eq. 23
with $Vol\%_{m,M}$ and $Vol\%_{i,M}$ respectively the measured and initial volume fraction of fuel ($X=\text{F}$) and matrix ($X=\text{M}$), $T_m$ and $T_i$ respectively the measured and initial meat thickness.

The meat thickness and the volume fraction occupied by the different phases in the meat can be measured during PIE (from SEM images) and using image processing software. Similar as for the Al cladding no contribution to the increase of plate thickness from the Al matrix is expected. If the assumptions stipulated here above are correct, the resulting net swelling of the matrix should be zero.

2.4.3 Restructuring

During the non-destructive post irradiation examination, the thickness of the fuel plate as well as of the oxide layer is measured. From the oxide corrected plate thickness and assuming that the cladding and matrix do not contribute to the thickness increase, the fuel swelling as a function of the burn-up can be plotted. (More detailed information can be found in the next chapters).

![Figure 48 Fuel swelling in function of fission density as measured on fuel plate U7MC4111. The red lines represent the linear fitting of the data prior and after the start of the restructuring.](image)

In 2.4.1 it was shown that the fission product swelling of fuel is a linear function of burn-up. However from several irradiation experiments and their PIE (NDT) campaigns, it is observed that at a fission density between $2.5 \times 10^{21}$ and $3.5 \times 10^{21}$ fissions/cm$^3$, the fuel swelling rate increases (Figure 48). Above that fission density also in the microscopy images of samples having different burn-ups, a visible change in the fuel microstructure is detected (Figure 49).

This microstructural change resembles what is coined the “rim effect” by the light water reactor fuel community. It consists of a transformation of the original grain of the fuel into a very refined grain structure with a much smaller grain size.

Currently still no consensus is reached on the terminology to define the process that takes place. Terms often used in Fuel literature are restructuring, high burn-up structure (HBS), recrystallization, grain refinement, ... This leads to confusion and it is suggested by Detavernier et al. [58] to use the well-defined terminology used in the metallurgical
literature. After cold work (e.g. rolling), the microstructure of a bulk material contains a lot of defects. During subsequent annealing several processes are known to take place within the deformed microstructure:

- **Polygonization**: Recovery consists of the annihilation of point defects and dislocations and the spontaneous rearrangement of dislocations into low-angle subgrain boundaries.
- **Recrystallization**: The formation of large defect-free grains that are separated from the defected regions by a high-angle grain boundary. The driving force for recrystallization is the stored energy in the form of point (vacancies and interstitials), line (dislocations), and planar (stacking faults) defects within the deformed grains, and is typically of the order of $100 \text{ J/cm}^3$.
- For some materials and sample geometries, secondary recrystallization has been observed. This process is characterized by a bimodal grain size distribution. Certain grains are believed to be able to grow much faster than the average grain because they have a boundary with a very large mobility and/or because they experience an additional driving force for grain growth (e.g., minimization of surface and/or strain energy in addition to the minimization of grain-boundary area).

![Image](image-url)

Figure 49 The influence of the fission gas on the microstructure of atomised and ground fuel at different burn-ups.

However in order to distinguish between polygonization or recrystallization extensive microscopy (e.g. TEM) is needed but this is not evident for irradiated materials. Despite the fact that most specialists seem to agree that the mechanism involved is a polygonization process [59], it is chosen to use the term recrystallization in the remainder of this thesis.

There have been various models developed to explain the restructuring [60]:

- **Model by Matzke and Spino and Kinoshita [61,62,63]**: recrystallization of the grains is a consequence of the overpressurization of the nm-sized bubbles due to fission gas
accumulation (see 2.3). This very high pressure in the nm-sized bubbles causes stress in the grain. Micro-cracking and cleavage into smaller sub-grains is the consequence, with grain sizes in the average distance between these nm-bubbles. The formation of the large µm-sized pores can be explained as a consequence of an athermal and fission induced diffusion of the fission gas to the large number of new grain boundaries of the subdivided grains. Some bubbles grow and, due to their size, get insensitive to the process of constant formation and annihilation (re-solution by fission fragments). They continue to capture gas, and therefore grow into µm-sized pores containing most of the fission gas.

- Model by Nogita and Une [64,65,66]: recrystallization is caused by accumulation of radiation damage (e.g. dislocations) and lattice strain (e.g. by Pu breeding). With increasing burn-up, the as-fabricated grains are divided in 20-30 nm small sub-grains with high-angle boundaries. These sub-grains act as nuclei for growth by recrystallization. The driving force for this recrystallization is the accumulated strain energy during creation of radiation induced defects. The small intra-granular nm-sized bubbles are formed by clustering of gas atoms and vacancies. These bubbles grow and during this grain growth, the moving grain boundaries sweep gas atoms and bubbles. They are coalescent at preferential sites within the matrix and form µm-sized pores (grain subdivision and Xe migration). The large number of new grain boundaries also enhance the gas diffusion to pores [67]. This model predicts the start of bubble formation at grain boundaries, which is well confirmed.

These two models indicate two different sequences of the formation of the pores and the sub-grains. However, experimentally these two features have been always observed together. There seem to be strongly interdependent mechanisms, and no evidence for the order of these processes has been described so far.

![Figure 50 Recrystallization starts at the cell boundaries(a) and progresses towards the cell center (b).](image)

Both models indicate that

- The initiation of restructuring occurs predominately along the preexisting grain boundaries (Figure 50a). Subsequently, the restructuring front moves toward the grain center eventually consuming the entire grain (Figure 50b). The volume fraction of recrystallized material is thus a function of irradiation time as well as the initial fuel grain size. The burn-up or fission density at which grain refinement is predicted to initiate is athermal and very weakly dependent on fission rate.
The large number of new grain boundaries causes enhanced diffusion of the fission gas to the µm-sized pores. Swelling caused by gaseous fission products will thus be higher in the recrystallized material than in the unrecrystallized fuel[68].

2.4.4 Total meat swelling

This section is based on following publication : [22]

Given that the swelling caused by the fabrication porosity and the formation of the interaction layer is negligible, the total meat swelling can be simplified to:

\[
\frac{\Delta V}{V_0} = \frac{\Delta V}{V_0}_g + \frac{\Delta V}{V_0}_s
\]

Eq. 24

This means that the swelling behavior of dispersion fuels can be generalized as follows (Figure 51): the solid fission products show a linear behavior up to high burn-up. However, the swelling curve resulting from the gaseous fission products shows two domains: at low burn-up there is an initial linear stage with a low swelling rate but, dependent on the type of fuel, after a critical burn-up the swelling rate will increase. As was shown above, this second linear stage is associated with restructuring of the fuel. Both stages can be considered to represent stable fuel swelling.

A third stage may occur when the fission gas bubbles link up and coarsen in either the fuel particles, fuel matrix reaction products and/or radiation damaged matrix material. This stage represents the unstable or breakaway swelling.

Figure 51 Schematic representation of the swelling behavior of irradiated dispersion fuel plates.

Kim et al [19] obtained from irradiation tests an empirical correlation on the swelling of U(Mo) fuel in both domains. However, these correlations are based on measurements
performed on monolithic fuel. Compared to dispersion U(Mo), monolithic fuel has no matrix and as such there is no formation of an interaction layer and the as fabricated porosity is also negligible.

They described the first domain in the swelling curve prior to restructuring (stage 1) as

\[
\left( \frac{\Delta V}{V_0} \right)_{\text{total}} = 5.0 f_d \quad \text{for } f_d \leq 3 \times 10^{21} \text{ f/cm}^3 \quad \text{Eq. 25}
\]

Of this 5% swelling, Kim et al state that 1% is resulting from μ-sized fission gas bubbles that can be measured from microscopy images (SEM or OM) on monolithic fuel. The remaining 4% swelling should be attributed to:

- Solid fission products: as shown in Table 3, this can amount to almost 1% if all solid fission products would precipitate. Those remaining in solid solution contribute by increasing the U(Mo) lattice parameter.
- Fission gas contained within nanobubbles.

After the critical burn-up of restructuring initiation (stage 2) an increase swelling rate is observed and fitted by the expression:

\[
\left( \frac{\Delta V}{V_0} \right)_{\text{total}} = 15.0 + 6.3(f_d - 3) + 0.33(f_d - 3)^2 \quad \text{for } f_d > 3 \times 10^{21} \text{ f/cm}^3 \quad \text{Eq. 26}
\]
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6589-6594.
Introduction to the experimental part

In the next chapters some of the irradiation experiments performed in the framework of qualifying a viable U(Mo) dispersion fuel for the conversion of several high power Research Reactors, are described. It concerns mostly European initiated programs for which SCK•CEN performed the irradiation at the BR2 reactor and/or post-irradiation examinations at the Laboratory for High and Medium Activity. Next to these irradiations campaigns SCK•CEN also performed several additional out of pile studies to gain a better understanding of the phenomena that were occurring.

It should however be emphasized that the qualification of a U(Mo) dispersion fuel is a collective theme to which many researchers all over the world have contributed. For more than a decade numerous irradiations programs were performed especially in the US (the RERTR experiments performed at ATR) each leading to a better understanding of the U(Mo) fuel behavior. The results of most of these programs and studies have been published in open literature or were presented at conferences such as the European Research Reactor Fuel Management (RRFM) conference or the International Reduced Enrichment for Research and Test Reactors (RERTR) meeting.
Chapter 4 The FUTURE experiment

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Summary

As reference fuel solution for the Jules Horowitz Reactor (RJH) project, the development of an optimized and reprocessable LEU fuel was (and still is) of high importance for the French Commissariat à l’énergie atomique (CEA). In order to reach these goals, CEA launched a large program on the development of dispersion U(Mo) fuels. The third experiment in this program (after the IRIS-1 and IRIS-2 experiments) was called FUTURE-UMO-1. Two low-enriched uranium fuel plates consisting of U–7wt%Mo atomized powder dispersed in an aluminum matrix, have been irradiated in the FUTURE irradiation rig of the BR2 reactor at SCK•CEN. The plates were submitted to a heat flux of maximum 353 W/cm² while the surface cladding temperature is kept below 130 °C. The objective of the irradiation was to reach a maximum local burn-up of 70% (5.3×10²¹ fissions/cm³). After 40 full power days, visual examination of the fuel plates revealed an increase of the plate thickness. In view of this observation, the irradiation campaign was prematurely stopped and the fuel plates were retrieved from the reactor, having at their end-of-life a maximum burn-up of 32% ²³⁵U (2.3×10²¹ fissions/cm³). Extensive post irradiation examinations (PIE) were performed on the fuel plates. The non-destructive analyses revealed the presence of important local swelling or pillowing in the highest burn-up locations of the fuel plates. The microstructure examination showed that the U(Mo) fuel particles interacted with the Al matrix, resulting in an interaction layer surrounding the fuel kernels. The growth of that interaction layer causes an increase of the fission products concentration at the interface of the interaction layer and the matrix. These halos were identified as weak spots in the meat structure where cracks would initiate if the local stresses, for example related to the normal gradual swelling of the fuel with burn-up accumulation, exceed the fracture strength of the interface.
Introduction to the Future-UMo-1 program [1,2]

The French Program for U(Mo) fuel qualification, launched in 1999, was a close collaboration between Compagnie pour l’Étude et la Réalisation de Combustibles Atomiques (CERCA), the Commissariat à l’énergie atomique (CEA), FRAMATOME Advanced Nuclear Power (ANP), TECHNICATOME and the Compagnie Générale des Matières Nucléaires (COGEMA). In the framework of U(Mo) dispersion fuel development, the French group irradiated two UMo-fuel plates U7MTBR06 and U7MTBR07 in the FUTURE rig (FUel Test Utility for REsearch reactors) in the BR2 reactor at SCK•CEN. The objective of the Future-UMo-1 program was to contribute to the qualification of the U(Mo) fuel for research reactors operating up to a surface power of maximum 353 W/cm². The work involved the production (CERCA), irradiation (CEA-SCK•CEN) and reprocessing (COGEMA) of full size UMo-fuel plates. In comparison to previous irradiations in other research reactors, full size plates with atomized powder UMo-fuel were used. The power level of 353 W/cm² would also exceed any previous U(Mo) irradiation experiment [1,3].

Fuel plate fabrication and fresh fuel characterization

Fuel plates consisted of low enriched (19.8% $^{235}$U) atomized U(Mo) fuel, dispersed in an aluminum matrix and surrounded by an aluminum alloy cladding. The plates had a U loading of 8.5 g/cm³ and were manufactured by CERCA. The atomized U7wt%Mo powder (supplied by the Korea Atomic Energy Research Institute (KAERI)), containing particles of less than 125 µm was mixed with aluminum powder (A5) according to a U(Mo)/Al mass ratio of 7.32. The mixed powder was successively compacted, placed into the aluminum cladding frames and hot rolled. The cladding consisted of AG3-NE, an aluminum magnesium alloy (2.81 wt% Mg) which corresponds to a nuclear grade Al 5754 alloy. The final fuel loading amounted to 8.47 U g/cm³ and a porosity of 1.1% was measured (Table 4).

The U-7wt% Mo atomized fuel plates have been irradiated in a flat plate configuration in the FUTURE rig (Figure 52).

During plate production, the fuel is submitted to several heat treatments. As a result, a part of the $\gamma$ U(Mo) phase might decompose to $\alpha$-U, which is known to exhibit instable irradiation behavior (swelling) if the irradiation does not lead to transform of the $\alpha$-U back to $\gamma$-U (see...
chapter 3). It can be postulated that preferential attack by AL matrix in decomposed areas may prevent γ reversion. To exclude the possibility that the observed deformation is resulting from swelling of α-U, the microstructure of the fresh fuel plates has been examined.

In addition, an annealing study was performed on the fresh fuel to compare the out-of-pile microstructure with the post irradiation. The results are discussed later in this chapter.

**Figure 53** X-ray diffraction pattern of the unirradiated sample shows that the U(Mo) powder contains an amount of α-uranium next to the desired γ-uranium. The indexed Al peaks (α₁, α₂) originate from the fuel matrix and/or cladding.

The phases present in the meat of the sibling sample were measured by X-ray diffraction. To obtain a larger analysis surface, the cladding at one side of the unirradiated sample was removed by polishing until the meat became visible. The measured X-ray diffraction pattern (Figure 53) shows that the powder, after fabrication but prior to irradiation, contains a low but significant amount of orthorhombic α-U in addition to γ-U. Diffraction peaks due to the Al of the cladding and matrix are also present.

**Figure 54** The cellular structure of the fuel particles in the unirradiated U–7wt%Mo fuel plate.

From the detailed optical microscopy image (Figure 54) of a U(Mo) fuel particle of the unirradiated sample in as-polished condition, the typical cellular structure of atomized
U(Mo) as described in chapter 2 can be seen. There is no indication of the formation of an interaction layer between the U(Mo) fuel particle and the Al matrix after fabrication, prior to the irradiation.

3 Irradiation history

The objective of the program was to test the behavior of this type of fuel at a surface heat flux up to 353 W/cm\(^2\) and a maximum fuel cladding temperature of 130 °C during operation. However, after the second irradiation cycle, visual examination of the fuel plates showed a local increase in plate thickness in the axial hot plane and the plates were retrieved from the reactor. After 40 FPD’s, the fuel plates had a maximum burn-up of approximately 32\% \(^{235}\text{U}\).

An extensive post irradiation campaign was performed on the fuel plates to find the underlying cause for the observed deformation.

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<tr>
<th>Plate Id.</th>
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<th>U7MTBR07</th>
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<td>AG3NE</td>
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<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Mean BU (%(^{235}\text{U})) (\text{f/cm}^3 \text{ U(Mo)})</td>
<td>(~21) (1.49\times10^{21})</td>
<td>(~21) (1.49\times10^{21})</td>
</tr>
<tr>
<td>Max BU %(^{235}\text{U})) (\text{f/cm}^3 \text{ U(Mo)})</td>
<td>(~32) (2.3\times10^{21})</td>
<td>(~32) (2.3\times10^{21})</td>
</tr>
<tr>
<td>Peak Heat Flux (W.cm(^{-2}))</td>
<td>370</td>
<td>367</td>
</tr>
</tbody>
</table>

Table 4 Fabrication and irradiation history of the FUTURE plates.

4 Post Irradiation Examination

4.1 Calculated burn-up profile [4]

An extended model of BR2 including detailed axial and radial fuel burn-up distributions in the core has been developed using MCNP-4C and ORIGEN-S codes. MCNP is a general-purpose Monte Carlo N-Particle code that can be used for neutron, photon, electron, or coupled neutron/photon/electron transport. Fuel depletion, actinide transmutation and fission product buildup and decay are calculated using ORIGEN-S.

The MCNP calculations of the reactor BR2 are validated on the benchmarks and experiments related to various irradiation programs, carried out in BR2. One of these experiments was already mentioned in chapter 3: thermal fluxes were calculated using the MCNP model of BR2 and compared to thermal fluxes measured using Co dosimeters in the FUTURE basket.

The main conclusions were:
• neutron fluxes can be predicted with an accuracy of better than ± 10% in comparison with the dosimeter measurements
• thermal power characteristics (fission rate, heat flux, linear power) in the irradiated advanced MTR fuel plates can also be predicted within the margin of ± 10% in comparison with the γ - spectroscopic methods

The MCNP-4C and ORIGEN-S codes were used to calculate the burn-up profile over the fuel plate U7MTBR07 (Figure 55).

Figure 55 Calculated burn-up profile for fuel plates U7MTBR07

Typically the burn-up resulting from the MCNP calculations is expressed in %\(^{235}\)U; it is the fraction of \(^{235}\)U atoms that have disappeared, either through fission or neutron capture \(^{235}\)U(n,\(\gamma\))\(^{236}\)U. To convert %\(^{235}\)U in a more physical parameter such as fission density (fissions/cm\(^3\) U(Mo)), one has to take into account the fissions of \(^{239}\)Pu, which is generated by neutron absorption by \(^{238}\)U (see chapter 3). In LEU fuel, \(^{238}\)U is one of the main constituents and as such the amount of bred \(^{239}\)Pu is significant.

Conversion %\(^{235}\)U to fission density :

\[
FD = \frac{N \times e \times B}{(1 + \alpha) \times \eta} \quad \text{Eq. 27}
\]

with \(\alpha\) the capture-to-fission cross section ratio (calculated as 0.17 in BR2 conditions by MCNP calculations [5]), \(\eta\) the fraction of \(^{235}\)U fissions over the total number of fissions (\(^{235}\)U, \(^{239}\)Pu and others), \(N\) the U atom density in at/cm\(^3\), \(e\) the enrichment and \(B\) the fraction of consumed \(^{235}\)U atoms.

The U atom density can be calculated using

\[
N = N_A \times \frac{\rho_u}{235 \times we + 238 \times (1 - we)} \quad \text{Eq. 28}
\]

with \(N_A\) = Avogadro’s number, \(\rho_u\) = the uranium density in g/cm\(^3\), \(we\) = the uranium enrichment by weight = \(\frac{235 \times e}{235 \times e + 238 \times (1 - e)}\)

For 19.75 % enriched U7wt%Mo the relation between fission density and %\(^{235}\)U is:

\[
FD = 6.86 \times 10^{21} \frac{B}{\eta} \quad \text{Eq. 29}
\]

What remains to be defined are the \(^{235}\)U fission to total fission ratios. These depend on the enrichment, the burn-up and the spectrum [6]. This ratio was calculated by an ORIGEN [7]
calculation based on 19.7% enriched fuel in a PWR spectrum [8]. Even if the use of a PWR spectrum, which differs from the spectrum in an MTR like BR2, neglects spectral influences in the fission ratio, it is considered sufficiently accurate for the purpose of this study. The fraction $\eta$ of $^{235}$U fissions over total fissions in function of the $^{235}$U consumed B can be fitted with a 5th order polynomial ($R^2>0.99$):

$$\eta = -4.00 \times B^5 + 8.35 \times B_{CNP}^4 - 6.21 \times B^3 + 1.88 \times B^2 - 0.28 \times B + 0.99$$  \text{Eq. 30}

The conversion of %$^{235}$U consumed B to fission density $FD$ for a 19.7% enriched fuel can then be described by a polynomial of 5th order ($R^2>0.99$):

$$FD = 4.03 \times 10^{12} \cdot B^5 - 8.04 \times 10^{14} \times B^4 + 5.60 \times 10^{16} \times B^3 - 1.48 \times 10^{18} \times B^2 + 8.42 \times 10^{19} \times B$$  \text{Eq. 31}

The burn-up was also determined using a combination of mass spectrometry and radiochemical measurement techniques [9]. A sample of the irradiated fuel plate was fully dissolved and the burn-up was quantified by determining the exact concentrations of various fission and activation products. Selected burn-up monitors were: neodymium isotopes, cesium-137 and cerium-144. Using the fission yields, cross-sections and decay constants a FIMA (Fissions per Initial Metal Atom) of 5.06% was derived. This result can also be converted into a fission density by using

$$FD = \%FIMA \times N$$  \text{Eq. 32}

Combining Eq. 28 and Eq. 32 results in $FD = 2.09 \times 10^{21}$ f/cm$^3$ which can be converted to a burn-up of 29.4 %$^{235}$U using Eq. 29 with $\eta=0.9677$.

The radiochemical measurements produces more local values than can be calculated by MCNP. It is therefore that the radiochemical burn-up value (29.4 %$^{235}$U ) is higher than the values obtained from the calculations (average 26.5 %$^{235}$U ).

4.2 Non-destructive analysis

Initially (in 2004) non-destructive examination was done only on fuel plate U7MTBR06 using a prototype measuring bench. After these examinations, samples were cut from this plate for microstructural analysis. However, with the development of the high precision BONAPARTE measuring bench (see 4.2.2) it was decided to redo the NDT examinations on the FUTURE plates. This could only be performed on the remaining intact plate U7MTBR07. Comparison of the old and new NDT results showed that both plates had almost identical characteristics and as such it can be safely assumed that all drawn conclusions from the NDT on U7MTBR07 and DT on U7MTBR06 apply for both plates.

The non-destructive examination campaign on the FUTURE plate U7MTBR07 included visual examination, plate and oxide layer thickness measurements.
4.2.1 Visual examination

The photographs of the irradiated fuel plate (Figure 56) show a clear delineation of the meat. Towards the central part of the plate a difference in color of the surface is seen which indicates a difference in oxide layer thickness or roughness. Looking in more detail a small deformation on the front and back side is observed (inside dotted circle in Figure 56) indicating a local pillowing.

![Front](front1.png)
![Back](back1.png)

*Figure 56 Photographs (taken through the hot cell window) of the front and back side of fuel plate U7MTBR07.*

4.2.2 BONAPARTE measuring bench [10]

SCK•CEN has developed a measurement bench designed for the non-destructive analysis of irradiated research reactor fuel plates, both in curved and flat geometry (see Figure 57). The BONAPARTE measurement bench (Bench for Non-destructive Analyses of Plate And Rod Type fuel Elements) is installed in a lead brick shielded (15cm) hot cell, licensed for accepting both intact and defective fuels (plates and pins). The bench consists of a fuel plate clamping system with plate rotation (only for curved fuel plates) and a mobile measurement head with motorized X- and Y-movement (Y-movement only for flat fuel plates). Positioning feedback is provided to the stepping motors by a magnetic ruler system based on the Sony Magnescale product line. This allows repeatable positioning of the measurement head to within ±100 μm (68% confidence interval) on the plate. The measurement head holds probes for plate thickness and oxide thickness measurements, the latter can be performed simultaneously on both sides of the fuel plate. In addition, it can also house a video camera for visual inspection of the fuel plate.

Oxide thickness measurements are based on the eddy current (EC) principle. The probes consist of a ferrite core with an electrical coil surrounding them; with a ceramic top pushed against the measured surface. The coil is fed by a high frequency current, producing a high frequency alternating magnetic field, inducing eddy currents in the fuel plate cladding. The magnitude of the induced eddy currents depends upon the distance between the ceramic probe tip and the electrically conductive cladding material or in other words the thickness of the oxide layer and crud if present.

Calibration is performed using certified Mylar foils with known thicknesses or an alternative, well-characterized oxidized surface of cladding material. Before and after each measurement session, a calibration check is performed to verify the stability and determine
the uncertainty of the system, resulting in a typical overall measurement uncertainty of ±3μm, expressed as a 68% confidence level.

Plate thickness measurements are done using 2 opposed, customized Sony Magnescale probes, whose measurement principle is based on a magnetic ruler (similar to the position encoders used). The system is calibrated with a certified ceramic standard of 1200 μm. Prior to and after each plate measurement, a calibration check is performed with standards ranging from 1000 μm to 1400 μm at different Magnescale ranges. The measurement uncertainty for the thickness measurement was thus determined to be ±5 μm, expressed as a 68% confidence level [10]

4.2.3 Thickness measurements

To measure the plate and oxide layer thickness, a measurement grid of 5 x 1 mm$^2$ is defined with measurements every 1 mm in the longitudinal plate direction. All positions are corrected to represent the absolute position on the plate with a reference point (0,0) to the upper left corner when the fuel plate engraved number is visible on the left side (Figure 58).

The plate and oxide layer thickness probes are in line in the Y direction, with a separation between the probe positions of 35.25 mm in the X direction (oxide probe leading in the
scanning direction). The zero position of the thickness probe is located at 23.60 mm from the real plate edge, which means the zero position of the oxide probes is at 58.85 mm from the edge.

4.2.3.1 Plate thickness
Twelve thickness measurements were performed over the length of fuel plate U7MTBR07, every 5 mm starting at ~ 5 mm from the side of the plate (Figure 58).

![Line scan Position (mm)](image)

Figure 59 Measured plate thickness profile.

The line scans in Figure 59 clearly show a deformed area with a maximum around 500 mm from the top of the plate. Locally a thickness up to 1500 µm is measured which is an increase of 270 µm compared to the nominal plate thickness of 1230 µm [11]. However, during irradiation an oxide layer will grow on the outer surface of the cladding. To convert plate thickness to swelling, the thickness will have to be corrected for the presence of the oxide layer as oxidation also leads to swelling. The growth rate of this layer is dependent on the temperature the cladding is submitted to.

The thickness scans at the plate edges (at 5 mm and 60 mm) clearly differ from the other scans in that no increase in thickness is observed. This is because these scans are located near the edge or even outside the meat area, in the constrained part of the fuel plate where the fuel meat shows less swelling due to the locally lower temperatures and larger constraints (proximity of cladding frame). In that respect, the scan located outside the meat area (at 60 mm) can be used to determine the initial plate thicknesses. It was however observed on fresh fuel plates that there is a 25–30 µm difference in initial plate thickness between the fuelled area of the plate and the out-of-fuel zone, related to a difference in spring back during production.

On average a thickness of 1206 µm is found, which is corrected for spring back and oxide layer thickness (measured outside the fuel zone) resulting in an initial plate thickness $T_i$ of
1225 µm. This is slightly less than the plate thickness of 1270 µm specified by the fuel plate manufacturer (CERCA) but the precision of this measurement is poor.

The scans on the outer sides of the fuel plate are not retained for further analysis, as they are influenced by edge effects, particularly for the eddy current based oxide thickness detection system. Due to the nature of the eddy current measurement technique, strong influences of defects in the material in the vicinity of the probe (the edge can be regarded as a defect) are to be expected.

4.2.3.2 Oxide layer thickness

As shown in chapter 3, aluminum alloys undergo oxidation if oxygen is available. At room temperature, an Al₂O₃ layer forms but its growth rate saturates in a short time. This protective oxide however, degrades in water by the formation of various oxide-hydrates at the outer surface in time. The formed oxide-hydrate layer of an irradiated fuel plate, collected by wiping the surface with a moist cloth, was characterized using X-ray Diffraction (XRD). Analysis of the recorded pattern shows that the major constitutes are Boehmite (AlO(OH)) and Bayerite (Al(OH)₃) ([Figure 60, [12]]).

Static corrosion experiments [13] on fresh AlFeNi alloy plates showed, that depending on the temperature of the leaching test, the thermodynamically stabilized crystalline phase was found to be different [17–19]: at 70 °C, bayerite Al(OH)₃ was identified while at 165 °C and 250 °C, boehmite AlO(OH) is stable. Their simultaneous presence in the oxide powder collected from the irradiated fuel plate can be linked to the variation of temperatures over the cladding between the center and the extremities of the fuel plate [13].

![Figure 60 Measured X-ray diffraction pattern of the oxide layer and the reference pattern JCPDS 021–1307 for boehmite AlO(OH) (*), JCPDS 077–0114 for bayerite Al(OH)₃ (o) and JCPDS 004–0787 for aluminum (x).](image)

Aluminum oxide-hydrates are soluble in water, especially in flowing water, meaning that even the hydrated oxide becomes less protective, further enhancing film growth. The measurement of the fuel plate thickness will thus be affected by the corrosion process. Axial scans of the outer oxide layer were therefore performed on each side of the fuel plate.
In Figure 61 the oxide layer thickness over the fuel plate is shown. The profile is based on the as-recorded oxide thickness that is corrected for a systematic bias created by the difference between the stationary probe conditions during calibration and the measurement with a moving probe. The bias is corrected by levelling of the average measured oxide thickness in the out-of-fuel calibration zone for each scan to the true value of the oxide layer at that location. This latter value is determined by a separate stationary probe measurement at that location. The probe used for that bias determination was separately calibrated on a sample of non-oxidized cladding material [10].

The maximum oxide layer thickness is observed in the deformed area and amounts to approximately 25 µm but it should be noted that the interpretation of the oxide thickness in the deformed area is not reliable.

4.2.4 Swelling

4.2.4.1 Plate swelling
To calculate the swelling, the thickness of the plate has to be corrected for the measured thickness of the formed oxide layer on the outer surface of the cladding. Boehmite has a density of 3.04 g/cc compared to the density of Al (AG3/AlFeNi have similar densities) which is 2.7 g/cc. Therefore if 1 mol of Al transforms to 1 mol of AlOOH, which has a 97.5% larger volume than the Al volume, a swelling of 97.5% with the formation of boehmite should thus be taken into account.

The plate thickness measurements therefore can be corrected using:

$$ T_{corr} = T_{raw} - \left(1 - \frac{1}{1.975}\right) \times (Ox_{up} + Ox_{low}) $$

Eq. 33
in which $T_{\text{corr}}$ is the corrected thickness, $T_{\text{raw}}$ is the measured plate thickness and $Ox_{\text{up}}$ and $Ox_{\text{low}}$ are the oxide thicknesses measured on both sides of the plate. This correction does not take into account porosity or cracks in the (hydr)oxide, which are known to exist. The cracks are a consequence of the dehydration of the in-reactor generated hydrated hydroxide layer after extraction from the water in hot cell. Due to the unpredictable nature of these microstructural features, it is not straightforward to correct for them. One should therefore keep in mind that it is likely that the oxide correction is an under-prediction. The thickness profile is corrected for oxide swelling in each point and divided by the as-fabricated plate thickness to obtain the plate swelling profiles (Figure 62).

A maximum swelling of 20 % is observed at the highest burn-up position.

4.2.4.2 Fuel swelling

Assuming that no clad swelling occurs (which can be expected), the swelling of the plate can be attributed to the swelling of the fuel. The fuel swelling can be calculated using:

$$S_F = \frac{S_p \times T_{i}}{V} = \frac{T_{\text{corr}} - T_i}{V \times t_i} = \frac{\Delta T_{\text{corr}}}{V \times t_i} \quad \text{Eq. 34}$$

with $S_F$ and $S_p$ the fuel and plate swelling respectively and $V$ the volumetric U(Mo) loading (52 vol%). Instead of the as fabricated plate thickness $T_i$, the average measured thickness of the plate outside the meat zone is taken (see 4.2.3.1) while for the meat thickness $t$, the initial value of 530 µm is used. The formula neglects meat porosity (for atomized fuel this is very low) and the effect of interaction phase formation on the swelling. It furthermore assumes a uniform meat thickness and fully homogenous U(Mo) dispersion.

Averaging fuel swelling values at positions with similar burn-up allows plotting the fuel swelling as a function of the burn-up. By converting the calculated burn-up given in %$^{235}$U consumed to fission density (4.1), the fuel swelling can be more appropriately visualized in function of local fission density.

In Figure 63, this is done for the fuel swelling data points of fuel plate U7MTBR07. The swelling increases almost linearly with the burn-up, but an excessive swelling is observed at $\sim 2 \times 10^{21}$ f/cm$^3$. 

![Figure 62 Plate swelling (filled) contour plots (after correction for oxide contribution to the thickness) overlaid with burn-up contour plot.](image)
4.2.5 Reliability and statistics

A number of effects can affect the absolute precision of the individual data points. Local variations in fuel density or meat thickness lead to local burn-up variations, which cannot be taken into account by the MCNP calculations as they are unknown. This leads to variations in the parameters of Eq. 34 as well as additional uncertainties in the local fission density. On the other hand, loose particles on the plate surfaces can affect the measurements and can create artefacts. If we consider these variations (and others like them) to have a normal distribution, the average values displayed in the fuel swelling evolution graphs are reliable, as each of them is based on a relatively large number of individual data points (typically 50-150). To provide insight in the reliability and variation of the data, the spread of the data points averaged to determine each of the fuel swelling data points in the graph can be used as a (over)conservative estimate for the error bar. Plotting the 1σ spread on the fuel swelling graphs (Figure 63) shows that the spread is fairly consistent throughout the complete dataset, which is what is expected if the origin of the spread are variations of the type described above and normally distributed. Only for those points that are in the pillowing area of the plate, one can observe a very clear increase in the spread of the data, indicating that the measured swelling is no longer related to the burn-up increase, but rather an effect of the mechanical forces producing plate failure in the pillowed area.

4.3 Destructive analysis

As mentioned earlier, non-destructive analysis was performed on fuel plate U7MTBR07 while microscopy was performed on samples cut from fuel plate U7MTBR06. The microstructure of the U(Mo) fuel was analyzed by optical microscopy (OM), scanning electron microscopy (SEM), electronprobe microanalysis (EPMA) and transmission electron microscopy (TEM) [1,2].

A slice over the complete width of the fuel plate was cut at the most deformed area characterized by a high burn-up (Figure 64).
From this slice, three samples were cut: samples A and B are characterized by OM, SEM and EPMA, while the third sample C was used for TEM.

In Figure 64 the location of the samples on the fuel plate U7MTBR06 are shown with reference to the measured fuel swelling and calculated burn-up of fuel plate U7MTBR07.

![Figure 64 Cutting scheme fuel plate U7MTBR06: location of the samples relative to the fuel swelling contour plot of fuel plate U7MTBR07 overlaid with the contours of the calculated burn-up profile (top graph) and relative to the fuel swelling plotted in function of the fission density (bottom graph).](image.png)

Two samples (A,B) were embedded in an epoxy resin in such a way that the complete section of the fuel plate (meat and cladding) can be observed. The samples were polished with SiC paper of successively finer grain size, finishing on cloth with diamond paste of 3 and 1 µm. Observations on the samples were made in as-polished and etched conditions. The etchant, consisting of 38 ml HNO$_3$ (65%), 1 ml HF (38%) and 100 ml H$_2$O [14] was used to reveal the cellular structure of the U(Mo) particles. The sample was immersed in the solution for up to a few minutes.

Sample C was polished down to a thickness of around 100 µm, after which it was cut into small fragments. One fragment was glued on a golden grid with an aperture of 1 mm. Final thinning of the sample was done with twin jet electropolishing using an electrolyte composed of 5% perchloric acid in methanol at -45°C applying a voltage of 20 V [15].

First optical examinations revealed large porosities in the meat of the most deformed sample B. It was found that these result from extensive pull-out during sample preparation. To obtain a more accurate image, the sample was impregnated with an epoxy resin and repolished using a low force. Although some pull-out was still unavoidable, most of the large porosities were no longer observed in the resulting micrographs.

4.3.1 Fuel behavior

The collage of optical micrographs in Figure 65 show that the microstructure of sample A is completely different from sample B although the difference in burn-up or heat flux is minimal (Figure 64, BU sample B ~ 2.15×10$^{21}$ f/cm$^3$ and sample A ~ 1.82×10$^{21}$ f/cm$^3$). The
deformation observed in the visual examination (Figure 56) and measured in the NDT analysis (Figure 59) is clearly recognized as the pillowed area observed in sample B. From the optical micrographs, the plate thickness (without the oxide layer) is measured on sample A and B of fuel plate U7MTBR06 and compared to the plate thickness measurements (corrected for oxide formation) obtained from NDT on an identical location on fuel plate U7MTBR07 (Figure 66).

Even though the measurements were performed on different fuel plates, a very good correlation of the trends between the DT and NDT results is obtained.

Figure 65 The composition of optical micrographs of the irradiated samples reveal the increase in fuel meat thickness.

The OM images in Figure 65 also show that the increase in plate thickness is caused by an increase in meat thickness as the cladding thickness is unaffected. In the pillowed area of sample B, near the center of the meat large porosities can be observed which, as already mentioned, are in part due to pull-out during sample preparation.

Figure 66 Plate thickness measured in NDT on fuel plate U7MTBR07 and DT on fuel plate U7MTBR06, at the same longitudinal position.
After irradiation, the cellular structure in the fuel particles as seen in Figure 54 can only be observed after etching of the sample (Figure 67). In the same micrographs (of sample A), it is seen that an interaction between the Al matrix and the U(Mo) fuel particle has occurred, resulting in a U-Mo-Al layer surrounding the fuel particle (see chapter 3). At the interface of the U-Mo-Al interaction layer and the Al matrix, small crescent shaped voids are observed (Figure 67 indicated by black arrows).

![Micrograph of fuel particle after etching](image1)

**Figure 67** Compared to the unirradiated fuel particle (Figure 54), the formation of an interaction layer, surrounding the fuel particle, has occurred during irradiation.

From detailed OM micrographs of sample B in as-polished condition several observations can be made:

- The cellular structure of the U(Mo) agglomerate becomes visible as the cell boundaries are delineated by fission gas related bubbles (Figure 68 a,b,c)
- Larger fission gas bubbles are observed in-between touching fuel particles and squeezed in-between touching interaction layers (Figure 68 a)
- Crescent shaped voids have formed in the interaction layer (Figure 68b) and cause a detachment of the fuel particle from the matrix
- In the pillowed area, the matrix is completely detached from the fuel particles (Figure 68 c).

![Optical micrograph of sample B](image2)

**Figure 68** Optical micrograph of sample B in as-polished condition showing the microstructure resulting from irradiation of U(Mo) particles dispersed in an Al matrix.

Vickers micro-hardness measurements of the cladding material, the U-Mo fuel, the aluminum in the meat and the interaction product formed between the fuel and the aluminum of the meat, were performed. Micro hardness measurements can give an
indication of the mechanical properties, which are based on the defect concentration. In Table 5 the average values (based on five measurements) are displayed. Considering that especially sample B has some weak spots where a decohesion between matrix and fuel/IL has occurred, the hardness values of the phases in the meat should not be treated as absolute, but they give an indication of the evolution of the microhardness with burn-up.

<table>
<thead>
<tr>
<th></th>
<th>FD (x10^{21} f/cm^3)</th>
<th>AG3NE Cladding</th>
<th>U(Mo) Fuel</th>
<th>U-Mo-Al IL</th>
<th>AIS Matrix</th>
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<td>63</td>
<td>353</td>
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<td>104</td>
</tr>
</tbody>
</table>

Table 5 Vickers hardness measurements of the different phases found in a plate containing atomized U(Mo) dispersion fuel.

The Al alloy cladding seems to remain unaffected during irradiation while for the matrix an increase of hardness with BU is observed. As the irradiation progresses, the fission fragments cause more and more defects in the matrix leading to an increase of the hardness, while the cladding only suffers from n bombardment which has less effect on Al. A similar effect is seen for the hardness of the U(Mo) fuel and the formed interaction layer.

Sample B

Figure 69 Secondary electron images of the meat taken at several positions on sample B. The locations of the SEM images are indicated on the collage of micrographs covering the complete sample.

However, as the amount of produced fission gas also increases with burn-up, the formed fission gas bubbles on the cell boundaries of the U(Mo) fuel particles will grow. This will cause a decrease in apparent fuel hardness.
From the SEM and OM images, it is confirmed that the increase in fuel plate thickness has to be attributed to an increase in the thickness of the fuel meat, as the cladding shows only minor corrosion, i.e. formation of an oxide layer (Figure 70). The thickness of the oxide layer on the outer surface of samples B amounts to 25 µm, which is in good correlation with the NDT measurement (~20 µm) performed on the sibling plate U7MTBR07.

Figure 70 Corrosion layer on the cladding.

4.3.2 Interaction layer

Figure 69 and the more detailed images in Figure 71, show that the thickness of the layer surrounding the fuel particles resulting from the interaction between fuel and matrix is thinner at the extremities of the plate than in the center.

Figure 71 The secondary electron image at a lower heat flux position (a) shows U(Mo) particles with a jagged edge surrounded by an interaction layer, dispersed in the Al matrix. The SE image of the fuel in the deformed area of the sample (b) reveals U(Mo) particles framed by a thick interaction layer. At this position the Al matrix has been completely consumed and voids appear in-between the fuel particles.

The thickness of the interaction layer of the fuel particles located at the picture frame (Figure 69 most left position, Figure 71a) is measured to be approximately 4 µm. Near the picture frame the fuel particles have undergone different thermo-physical conditions
compared to those located more towards the center of the fuel plate. The values measured there should not be taken as typical.

In the deformed high heat flux area (Figure 69 most right position, Figure 71b), a complete consumption of the aluminum matrix is observed and the thickness of the interaction layer at this position has increased to \(\approx 11\ \mu\text{m} \).

Using the equation
\[
Y^2 = 2.6 \times 10^{-16} \cdot f^{0.5} \cdot t \cdot \exp \left( -\frac{3850}{T} \right)
\]
Eq. 35

described in chapter 3 and assuming for sample A and B a fission rate of respectively \(5.26 \times 10^{14}\) and \(6.22 \times 10^{14}\) fissions/cm\(^3\).s, a fuel temperature of \(\sim 115\ \degree\text{C}\) would generate an IL of \(\sim 10.0\ \mu\text{m}\) for sample A and an IL of \(\sim 10.5\ \mu\text{m}\) for sample B. This is in good correlation with the measured values of 9.5 \(\mu\text{m}\) for sample A and 10.7 \(\mu\text{m}\) for sample B (Figure 72).

![Image 72](image)

**Figure 72** Calculated and measured interaction layer thickness at different fuel temperatures in the FUTURE U7MTBR06 fuel plate.

The Mo X-ray map recorded by EPMA illustrates that the two-phase structure of the U(Mo) particle, consisting of U(Mo) cells surrounded by a boundary which has a lower Mo content (Figure 73) is retained after irradiation. The layer resulting from the interaction between the U(Mo) fuel and Al matrix is clearly observed in the U, Mo and Al maps Figure 73.

![Image 73](image)

**Figure 73** Secondary electron image and X-ray mappings of the matrix, fuel particle and interaction layer.
A quantitative linescan is defined to measure (in point mode) the local composition of the fuel, matrix and interaction layer (Figure 74). Such analysis is performed at several locations on sample B. The averaged composition of 5 IL’s is summarized in Table 6.

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<th>Mo (wt%)</th>
<th>U (wt%)</th>
<th>Al (at%)</th>
<th>Mo (at%)</th>
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<tr>
<td></td>
<td>39.4</td>
<td>5.1</td>
<td>61.2</td>
<td>82.5</td>
<td>3.0</td>
<td>14.5</td>
<td>4.7</td>
<td></td>
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<tr>
<td></td>
<td>29.8</td>
<td>5.5</td>
<td>64.3</td>
<td>77.2</td>
<td>4.0</td>
<td>18.8</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 6 Composition of the interaction layer measured at several locations on sample B

Over the width of the IL, the composition is found to be rather homogenous as can be seen in Figure 75. A nearly constant Al/U+Mo ratio is measured, with a slight increase in Al content towards the interface IL/matrix. At both interfaces (matrix and fuel kernel) the ratio changes abruptly.

There is no indication of ternary compound with higher Al content (UMo$_2$Al$_{20}$ and U$_6$Mo$_4$Al$_{43}$).
A sample of a sibling unirradiated fuel plate was submitted to an out-of-pile experiment. In Figure 76 the SEM images of the fuel plate as received (Figure 76a) and after annealing at 550 °C for 2 hours (Figure 76b). No interaction between the fuel and matrix was present in the as received state, even though the fuel plate was submitted to ~ 425 °C for 2 hours during plate production (blister test). At higher annealing temperature, a thick uniform interaction layer is formed similar to the observation made in the PIE.

However, during the heat treatment, not only an interaction occurs at the interface of the fuel kernel and the matrix but also a reaction in the kernel happens. It appears that the cell boundaries, which are depleted in Mo, are the preferred diffusion pathways for Al. It has been shown [16] that, in the ternary system U-Mo/Al, the cell interiors which are richer in Mo show a slower diffusion of Al.

Quantitative analysis of the interaction layers formed after annealing at 550 °C for 2h (Table 7) reveals a composition similar to the one found in-pile.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Mo</th>
<th>U</th>
<th>Al</th>
<th>Mo</th>
<th>U</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>(at%)</td>
<td>(at%)</td>
<td>(wt%)</td>
<td>(at%)</td>
<td>(at%)</td>
<td>(at%)</td>
<td>U+Mo</td>
</tr>
<tr>
<td>34.2</td>
<td>6.1</td>
<td>55.3</td>
<td>80.3</td>
<td>4.3</td>
<td>15.5</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>31.5</td>
<td>7.9</td>
<td>66.9</td>
<td>75.0</td>
<td>5.7</td>
<td>19.3</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>31.7</td>
<td>5.1</td>
<td>64.6</td>
<td>77.2</td>
<td>3.8</td>
<td>19.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>31.0</td>
<td>6.7</td>
<td>65.7</td>
<td>73.8</td>
<td>5.2</td>
<td>20.9</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 7 Composition of the interaction layer after submitting the unirradiated fuel to a temperature treatment of 500 °C for 2 hours.

The composition is however not homogeneous over the width of the IL (Figure 77) and reflects the solid state reaction that occurs between U(Mo) and Al. This reaction will start
with the formation of nuclei of UAl$_2$ near the U(Mo)/Al boundary but in the U phase. Next, the diffusion of U(Mo) in Al and vice versa will lead to formation of UAl$_3$ and UAl$_4$ phases in the aluminum phase, while in the U phase the UAl$_2$ grains will grow into the bulk material [17,18].

Figure 77 Al/U+Mo ratio over the width of the interaction layer formed during annealing.

As seen in the previous chapter, if sufficient Al is available, the formation of ternary compounds UMo$_2$Al$_{20}$ and U$_6$Mo$_4$Al$_{43}$ can be observed at the interface IL and matrix. Therefore, the Al/U+Mo ratio of the IL closest to the Al matrix ranges theoretically between 3 and 9, while for the layer close to the fuel the ratio Al/U+Mo ranges between 2 and 4. This is confirmed by the measurements in Figure 77.

When comparing the microstructure of the interaction layer formed in-pile and in out-of-pile experiments, several differences are observed:

- In both experiments a uniform layer is formed around the kernels. However the penetration of the Al into the fuel kernel is only observed in the out-of-pile experiment (Figure 78).
- The interaction layer formed during irradiation has an amorphous character, while in the anneal study it stays crystalline [19].

This shows that the thermal anneals are not an ideal simulation of the in-pile behavior. During irradiation, as was discussed in the previous chapter, the main origins for the fuel-
matrix intermixing are the fission fragment induced displacement spikes. In the out-of-pile study, thermally driven diffusion between U, Mo and Al lead to the formation of the IL. However, the composition of the formed IL is nearly the same in both experiments.

![U, Mo, Al Ternary diagram](image)

The compositions of the IL’s formed in the in- and out-of-pile study and shown in Figure 75 and Figure 78, are plotted in a ternary diagram (Figure 79). Not only is there no difference between the in-pile and anneal formed IL’s but all measured compositions lie on the tie line between U7wt% Mo and pure Al. No pure phases such as UAl$_2$, UAl$_3$, UAl$_4$ or the higher Al containing compounds UMo$_2$Al$_{20}$ and U$_6$Mo$_4$Al$_{43}$ are formed but it seems that the U(Mo) alloy can accommodate large amounts of Al.

4.3.3 Fission products

The Xe X-ray map in Figure 80 reveals that some of the generated fission gas has precipitated into bubbles. These bubbles, as seen in the combined Al, Mo and Xe color map, can be found on the cell boundaries. At the interface interaction layer/matrix, an elevated concentration of Xe and other fission products (e.g. Nd) is measured. At some locations on this interface it also seems that Xe is concentrated into larger bubbles. Inside the interaction layer no fission gas bubbles or other fission product precipitates can be observed.
These observations are also reflected in the semi-quantitative linescan presented in Figure 81. The linescan was recorded at a position with a lower burn-up, which is reflected in the abrupt transition between matrix and fuel kernel as only a very thin interaction layer has formed. To see the distribution and quantify the fission products, xenon and neodymium are used. Xe is selected as it is the most important fission gas but care must be taken because it can precipitate into bubbles which can get opened during sample preparation affecting the result. The rare-earth solid fission product Nd is selected to monitor as it is immobile in the fuel (making it also usable as indicator of local burn-up) and stays in solid solution up to higher burn-up.

Inside the U(Mo) fuel kernel, the measured Mo signal fluctuates between 6 and 9 wt%, reflecting the cellular structure of the fuel particle. It should also be noted that inside the Al matrix, the concentration of Mo is on average 0.5 wt%. This Mo is not from the U(Mo) alloy but it is the fission product Mo that gets ejected out of the fuel kernel.

In the U-Mo-Al reaction layer the concentration of fission products is lower but at the interface with the Al matrix (and cladding) a clear rise in fission product concentration is observed, producing a halo around each U-Mo-Al coated fuel particle. This effect is caused by the growing IL snowplowing (or sweeping up) the solid fission products that got ejected out of the fuel kernel (chapter 3).

The Xe and Nd X-ray maps and semi-quantitative linescans (Figure 81) show the homogeneous distribution of fission products inside the U(Mo) fuel particle. The ratio Xe/Nd inside the fuel kernel is around 1.7 which is close to the theoretical ratio of 1.8 [7]. This indicates that almost no precipitation of fission gas in bubbles with sizes > 100nm occurred.
TEM examinations on sample C allowed to identify for the first time the formation of an ordered superlattice of nanosized fission gas bubbles (chapter 3, [2]).
diffraction spots. As already mentioned in chapter 3, the U(Mo) fuel remained crystalline, while an amorphization of the IL had occurred. The amorphous interaction phase is not a good host for the bubble superlattice, and the reaction between the pure Al matrix and the U(Mo) particles will lead to the release of the stored gas. Furthermore, the fission gas in the glassy interaction product can have a high mobility and will migrate towards the porosities forming at the IL/matrix interface [2].

4.3.4 Swelling

From the SEM images the volume fraction occupied by the different phases in the meat (matrix, fuel and interaction layer) can be calculated using image processing software (Figure 83). Comparing the measured volume fraction to their initial values would be biased as the volume occupied by the phases scales with the meat thickness which can vary locally in the fuel plate.

![Image processing based on intensity thresholds is used to determine the volume fractions occupied by the matrix, IL and fuel.](image)

Figure 83 Image processing based on intensity thresholds is used to determine the volume fractions occupied by the matrix, IL and fuel.

However by multiplying the measured volume fractions with the measured local meat thickness, the evolution of the volume of the different phases in function of the burn-up can be calculated (Table 8).

<table>
<thead>
<tr>
<th>Analyzed volume</th>
<th>Vol% matrix</th>
<th>Vol% IL</th>
<th>Vol% fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fission density</td>
<td>Volume fraction (%) $\times$ Meat thickness (µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>fresh</td>
<td>254</td>
<td>0</td>
</tr>
<tr>
<td>sample A</td>
<td>$1.9 \times 10^{21}$</td>
<td>95</td>
<td>209</td>
</tr>
<tr>
<td>sample B</td>
<td>$2.2 \times 10^{21}$</td>
<td>117</td>
<td>262</td>
</tr>
</tbody>
</table>

Table 8 Evolution of the matrix, IL and fuel volume based on the measured meat thickness and volume fractions occupied by the different phases.

When comparing the volume of the phases to their initial values, it becomes clear that the interaction layer grows at the expense of the matrix. The evolution in the fuel volume remains nearly constant which is the result of two evolutions cancelling out each other.
namely fuel swelling and interaction layer formation. Considering the limited number of data points, no further analysis on the contribution of the phase to the overall swelling is made.

5 Conclusion

From the FUTURE irradiation experiments it has become clear that the growing interaction layer is the underlying cause of the excessive plate swelling which could in the end lead to fuel plate failure. As irradiation progresses and fission density accumulates, the growing interaction layer sweeps up (‘snowplowing’) the ejected fission products piling them up at the interaction layer / matrix interface, creating a fission product halo around the fuel kernels with their interaction layers. These halos cause decohesion of the matrix from the fuel, severely weakening the structure of the meat and hindering thermal conductivity. If local stresses, for example related to the normal gradual swelling of the fuel with burn-up accumulation, exceed the yield strength of the weakened interfaces, cracks start to develop. In high loading fuel plates, these defects can interconnect to allow formation of large, pressurized fuel meat pores. This mechanism can eventually lead to pillowing of the fuel plate which might result in plate failure (release of fission products to the reactor environment).

The goal of reaching a maximum local burn-up of 70% (5.3×10\(^{21}\) fissions/cm\(^3\)) was not met in the FUTURE-UMO-1 experiment. It was however hypothesized that stabilizing the in-pile behavior of U(Mo) dispersion fuel would require inhibiting the formation of an interaction layer (or at least to limit its growth) and to stabilize fission gas behavior.
References

Chapter 5 An old solution for a new problem: BR1 fuel

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Summary

The interaction between uranium and aluminum was also found to be the detrimental problem with the first aluminum canned uranium fuel rods produced to power the ORNL graphite reactor X-10. To limit this interaction, a so-called AlSi bonding layer and a U(Al,Si)₃ anti-diffusion barrier were applied on the natural uranium fuel slug. The core of the BR1 research reactor at SCK•CEN, Mol (Belgium) has a graphite matrix loaded with such fuel rods. The reactor has been in operation since 1956 and still contains its original fuel rods. After more than 50 years irradiation at low temperature, some of the slugs have been examined and compared to the fresh fuel rods.

The microstructure of the (fresh) fuel, bonding and anti-diffusion layer and cladding were analyzed. It was observed that the AlSi bonding layer provides a tight bond between fuel and cladding. The applied anti-diffusion barrier, however, was not a homogenous U(Al,Si)₃ layer, as was assumed at fabrication. Instead a USi coating layer covering the U slugs and adjacent a second UAl₃-USi₃ reaction layer had formed. Comparing the fresh to the irradiated fuel rod it was found that irradiation at moderate temperature causes Si to diffuse through the UAl₃-USi₃ reaction layer, after which it reacts with the USi coating layer and the uranium slug, resulting in the increase in thickness of the coating layer and the change in stoichiometry to USi₂. The source of this additional Si was identified as the AlSi bonding layer. The composition and thickness of the UAl₃-USi₃ reaction layer remained unchanged.

It was concluded that the application of silicide layers on a U surface is an effective means to counteract the interaction of the metallic uranium with an aluminum cladding under low-flux, low-temperature irradiation conditions.

To investigate if the application of an anti-diffusion barrier would also be efficient in modern fuel system, the solid state reaction between U(Mo) and Si, leading to the formation of silicides, has been studied using in situ X-ray Diffraction. In a similar way, the reaction between U(Mo) and Al was examined. Kissinger analysis on ramp anneals with ramp rates of 0.2, 0.5, 1 and 3 °C/s have been performed to investigate the kinetics of the formed aluminides and silicides. Using this method, the apparent activation energy Eₐ for the formation of UAl₄, UAl₃ and UAl₂ was determined and is respectively 3.6 ± 0.55 eV, 2.74 ± 0.27 eV and 1.56 ± 0.08 eV. For U₃Si₅, USi₃ and U₃Si an apparent Eₐ of respectively 3.51 ±0.53 eV, 3.17 ± 0.3 eV and 2.52 ± 0.26 eV is found.

Using the effective heat of formation rule, a prediction was made on the first phase formed and the subsequent phase sequence. In the Al-U system, the subsequent growth of a UAl₄, UAl₃ and UAl₂ can be observed. The growth of U₃Si₅ and USi₃ phase is measured during the anneal of a Si substrate covered with a U(Mo) layer while a U₃Si₅ followed by a U₃Si phase appeared during heating of a U(Mo) substrate covered with a thin Si layer. This out-of-pile study confirmed that it is the high affinity of Si for U (larger heat of formation for silicides compared to the aluminides) that allows Si to limit the interaction between the U(Mo) fuel and the Al matrix.
1 BR1 fuel [1]

1.1 Introduction

The interaction between uranium and aluminum is not a new problem. The ORNL graphite reactor X-10 [2], was powered by natural uranium fuel rods (enrichment 0.7% $^{235}\text{U}$) clad with aluminum and sealed with a cap (Figure 86). The first U slugs for the ORNL reactor were simply canned by forcing the slug in the aluminum can. However, in-pile the slugs swelled, got stuck in the channels and blocked the flow of air coolant. In cases where the can ruptured, the air became polluted. The failures were due to

- air leaks in the welds, causing the formation of uranium oxide which has four times the specific volume of the initial metal from which it formed

Figure 84 The SEM images (Backscattered electron mode) of the fuel located at the split cladding shows the formation of an $\text{UO}_x$ layer ([3]

- penetration of the aluminum-can wall because of interaction of uranium and aluminum at 250°C [2]

Figure 85 Can rupture caused by a diffusion blister (from [4])

In those days the problem was solved by applying diffusion barriers and bond aids during the production of the fuel rods. The barriers were intended to inhibit the interdiffusion of uranium and aluminum at temperatures around 250 °C, whereas bonding layers were needed to enhance the heat flow across the fuel-cladding interface [2].

It was therefore decided [5], at the manufacturing stage of the fuel rods, to apply an AlSi bonding layer (BL) and an $\text{U(Al, Si)}_3$ anti-diffusion layer (ADL) on the natural uranium fuel slug.
In 1963, the ORNL reactor was shut down, but the Belgian research reactor BR1, which is of similar design, still uses these fuel rods. The BR1 reactor has been in operation since 1956 and is mainly used as a neutron source for reactor physics experiments, neutron activation analysis, and calibration of nuclear detectors and instruments. The reactor core consists of a graphite matrix, serving as moderator, in which the fuel rods are loaded in horizontal channels.

For the past 20 years, the BR1 reactor has been operational for 3 days per week at a power of 700 kW for a maximum of 8 hours a day. BR1 is cooled by forced air convection with the help of a fan. In this way, the fuel temperature in the reactor is kept well below 200 °C. After more than 50 years, the average fuel element burn-up is calculated to be only 0.07% FIMA (12% $^{235}$U or 3.2 $10^{19}$ f/cm$^3$ U).

The reactor still contains its original fuel rods and after more than 50 years of irradiation at low temperature some of the rods were unloaded and submitted to a post irradiation campaign.

1.2 Fuel fabrication

In the canning operation, three molten metal baths were used (Figure 87), the first one being an Al-Si coating bath to deposit the anti-diffusion layer on the U slug. The bath was held between 590 °C and 615 °C and consisted of 3 layers : a Pb layer on the bottom to preheat the slug; an intermediate layer of Al-Si alloy (11.2 - 11.5 wt% Si) to coat the preheated slug and on top, a flux layer to provide a protective cover for the bath. Dipping the heated uranium slug in a molten aluminum-silicon alloy of eutectic composition produced the anti-diffusion layer of U(Al,Si)$_3$ on the surface (Figure 87a).

In the second bath, consisting of Al-Si alloy (11.2 - 11.5 wt% Si) at a temperature of 595 °C ± 5 °C, the coated slugs were rinsed for 3 seconds to avoid contamination of the final Al-Si canning bath (Figure 87b). The use of a molten aluminum-silicon alloy in the third bath during the subsequent canning of the slug (Figure 87c) was intended not only to assure good
thermal bonding between the uranium rod and the aluminum can but also to provide intimate contact between cap and can. The layer applied in the third bath is henceforth referred to as the bonding layer. The completed assembly was then taken out of the bath and the excess Al-Si was removed. Finally, a weld bead was run around the exposed braze line at the top of the rod using an argon-shielded arc, without filler rod. More details of this process, called the flux-alpha canning process, can be found in [6].

![Figure 87 Schematic overview of the flux-alpha canning process. The uranium slugs are first coated (a), then rinsed (b) and finally inserted into an Al can (c).](image)

It should be noted that the slugs were dipped in the respective baths for a fixed period of time to assure a good reproducibility in coating thickness and composition.

### 1.3 Microstructure

The microstructure of an irradiated BR1 fuel rod used for over 50 years has been analyzed. For comparison, the microstructure of an unirradiated rod (referred to as "fresh" fuel rod and originating from the same production batch as the irradiated rod) has also been investigated.

![Figure 88 Backscattered electron images of (a) the complete section of top of the fuel rod revealing (b) the Al-Si bonding layer; (c) composition of the alloy from the X-ray maps.](image)
The backscattered-electron image of the top of the fresh fuel rod (Figure 88a,b) reveals the bonding layer between the aluminum cladding/cap and uranium. The EDX maps of a small area in the bonding layer, confirm the eutectic microstructure (Figure 88c).

It should be noted that the observed white needle-shaped inclusions (Figure 88a,b) are probably peeled-off flakes of the U-Al-Si anti-diffusion layer. This layer is reported to be very brittle [2]. The flakes probably peeled off during the canning process.

The detailed SEM image and the combined EDX maps (Al=green, Si=red, U=blue) of the fresh fuel (Figure 89a) show the anti-diffusion layer (ADL) between the uranium slug and the bonding layer (BL) and the large pure-aluminum zones at the interface of both layers. From the combined X-ray map, it is clearly seen that the anti-diffusion layer actually consists of two layers which were labeled coating layer (CL) and reaction layer (RL). Such a duplex anti-diffusion layer is also observed in the irradiated fuel (Figure 89b).

Comparing the thickness of the anti-diffusion layer formed in the fresh fuel and in the irradiated fuel, it is observed that the CL has tripled in size during irradiation, while the RL is unchanged.

The increase in the coating-layer thickness is also clearly observed in the optical micrographs taken of the fresh and irradiated fuel (Figure 90).
The optical micrographs also demonstrate that the pure-Al zones at the anti-diffusion and bonding-layer interface in the irradiated fuel rod are noticeably larger than in the fresh fuel.

A quantitative linescan starting in the fuel slug, covering the complete anti-diffusion layer (i.e. coating layer and reaction layer) and ending in the bonding layer has been defined. The measured composition at each point in the linescan is plotted in a ternary diagram (Figure 91). From the diagram the formation of the CL (blue line) and RL (green line) during fuel rod production can be derived. When the fuel slug comes in contact with the molten Al-Si alloy in the first bath, it will preferentially react with silicon from the eutectic melt. This high affinity of Si for U is supported by the fact that the energy of formation of all uranium silicides is larger than that of the uranium aluminide. Comparing the $\Delta H_f$ of all uranium silicides, $U_3Si_5$ is the phase most easily formed. However, a homogeneous layer of $U_3Si_5$ will not be formed as the eutectic layer touching the CL will get depleted in Si and zones of Si-free Al will form [7].
Table 9 Enthalpy of formation of several uranium silicide and aluminide phases [8].

<table>
<thead>
<tr>
<th>Silicide phase</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>Aluminide phase</th>
<th>$\Delta H_f$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USi</td>
<td>-83.7</td>
<td>UAl$_2$</td>
<td>-98.7</td>
</tr>
<tr>
<td>USi$_2$</td>
<td>-129.7</td>
<td>UAl$_3$</td>
<td>-114.2</td>
</tr>
<tr>
<td>USi$_3$</td>
<td>-130.5</td>
<td>UAl$_4$</td>
<td>-130.5</td>
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<tr>
<td>U$_3$Si$_2$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>U$_3$Si$_5$</td>
<td>-343.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$_3$Si</td>
<td>-134.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

U$_3$Si, U$_3$Si$_2$ and USi can dissolve only a small amount of Al in solid solution, but the higher silicides U$_3$Si$_5$, USi$_2$ or USi$_3$ dissolve increasingly larger amounts of Al [9]. The CL, having a composition lying on the tie line between U$_3$Si$_5$ and UAl$_2$ (Figure 91 red dotted line) will start to dissolve Al. As a result, the composition of the coating layer will evolve towards a solid solution [9] of USi$_3$ and UAl$_3$ (represented by the second red dotted tie line in Figure 91).

The formation of the reaction layer in the ADL occurs during the canning process when the bonding layer is applied (third bath Figure 87). At this point, the surface of the coated U slug is again heated to almost 600°C, allowing the eutectic melt to interact with the USi$_3$-UAl$_3$ CL on the slug and form the IL. The composition of the IL will remain a solid solution of USi$_3$ and UAl$_3$, but the Al/Si ratio will evolve from ~2 (at the interface with the CL) to ~1 (at the interface with the eutectic melt). As again the eutectic layer touching the RL will get depleted in Si, the USi$_3$ and UAl$_3$ layer will get exposed to pure Al zones and USi$_3$ will start to dissolve more and more Al.

The observations of the irradiated specimen show those 50 years at moderately low temperature (~140 °C) has caused the anti-diffusion layer to grow. Quantification of the two-part ADL (Figure 89, Figure 90) shows that the CL has increased in size (from ~5 µm to ~21 µm thick). Compared to the CL on the fresh fuel slug, the part of the layer close to the U rod evolved to a nearly pure U$_3$Si$_5$ (Figure 92). Again, only very small amounts of Al, increasing slightly towards the reaction layer, are found in the layer.

The RL is still USi$_3$-UAl$_3$ but compared to the measurements on the fresh fuel rod, the Al/Si ratio has changed from ~0.75 (at the interface with the CL) to ~0.5 (at the interface with the eutectic melt) and the eutectic layer touching the RL remains depleted in Si. The thickness of the reaction layer (~6 µm) is virtually unchanged during the 50 years of irradiation.
These results indicate that irradiation for an extended period, has caused diffusion of Si into the ADL (diffusion barrier for Al). The proposed mechanism for the Si diffusion, and according to the binary diagram [9], is that at low temperature the CL (initially a mixture of U₃Si₅ and UAl₂), reacts with the silicon of the USi₃-UAl₃ RL and forms a nearly pure U₃Si₅ layer (Figure 92). The Si reduction in the USi₃-UAl₃ layer is counterbalanced by a supply of silicon coming from the Al-Si bonding layer. As the latter is a rich source of free silicon, the diffusion mechanism continues. As a result, the U₃Si₅ layer grows into the uranium slug and the bonding layer becomes progressively depleted in Si, resulting in the growth of the pure Al zones.

Simultaneous supply of Si from the bonding layer and supply of Si to the coating layer causes the width of USi₃-UAl₃ layer (RL) to remain virtually unchanged. The Al from the USi₃-UAl₃ RL
only partly diffuses into the CL. On average, the composition of the USi3-UAl3 RL remains the same but the ratio Al/Si changes in favor of Si.

The unintended growth of a thin U3Si5 – UAl2 layer on the uranium slug during fabrication, which during irradiation evolves to a pure U3Si5, served to limit interaction between the uranium and the aluminum cladding.

These results can be related to modern U(Mo)-based dispersion fuel, where during irradiation an (U,Mo)Alx reaction layer develops between the fuel and the aluminum matrix. However, it should be noted that, considering the low burn-up (0.07% FIMA) of the BR1 fuel rods, hardly any fission gas has been created. The behavior of fission gas in the silicides cannot be deduced from these observations, but can be from the PIE on irradiated U3Si2 fuel plates [10]. It was observed here that most of the fuel particles were a mixture of U3Si2 and USi. Detailed analysis of the SEM and BSE images in combination with the EPMA results showed very clearly that the size of the fission gas bubbles is related to the composition of the fuel particles in which they are generated. The fission gas bubbles in the USi fuel were numerous and very small (100-300 nm), while in the U3Si2 zones, the bubble diameter could be as large as a few micrometers, but fewer bubbles were found. All the observed bubbles in USi and U3Si2 had a nearly perfect round shape and no evidence of bubble coalescence is seen, indicating very stable fission gas behavior. Only for the silicides with higher uranium contents (U3Si), unstable fission gas behavior is observed under some irradiation conditions [11].

Based on thermodynamic and metallographic analysis, it is suggested [12] that addition of silicon to the Al matrix would inhibit the growth of the (U,Mo)Alx interaction layer. The first irradiation tests indeed show that the average plate swelling decreases with increasing Si content in the matrix [12].

Adding Si to the U(Mo)/Al systems seems to be a solution to limiting the growth of interaction layer. This solution is based on the preferred interaction of U(Mo) with Si instead of with Al. To obtain a better understanding of this mechanism, the kinetics of the solid state reactions in thin layer systems U(Mo)/Al and U(Mo)/Si are studied using in-situ X-ray diffraction and Kissinger analysis [13].

2 The U(Mo)/Al and U(Mo)/Si solid state reaction [13]

2.1 Introduction

When two materials are brought into contact with each other, the resulting system is typically not thermodynamically stable. A reduction of the Gibbs free energy is achieved by intermixing or compound formation. Completely miscible materials will evolve to a solid solution. However, most materials have only limited mutual solubility and in that case intermixing can lead to the formation of new phases. Theoretically, it is expected that all phases which are stable at a certain temperature T in the phase diagram, will also form in a binary bulk diffusion couple kept at the same temperature T. In most thin films experiments
however simultaneous growth of multiple phases is uncommon as usually the formation of only one compound is observed at the initial stages of the solid state reaction. This is commonly attributed to kinetic constraints or nucleation problems induced by the limited dimensions of the thin film system. First, the new compound formed during the thin film solid state reaction needs to overcome a thermodynamic barrier to enable the formation of very small nuclei of the new phase. After the nucleation, the formed nuclei need a continuous influx of new material to facilitate their growth. If the thickness of this phase can reach a certain critical value before one of the reactants is completely consumed, the formation of a second phase becomes possible and both phases will grow simultaneously. However if one of the reactants is consumed before the critical thickness of the new phase is reached, this new phase becomes the seeding layer for the growth of a second phase and sequential growth of different phases can be observed. The sequence of phases does not necessarily follow the sequence of phases found in the equilibrium diagrams.

2.2 Effective heat of formation rule

For the thin film diffusion experiments, the effective heat of formation (EHF) rule can be used to predict the first phase formed and the subsequent phase sequence for thin films on thick substrates $[14,15,16,17]$. To predict phase formation using the EHF rule, one needs to know the effective concentration of the reactants at the growth interface. Thin film solid state interaction is a non-equilibrium process and the effective concentration is independent of the thicknesses of the interacting components but it can be affected by factors such as impurities, diffusion barriers, atomic mobility, oxidation, ... The effective concentration is assumed to be at the concentration leading to the highest mobility and is thus given by the composition at the liquidus minimum of the binary system.

The effective heat of formation is defined as:

$$\Delta H' = \Delta H^* \times \left( \frac{\text{effective concentration limiting element}}{\text{compound concentration limiting element}} \right)$$  \hspace{1cm} \text{Eq. 36}

with $\Delta H^*$ the standard heat of formation (kJ/mol). The rule for the first phase formation and sequence states that the first compound phase to form during the interaction is the phase with the most negative effective heat of formation ($\Delta H'$) at the concentration of the lowest temperature eutectic of the binary system. The subsequent phase to form at the interface between the compound phase and remaining element is the next phase richer in the unreacted element which has the most negative effective heat of formation.

2.3 Kissinger analysis

In general, the kinetics of thermally activated processes can be described by means of the Arrhenius equation

$$k = A e^{-\frac{E_a}{k_b T}}$$  \hspace{1cm} \text{Eq. 37}

in which $k$ is the growth rate coefficient, $A$ is the pre-exponential factor (reaction coefficient) and $E_a$ the apparent activation energy of the observed process. In order to experimentally
determine the \( E_a \) of the reaction, typically a series of isothermal measurements combined with e.g. Rutherford backscattering spectroscopy (RBS) and/or in-situ ramped resistance measurements can be used \([18,19,20]\). However, Kissinger analysis on the results obtained from in-situ X-ray diffraction (XRD) or resistance measurements proves to be a more time efficient alternative to determine \( E_a \) \([21,22]\). Instead of measuring the time needed at a fixed temperature to initiate the formation, ramp anneals at different fixed heating rates are used to determine the apparent formation temperature at each ramp rate. The ramp rate determines the integrated thermal budget to which the sample has been exposed prior to reaching a certain temperature. The integrated thermal budget spent to reach a certain temperature will be much higher when using a relatively slow heating rate e.g. 0.2 °C/s instead of a faster heating rate e.g. 3 °C/s, because the sample will spend a longer time at each temperature. As a result, the value of the apparent formation temperature will depend on the ramp rate. By using the Kissinger equation \([23]\), which according to Colgan and d’Heurle \([19]\) is applicable to ramp anneals,

\[
\ln \frac{dT}{dt} = - \frac{E_a}{k_b T_f^2} + cst \tag{Eq. 38}
\]

the apparent \( E_a \) of the silicide formation process can be determined by plotting \( \ln \frac{dT/dt}{T_f^2} \) as a function of \( \frac{1}{k_b T_f} \). In this equation, \( T_f \) stands for the apparent temperature of formation, which is taken as the temperature at which the rate of increase of the corresponding XRD peak intensity is maximal.

### 2.4 Experimental

To study the kinetics of the U(Mo)/Si and U(Mo)/Al reaction, 3 sets of samples have been prepared: U(Mo) layer / Si substrate, Si layer / U(Mo) substrate and Al layer / U(Mo) substrate.

A 500nm thick layer of U(Mo) (with 8 wt% Mo) has been deposited by the Technische Universität München (TUM) on HF-cleaned Si substrates using physical vapor deposition (PVD) \([24]\). On the surface of this system, a 30 nm Si capping layer was deposited to prevent oxidation of the U(Mo) layer.

As part of the SELENIUM (Surface Engineered Low ENriched Uranium-Molybdenum fuel) project \([25]\), a sputter deposition setup was constructed in a collaboration between the University of Ghent and the SCK•CEN \([26]\). This PVD coater has been used to deposit ~200nm thick Si and Al layers on U(Mo) substrates containing 8 wt% Mo. The U(Mo) substrates were kindly provided by the Atomic Energy of Canada Limited (AECL).

High temperature in-situ X-ray diffraction measurements are performed on a Brucker D8 Advance system equipped with a Cu tube (Cu Kα1,2=0.1541 nm) and a Våntec detector which allows for fast simultaneous recording of X-ray patterns over a wide 2θ angular range \([22,27]\). The detector was used in snap shot mode, with a fixed 2θ range (25° - 45° 2θ).
Phase transformation of the films was studied by ramp anneals from room temperature up to >850 °C at rates of 0.2, 0.5, 1 and 3 °C/s.

2.4.1 Uranium-aluminum solid state reaction

2.4.2 U(Mo) substrate / Al layer

The XRD data collected during the annealing (ramp rate 1°C/s) of a thin layer of Al on a U(Mo) substrate is presented as contour plot in Figure 94. Initially only two 2 reflections can be observed, the one at 2θ≈37° is resulting from the U(Mo) substrate (γ-U (110) line) while at 2θ≈38.5° the Al (111) reflection from the Al film is measured. At 600 °C, both the γ-U and Al diffraction peaks start to disappear. This indicates that a reaction has taken place and the reflections at 2θ=28°, 36°, 39°, 41°and 44° mark the formation of a UAl₄ phase. Increasing the annealing temperature to above 660°C results in the fading of the UAl₄ peaks and the appearance of diffraction lines at 2θ=29.5°, 36.5° and 42.5°, which is the fingerprint of a UAl₃ phase.

At higher temperatures (860 °C), the UAl₃ phase diminishes and the reflections at 2θ=32.5° and 38° indicate the nucleation of a UAl₂ phase. The other observed reflections could not be indexed but are most probably U or Al –oxides.

The phase-sequence is significantly different from the one obtained in bulk diffusion experiments. There, the solid state reaction between uranium and aluminum will start with the formation of nuclei of UAl₂ near the U/Al boundary but in the U phase. Next, the diffusion of U in Al and vice versa will lead to formation of UAl₃ and UAl₄ phases in the aluminum phase, while in the U phase the UAl₂ grains will grow into the bulk material [28].

A prediction can be made on the first formation in the U/Al system. From the U-Al diagram (Figure 95) it can be seen that the lowest temperature on the liquidus curve is 641°C, with compound concentration of U₀.₀₁₇Al₀.₉₈₅.
The effective heat formation diagram for compound phase formation (top) and the phase diagram for the Al-U system. Each triangle of the effective heat of formation diagram represents the energy released during formation of a particular uranium aluminide phase as a function of concentration.

In Table 10 the effective heats of formation (ΔH') for the uranium-aluminum compounds are given.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>ΔH° [kJ/mol at.]</th>
<th>Limiting element</th>
<th>ΔH' [kJ/mol at.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest eutectic =</td>
<td>U₀.₀₁₇ Al₀.₉₈₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UAl₄</td>
<td>U₀.₂₀ Al₀.₈₀</td>
<td>-26.1</td>
<td>U</td>
<td>-2.22</td>
</tr>
<tr>
<td>UAl₃</td>
<td>U₀.₂₅ Al₀.₇₅</td>
<td>-28.5</td>
<td>U</td>
<td>-1.94</td>
</tr>
<tr>
<td>UAl₂</td>
<td>U₀.₃₃ Al₀.₆₇</td>
<td>-32.9</td>
<td>U</td>
<td>-1.69</td>
</tr>
</tbody>
</table>

Table 10 Heat of formation (ΔH°) and effective heats of formation (ΔH') for various uranium aluminides. The ΔH' have been calculated at the concentration of the lowest temperature eutectic of the binary systems.

From the calculations in Table 10, UAl₄ is expected to form first as it has the most negative ΔH' (2.22 kJ/mol at.). The next phase to form needs to be richer in uranium and has the most negative effective heat of formation. In the current system this would be UAl₃ and subsequently UAl₂. This analysis is in agreement with the observation made in Figure 94.

In Figure 97, the in-situ diffraction contours at different ramp rates are shown. It can be observed that the formation temperature of UAl₄, UAl₃ and UAl₂ increases with increasing ramp rate.
The $T_f$ (temperature of formation) values for the different ramp rates and phases were consistently derived from the plots as the temperature at which the integrated peak intensity shows a steep increase (Figure 96).

Figure 96 The temperature at which the integrated intensity of the UAl$_4$ (112) reflection shows a steep increase, is taken as $T_f$(temperature of formation) of the UAl$_4$ phase formed at a ramp rate of 0.5 °C/s.

Figure 97 In-situ XRD results for ramp anneal of a U(Mo) substrate/Al thin film layer at a rate of 0.2 °C/s, 0.5 °C/s, 1°C/s and 3 °C/s. The dashed lines indicate the growth of the UAl$_4$, UAl$_3$ and UAl$_2$ phases.
These values for $T_f$ are used to perform the Kissinger analysis (Eq. 38) in order to determine the apparent activation analysis for the aluminide formation. In Figure 98, for each of the phases, $\ln \frac{dT/dt}{T_f^2}$ is plotted as a function of $\frac{1}{k_B T_f}$.

The apparent activation energy for UAl$_4$, UAl$_3$ and UAl$_2$ is determined from the slopes of the plotted lines and is respectively $3.6 \pm 0.55$ eV, $2.74 \pm 0.27$ eV and $1.56 \pm 0.08$ eV. In the determination of $E_a$ several errors have been taken in account: the systematic error introduced by the thermocouple calibration and a statistical error caused by the linear regression analysis. As total error on the activation energy, the largest of the errors is taken. In all the measurements this was the systematic thermocouple error.

![Kissinger plot of the uranium aluminide phases observed during the solid state reaction between U(Mo) and Al using ramp anneals at 0.2, 0.5, 1 and 3 °C/s.](image)

Figure 98 Kissinger plot of the uranium aluminide phases observed during the solid state reaction between U(Mo) and Al using ramp anneals at 0.2, 0.5, 1 and 3 °C/s.

### 2.5 Uranium-Silicon solid state reaction

#### 2.5.1 Si substrate/U(Mo) layer

![Variation of XRD intensities in function of temperature](image)

Figure 99 Contour plot of the XRD data acquired during annealing at ramp rate of 1 °C/s. First the growth of an oxide layer can be seen (USiO$_4$), next the USi$_2$ and USi$_3$ phase is formed.
Figure 99 shows the contour plot resulting from the in-situ HTXRD measurement of a Si substrate covered with a 500 nm U(Mo) layer/30 nm Si layer (ramp rate 1°C/s).

A pure unreacted U(Mo) film (γ-U(110) at 2θ=37°) and Si substrate (Si(200) at 2θ=28°) were observed up to temperatures as high as 600 °C. Above 600 °C, a reaction with the U(Mo) film results in the formation of a USiO₄ layer (major peaks at 2θ=24.5°, 31°, 34° and 41°). This indicates that even the deposition of a Si capping layer cannot prevent the U(Mo) layer from oxidation. At ≈630 °C, the USiO₄ lines disappear as well as the γ-U(110) line at 2θ=37° and the formation of a U₃Si₅ layer⁶ is seen (reflections at 2θ=26°, 34° and 44°). Simultaneously, the measured reflections of a UO₂ phase indicates that further oxidation of the U(Mo) layer has occurred. The U/VO₂⁺ equilibrium line is located at an extremely low oxygen potential (at 450 °C \( \mu_{O_2} \) is ~-960 kJ/mol). In that respect the high sensitivity of uranium for oxygen can be understood. However, the annealing of the samples has been done either in vacuum or purified He (oxygen content <ppm) so it is not clear where the oxygen originates from. A possible source of oxygen could be any oxygen dissolved in the U(Mo).

Around 750°C, additional lines appear around 2θ=31°, 38.5° and 44.5°, which can be attributed to the formation of a USi₃ phase. The other observed reflections could not be indexed but are most probably U or Si –oxides.

Also for the uranium-silicon system, a prediction of the first phase formation and sequence can be made. However, for silicide formation, it is recognized that non-congruent silicide phases do not nucleate easily at a moving interface and they are usually skipped except if it is an end phase [14,15]. A rule for silicide first phase formation based on the effective heat of formation model was therefore formulated as the first silicide compound to form during metal-silicon interaction is the congruent phase with the most negative effective heat of formation (\( \Delta H' \)) at the concentration of the lowest temperature eutectic of the binary system. For the various uranium silicides, only U₃Si₂ and U₃Si₅ melt congruently⁶ [29]. According to the calculation in Table 11 and Figure 99, the first phase to form would be U₃Si₂.

This does not correlate with the observation made in Figure 99. Oxygen is expected to decrease the effective concentration of U at the growth interface, thereby favoring the formation of a more silicon rich phase [14].

⁶ In the paper by Leenaers et al. on the “Determination of activation energies of the U(Mo)/Si and U(Mo)/Al solid state reaction using in-situ X-ray diffraction and Kissinger analysis”, the authors were misled by the paper H. Shimizu, Atomics International Report NAA-SR-10621 (1965) in which was stated that only U₃Si₂ and USi₂ melt congruently. Since the diffraction pattern of U₃Si₅ (in the 2 theta domain measured) is almost similar to the one of USi₂, the authors have misinterpreted the first phase formed in the experiment as USi₂. However it has become clear the USi₂ forms peritectic while it is U₃Si₅ that melt congruent.
Table 11 Heat of formation ($\Delta H^\circ$) and effective heats of formation ($\Delta H'$) for various uranium silicides. The $\Delta H'$ have been calculated at the concentration of the lowest temperature eutectic of the binary systems.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Congruency</th>
<th>$\Delta H^\circ$ kJ/mol at.</th>
<th>Limiting element</th>
<th>$\Delta H'$ kJ/mol at.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest eutectic</td>
<td>$U_{0.91}Si_{0.09}$</td>
<td>=</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USi</td>
<td>$U_{0.50}Si_{0.50}$</td>
<td>NC</td>
<td>-42.3</td>
<td>Si</td>
<td>-7.53</td>
</tr>
<tr>
<td>USi$_2$</td>
<td>$U_{0.33}Si_{0.67}$</td>
<td>NC</td>
<td>-43.2</td>
<td>Si</td>
<td>-5.89</td>
</tr>
<tr>
<td>USi$_3$</td>
<td>$U_{0.25}Si_{0.75}$</td>
<td>NC</td>
<td>-32.6</td>
<td>Si</td>
<td>-3.91</td>
</tr>
<tr>
<td>U$_3$Si</td>
<td>$U_{0.75}Si_{0.25}$</td>
<td>NC</td>
<td>-23.0</td>
<td>Si</td>
<td>-11.94</td>
</tr>
<tr>
<td>U$_2$Si$_2$</td>
<td>$U_{0.60}Si_{0.40}$</td>
<td>C</td>
<td>-34.1</td>
<td>Si</td>
<td>-7.67</td>
</tr>
<tr>
<td>U$_2$Si$_5$</td>
<td>$U_{0.375}Si_{0.625}$</td>
<td>C</td>
<td>-44.2</td>
<td>Si</td>
<td>-6.34</td>
</tr>
</tbody>
</table>

Since uranium is highly sensitive to oxidation and the observation of such oxidation phase (USiO$_4$ and UO$_2$) is made (Figure 99), the next possible (congruent) first silicon rich phase would thus be U$_3$Si$_5$. Concerning phase formation sequence, the subsequent phase should be richer in the unreacted element (Si) and has the most negative heat of formation. According to Figure 99 and Table 11 this would be USi$_3$ which is non-congruent but it is an end phase.

Figure 100 The effective heat formation diagram for compound phase formation (top) and the phase diagram for the Si-U system. Each triangle of the effective heat of formation diagram represents the energy released during formation of a particular uranium aluminide phase as a function of concentration. The dashed triangle indicates a non-congruent phase that has difficulty in nucleating.
From the in-situ diffraction results at different ramp rates in Figure 101 it is seen that the formation temperature of the $U_3Si_5$ and $USi_3$ phases increases with increasing ramp rate as expected.

![Figure 101 In-situ XRD results for ramp anneal of a Si substrate/U(Mo) thin film layer at a rate of 0.2 °C/s, 0.5 °C/s, 1 °C/s and 3 °C/s. The dashed lines indicate the growth of the $U_3Si_5$ and $USi_3$ phases](image)

2.5.2 U(Mo) substrate / Si layer

Figure 102 shows the contour plot resulting from the in-situ HTXRD measurement of a U(Mo) substrate covered with a Si layer (ramp rate 0.2°C/s). The transformation of the U(Mo) substrate from gamma phase to alpha U is measured between 500 and 650 °C. Around 700 °C, the $\gamma$-U (110) reflection at $2\theta=37^\circ$ starts to diminish and a $U_3Si_5$ layer is formed. At a slightly higher temperature, the fingerprint of a $U_3Si$ phase is measured (reflections at $2\theta=29^\circ$, $36^\circ$ and $42^\circ$). Figure 103 is an overview of the recorded contour plots at different ramp rates and indicate the increasing formation temperature of the different phases with increasing ramp rate.
Figure 102 Contour plot of the XRD data acquired during annealing at ramp rate of 0.2 °C/s. The growth of an uranium oxide layer can be seen (UO$_2$) as well as the growth of a USi$_2$ and U$_3$Si phase.

Figure 103 In-situ XRD results for ramp anneal of a U(Mo) substrate/Si thin film layer at a rate of 0.2 °C/s, 0.5 °C/s, 1 °C/s and 2 °C/s. The dashed lines indicate the growth of the USi$_2$ and U$_3$Si phases.

Similar arguments as used in 2.5.1 (Si substrate / U(Mo) layer) concerning prediction of first phase using the EHF rule can be made to this system. According to Table 11 and Figure 99, the first phase predicted to form will be U$_3$Si$_5$, while the next phase needs to be richer in the unreacted element, here uranium, thus resulting in an U$_3$Si phase. This is in agreement with the observations made in Figure 102.
From Figure 101 and Figure 103, the temperature of formation $T_f$ of each phase at the different ramp rates is derived and used to perform the Kissinger analysis. From the plot in Figure 104, the apparent activation energy for $U_3Si_5$, is found to be $3.51 \pm 0.53$ eV based on the analysis on the U(Mo) substrate/ Si layer and $3.47 \pm 0.54$ eV based on the Si substrate / U(Mo) layer system.

Figure 104 Kissinger plot of the uranium silicide phases observed during the solid state reaction between U(Mo) and Si using different ramp anneals.

For USi$_3$ and U$_3$Si an apparent $E_a$ of respectively $3.17 \pm 0.3$ eV and $2.52 \pm 0.26$ eV is found. In literature [27] the activation energy for $U_3Si$ is found to be $2.17 \pm 0.04$ eV.

The oxidation of the Si / U(Mo) thin film system will influence the formation of the first phase and has an impact on the absolute value of formation temperature $T_f$ of the different phases formed. The influence of the oxides will however be similar at the different ramp rates, therefore it can be assumed that oxidation will not affect the value of the activation energy $E_a$.

3 Conclusion

Since the failures of the U(Mo)-Al dispersion fuel (e.g. Chapter 4 : The FUTURE-UMo1 experiment) much effort has been devoted to the search for the root cause of these failures and, more importantly, a remedy. It became generally accepted that the properties of the interaction layer formed between the U(Mo) kernels and the Al matrix plays an important factor in these failures.

From the examination of natural uranium aluminum clad fuel rods irradiated for more than 50 years in the BR1 reactor but also miniplate RERTR irradiations conducted at INL, where an observed locally reduced interaction layer thickness was considered to be related to the presence of Si in the Al6061 alloy cladding, it was concluded that the application of silicide layers on a uranium surface is an effective means of counteracting the interaction of the metallic uranium and the aluminum cladding or, in modern fuel, the aluminum matrix.

The solid state reaction between Al - U(Mo) and Si - U(Mo) was studied using in-situ X-ray diffraction. In the Al-U system, the subsequent growth of a UA$_4$, UA$_3$ and UA$_2$ can be observed. The growth of $U_3Si_5$ and USi$_3$ phase is measured during the anneal of a Si
substrate covered with a U(Mo) layer while a $\text{U}_3\text{Si}_5$ followed by a $\text{U}_3\text{Si}$ phase appeared during heating of a U(Mo) substrate covered with a thin Si layer. The effective heat of formation rule has been successfully used to explain the first phase formation and subsequent phase sequence in the uranium-aluminum system and the uranium-silicon system. It was furthermore found that the oxidation of the U(Mo)/Si system results in the formation of a $\text{U}_3\text{Si}_5$ phase instead of a $\text{U}_3\text{Si}_2$ phase. This is mainly due to a decrease of the effective U concentration at the growth interface.

The apparent activation energy $E_a$ for the formation of $\text{UAl}_4$, $\text{UAl}_3$ and $\text{UAl}_2$ is determined with the use of Kissinger plots and is respectively $3.6 \pm 0.55$ eV, $2.74 \pm 0.27$ eV and $1.56 \pm 0.08$ eV. For $\text{USi}_2$, $\text{USi}_3$ and $\text{U}_3\text{Si}$ an apparent $E_a$ of respectively $3.51 \pm 0.53$ eV, $3.17 \pm 0.3$ eV and $2.52 \pm 0.26$ eV is found.

It is the affinity of U for Si (larger heat of formation for silicides than for aluminides) that allows Si to stop the interaction between U and Al. In the in-pile situation, Si covalent bonds may reduce the amount of free volume in the amorphous U-Al(-Mo) interaction phase and as such improve its properties.

The most straightforward method of adding Si to the Al matrix for plate production is to mix the Si with Al powder. During hot rolling and blister anneal, the fuel plate is submitted to higher temperatures inducing a thermally driven diffusion of Si atoms from the matrix towards the U(Mo) fuel particles leading to the formation of Si rich preformed layers around the kernels. Several irradiation experiments of U(Mo) fuel plates containing various Si amounts added to the Al matrix, were performed.
References


Chapter 6 Adding Silicon to the system: IRIS-3, (IRIS-TUM), E-FUTURE-I, (E-FUTURE-II)

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3 AlSi matrices for U(Mo) dispersion fuel plates [23]

3.1 Properties of AlSi alloys

3.1.1 Microstructure and hardness measurements

3.1.2 X-ray diffraction analysis

3.1.3 Annealing study of U(Mo) dispersed in an Al, Al-Si mixed or AlSi alloy matrix

3.2 E-FUTURE-II

3.3 Conclusion

4 General conclusion

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Summary

The FUTURE-UMo experiment described in chapter 4 showed that the classical atomized U(Mo) fuel dispersed in a pure Al matrix, cannot withstand demanding operating conditions required for high power research reactors (HPRR). Excessive local swelling (pillowing) was observed in the high power zones of the fuel plates. It turned out this was the consequence of excessive interaction between the UMo kernels and their surrounding matrix, leading to the formation of an amorphous interaction phase. The growth of that layer and its apparent low fission product solubility, causes accumulation of fission products at the interface between fuel kernel and matrix, weakening the matrix structure. Combined with an increase in stress in the fuel plate, this will eventually lead to pore formation and interconnection followed by the observed pillowing. A possible solution to improve the behavior of atomized U(Mo) dispersion fuel, as shown in chapter 5 and in [1,2,3], is to add silicon to the system and as such impede the growth of the U-Mo-Al IL in favor of the U-Mo-Al-Si IL. In that framework, the IRIS-3 and IRIS-TUM irradiation programs were started and several full size, flat plates containing atomized (IRIS-3) or ground (IRIS-TUM) U(Mo) dispersion fuel in an aluminum matrix, with and without addition of silicon, were irradiated in the OSIRIS reactor. During fabrication, the plates are submitted to a heat treatment which causes the formation of Si rich layers on the surface of the U(Mo) kernels. The microstructural observations of the fuels in these experiments revealed the positive effect of Si on the IL thickness. A markedly thinner IL was formed and larger quantities of matrix were found to remain at high burn-up. Nevertheless, at higher burn-ups, still important quantities of interaction phase were observed and the formation of the characteristic crescent shaped voids was seen in some samples. Since Si is not soluble in Al, it was present as precipitates in the Al-2.1w%Si matrices used in these experiments. The Si distribution was translated in a particular microstructure after irradiation where it was clearly established that, whenever important concentrations of Si were present in close proximity to the UMo-matrix interface, the local U-Mo-Al IL formation would be very small or even non-existent. On other locations on the interface, local Si concentrations were lower and a thicker IL would form.

Based on these findings, a new set of U(Mo) / Al-Si matrix irradiations at a high power level was defined by the European LEONIDAS consortium. The first irradiation campaign was called E-FUTURE and was performed to select an optimum Si concentration and fuel plate heat treatment parameters for further qualification. It consisted of the irradiation of 4 distinct (regarding Si content and heat treatments), full size flat fuel plates in the BR2 reactor under bounding conditions (470 W/cm² peak BOL power, ~70% peak burn-up). Although the plates were irradiated up to the foreseen burn-up level at elevated powers without fission product release indicating cladding failure, the post-irradiation examinations (PIE) did reveal important pillowing had occurred at the highest power locations on all 4 plates during the last cycle. Although the higher Si concentrations and higher powers, the evolution of the fuel microstructure was found to be very similar to what was observed in IRIS-3. Interaction layer growth is reduced by the presence of Si but at the highest burn-up locations, still important
quantities of interaction phase are formed and matrix concentrations drop below 10%. Due to the (required) high fuel loading, clustering of the U(Mo) fuel kernels occurs, leading to insufficient coverage of the fuel particle surface with Si during the thermal treatment prior to irradiation. The interaction between uncovered U(Mo) particle surfaces (or those that do not possess the protection of a sufficiently Si-rich preformed layer) and the Al matrix leads to the formation of the classical U(Mo)Al₅ layer. The ejected fission products are snowplowed by this growing interaction layer to the interface of the IL with the matrix. It is this accumulation of fission products at interface that leads to weakening of the core structure of the fuel plate, which eventually causes the pillowing to appear.

PIE also revealed that around $2.5 \times 10^{21}$ f/cm³, the U(Mo) particles start to undergo recrystallization. This grain refinement usually starts at grain boundaries, but in the case of atomized U(Mo) fuel it begins at the cell boundaries where the Mo concentration is lower. As the burn-up accumulation progresses further, also the cell interiors are recrystallized, but not all cells undergo grain refinement at the same burn-up. As such, a particular microstructure is produced, in which cells showing no bubbles in the SEM image (the nanobubble superlattice is presumed to exist) and cells that have completely restructured are sometimes both present in the same kernel. The transformation of the entire U7Mo fuel kernels appears complete at fission densities of $4.5-5 \times 10^{21}$ f/cm³.

One of the consequences of recrystallization is the coalescence of released fission gas in larger bubbles which are located on the new grain boundaries. This will lead to an increased swelling rate of the fuel.
1  IRIS-3 irradiation

1.1  Introduction

The IRIS-3 and IRIS-TUM experiment consisted of the irradiation of full sized fuel plates containing either atomized (IRIS-3) or ground (IRIS-TUM) U(Mo) powder dispersed in either a pure Al or Al-2.1wt%Si alloy matrix. At room temperature, the Si added to the matrix will be mainly present in the form of precipitates because of its low solubility in Al. However, during the manufacturing of the fuel plates, some of the Si will be thermally transported from the matrix to the fuel kernel surfaces [4,3], producing preformed U-Mo-Al-Si layers around the fuel particles [5]. The preformed Si rich layers limit the interaction between uranium and aluminum.

Adding ground fuel to the experiment is related to the fact that, compared to atomized fuel, ground fuel behaves differently under irradiation and it is not completely understood why. However, as ground fuel is somewhat outside the scope of this thesis (although there are lots of similarities to atomized U(Mo) fuel), the reader is referred to ANNEX 1 for the results on the IRIS-TUM irradiation.

1.2  Fuel plate fabrication and irradiation history

Four full sized fuel plates were irradiated in the IRIS-device in the OSIRIS reactor [6]. The plates had a fissile material loading of 7.8-8.0 g U$_{tot}$/cm$^3$ and a uranium enrichment of 19.8% $^{235}$U. The meat of the fuel plates consisted of U 7.3 wt%Mo particles dispersed in an aluminum matrix to which 2.1 wt% Si (2 plates) or 0.3 wt% Si (2 plates) was added. The cladding of the fuel plates was made of AG3NE Al-Mg alloy (2.81 wt% Mg) which corresponds to a nuclear grade Al5754 alloy.

In this thesis, the irradiation and subsequent post irradiation examination of only two of the four fuel plates will be described. Fuel plate U7MV8011 contains an Al-0.3wt%Si matrix while fuel plate U7MV8021 has Al2.1 wt% Si alloy as matrix (Table 12). Thanks to the availability of a specialized device it was possible to measure the plate thickness between cycles. After the 5$^{th}$ irradiation cycle, break away swelling for fuel plate U7MV8011 was observed and the plate was unloaded. At its end-of-life (EOL) the plate had an average burn-up of 33.9 % $^{235}$U (2.5×10$^{21}$ fissions/cm$^3$ U(Mo)) with a peak burn-up at maximum flux plane of 42.6 % $^{235}$U (3.1×10$^{21}$ fissions/cm$^3$ U(Mo)). Fuel plate U7MV8021 was kept in the reactor for 7 cycles, reaching an average burn-up of 48.8 %$^{235}$U (3.6×10$^{21}$ fissions/cm$^3$ U(Mo)) with a peak burn-up of 59.3 %$^{235}$U (4.4×10$^{21}$ fissions/cm$^3$ U(Mo)).
1.3 Post-irradiation examination

1.3.1 Non-destructive testing

A measuring bench located in one of the channels of the OSIRIS reactor, makes it possible to measure the plate thicknesses between cycles.

The longitudinal scans contain 250 data points measured every 2.5 mm, while the transversal measurement comprises 116 data points measured every 0.5 mm. The line scans over the plate length are located at the edge of the meat (-26 mm and 26 mm), the center (0

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7 These measurements are not published in open literature. They were kindly made available by M. Ripert and M-C. Anselmet from CEA for this thesis.
mm) and at -13, -21 mm, a location on the plate where in a previous irradiation experiment (IRIS-1) a deformation was measured.

The transversal scan is taken at 307 mm which corresponds to the max flux plane (MFP).

The transversal scans for plate U7MV8011 obtained after the first four cycles (Figure 106a), show a gradual increase in plate thickness as expected. The value of the thickness is nearly constant over the width of the plate but in the scan after the 4th cycle a slight increase in thickness is observed at position ~+21 mm (near the edge of the plate). The measurements after cycle 5 clearly show a steep increase in thickness at this location (Figure 106b). The location of the deformation is at the opposite side of the plate than was expected from a previous experiment (IRIS-1). As such, no longitudinal scans covering this deformation were recorded. It was decided to record more detailed transversal scans between 292 and 356 mm (every 4 mm).

![Figure 106 Transversal scans for fuel plate U7MV8011 after the first 4 cycles (a) and after 5 cycles (b).](image)

In Figure 107, the contour plot resulting from the detailed transversal scans is added to the contour plot obtained from the longitudinal measurements after the last cycle (5th).

![Figure 107 Plate thickness contour plot obtained from the transversal scans (in-between dotted lines) added to the contour plot resulting of the longitudinal scans.](image)

Based on these measurements, it was decided to unload fuel plate U7MV8011 after the 5th cycle.

For fuel plate U7MV8021 (with the Al/2.1%Si matrix), the transversal scans at 307 mm show after each of the 7 cycles a gradual increase of the plate thickness (Figure 108).
Figure 108 Transversal scans for fuel plate U7MV8021 after each of the 7 cycles.

In Figure 109 the plate thickness contour plot based on only the longitudinal scans recorded after the last cycle, is displayed.

For both plates, the fuel swelling is calculated based on the average plate thickness measured at the MFP after each cycle and corrected for corrosion of the cladding. As no oxide thickness measurements were performed, except for the oxide thickness at EOL (can be measured in the DT), an estimation of the thickness after each cycle is taken.

Figure 109 Plate thickness contour plot of U7MV8021.

It should be noted however that the influence of the oxide layer thickness on the plate thickness calculation is very small. For fuel plate U7MV8011, the total oxide layer thickness varies from 6 µm (at low power locations, assumption) up to 20 µm (at max flux plane (MFP) and measured on the SEM images), while for U7MV8021 which has been irradiated longer, the oxide thickness ranges between from 6 µm (at low power locations, assumption) and 40 µm (at MFP and measured on the SEM images).

The average burn up the plates had reached after each cycle was calculated and verified with gamma spectrometry after the last irradiation cycle.

In Figure 110 the fuel swelling measured on the FUTURE U7MTBR07, IRIS-3 U7MV8011 and U7MV8021 plates is plotted in function of the fission density. Both the FUTURE plate and the IRIS-3 U7MV8011 plate show excessive swelling. For the latter one, for which 0.3 wt% Si was added to the Al matrix, this appears at a slightly higher fission density. This could be the effect of adding (even a very small amount) of Si or the lower power at which fuel plate U7MV8011 has been irradiated.
The real benefit of adding Si to the matrix is seen from the fuel swelling curve of plate IRIS-3 U7MV8021 (2.1 wt% Si added), which shows an almost linear increase up to $\sim 4 \times 10^{21}$ fissions per cm$^3$. It should be noted that above a fission density of $3 \times 10^{21}$ fissions per cm$^3$ the swelling of fuel plate U7MV8021 seems to slightly accelerate. This can also be seen when a linear regression is performed on the data points below and above $3 \times 10^{21}$ fissions per cm$^3$. This all appears very artificial but this reasoning will become clear in the remainder of this section.

The points in Figure 111 are fitted using two linear relationship but they can of course also be described as a single non-linear evolution.

After unloading and non-destructive characterization at CEA, a slice of the fuel plate was cut at the maximum burn-up plane (MFP) and transferred to the Laboratory for High and Medium Activity (LHMA) at the SCK•CEN site for microstructural examination.

1.3.2 Destructive testing

The as received samples were too large for embedding and needed to be cut in smaller pieces. To limit the forces applied on the fuel sample during cutting and prevent falling apart of the damaged fuel plate, the slice was put in a stainless steel envelope and fixated with epoxy glue. Next, the slice was cut into several smaller samples which were embedded in an
epoxy resin by hot mounting in such a way that the complete section of the fuel (meat and cladding) can be observed. The mounts were polished with SiC paper of successively finer grain size, finishing on cloth with diamond paste of 3 µm and 1 µm.

The microstructure of the U(Mo) fuel was analyzed by optical microscopy (OM), scanning electron microscopy (SEM), and electronprobe microanalysis (EPMA).

1.3.2.1 Fuel behavior
As can be seen from the photograph (Figure 112) of the as received sample from fuel plate U7MV8011, the deformation measured on the fuel plate can be identified as a pillow.

![Figure 112 Photograph of a slice cut from fuel plate 8011 showing the deformed or pillowed area.](image)

From the photograph in Figure 112, it is seen that the deformed area on the plate is located near the edge of the plate. Similar observation is seen in the collage of OM images in Figure 113 but it furthermore shows some porosity at the other edge of the fuel plate. By representing the fuel parts as shown in Figure 113, it is clearly seen that the effects occur at positions located symmetrically on both edges of the fuel plate.

![Figure 113 Overview of the complete fuel plate width, with the edges pointing in the same direction.](image)

The microstructure of the plate bears much resemblance to the plates of the FUTURE irradiation (chapter 4), which were irradiated at higher power (340 W/cm²) but reached a lower burn-up 33% ²³⁵U before pillowing.

Looking in more detail (Figure 114 a,b) there is a very clearly observable interaction between the U(Mo) kernels and the matrix material and also large crescent shaped porosities are seen at the interface between the interaction layer (IL) and the matrix. The large number of porosities observed is associated to a weakening of meat, but it is an internal or external mechanical force is required to pull the plates apart. Three probable mechanism have been studied by S. Dubois [6]:

- An immediate deformation due to a high pressurization of the cavities driving to plastic deformation. Even with very high pressures, the calculated swelling does not
comply with the observed one. Plasticity modelling is thus not sufficient to induce plate tearing.

- A delayed deformation due to creep: The deformation would reach ~500 µm in 20 days (approximately one cycle), for a ~15 bars pressure gradient. These values are more in line with the observations and as such, creep can thus be considered as a possible mechanism inducing plate deformation.

- Buckling: local thermal buckling due to a thermal gradient seems improbable, since a high temperature should be necessary. However, as the plate cools down at the end of the irradiation an additional buckling mechanism due to cladding compression could increase the plate deformation. It is unlikely that this would be the primary cause, but it may contribute.

Figure 114 Detailed micrographs of the meat at the locations indicated a,b in Figure 113.

The composite image of optical macrographs of the sample from fuel plate U7MV8021 (with Al2.1wt%Si matrix) show a homogeneously thick (~600 µm) meat layer in-between the cladding (Figure 115).

Figure 115 Composite of micrographs showing a transverse cross section of the plate at maximum flux plane.
From the more detailed optical images, it is generally observed that plenty of the aluminum matrix is left and the silicon particles dispersed in the matrix can be readily observed (Figure 116).

Figure 116 Optical microscopy images showing a string of particles at the interface with the cladding (a). The Si particles added to the matrix are readily seen (b).

The 2.1 wt% Si added to the Al matrix is seen as particles randomly dispersed in the matrix, which is expected since Si is insoluble in Al. At the interface between the cladding and the meat, a string of particles is seen. It is also viewed that the matrix at the interface between cladding and meat contains less Si particles. It is therefore reasonable to assume that the string of particles consists of silicon originating from the matrix forming a secondary precipitate with the dissolved Mg from the AG3NE (2.81 wt% Mg) cladding typically Mg2Si as formed in Al-Mg-Si alloys (6XXX series). Also close to some of the fuel particles, the matrix contains less silicon particles (Precipitate free zone (PFZ)). It is believed that this is the result of the destruction of the silicon particles by fission fragment tracks (irradiation assisted dissolution) and irradiation assisted diffusion to the U(Mo) kernels.

Micro hardness measurements of different phases contained within a fuel plate irradiated to different burn-ups can give a good indication of the evolution of the mechanical properties of those phases. In Table 13 the results of the Vickers hardness measurements for fuel plates U7MTBR06 (FUTURE) and U7MV8011, U7MV8021 (IRIS-3) are shown.

Comparing the hardness measurements obtained in each of the different phases (cladding, matrix, fuel, interaction layer) in all plates (Table 13), a good agreement is found for the cladding and the interaction layer. For the matrix, increasing hardness is found for U7MV8021. This difference is most probably due to the addition of silicon to the matrix, in addition to the higher damage concentration because of the higher burn-up. For the U(Mo) fuel a further softening is observed which can be explained by the difference in burn-up of the fuel plates and as such the amount of fission gas bubbles formed.
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FD \times 10^{21} f/cm^3_{U(Mo)}

AG3NE Cladding

U(Mo) Fuel

U-Mo-Al IL

Matrix

Unirradiated

70

396

48

U7MTBR06 A (no Si)

1.9

64

482

306

92

U7MTBR06 B (no Si)

2.2

63

353

400

104

U7MV8011 (0.3wt%Si)

3.1

64

307

325

113

U7MV8021 (2.1wt%Si)

4.4

71

265

368

141

Table 13 Results of the Vickers hardness measurements for the FUTURE plate (samples A,B) with no Si added and the IRIS plates with respectively 0.3%Si and 2.1wt%Si added to the matrix.

1.3.2.2 Interaction layer

The secondary electron image of the sample from fuel plate U7MV8011 (no Si) (Figure 117a) shows the formation of porosities at the interface of the matrix and the IL. Similar as in the FUTURE irradiation, the fission products were snowplowed by the growing IL. The weakened interaction layer–matrix interface will thus be the location where decohesion occurs once mechanical separation forces are applied. The possible origin of those forces is discussed above.

Figure 117 Secondary electron (SE) image showing the porosities that have formed at the interface IL and matrix in plate U7MV8011 (0.3% Si). The SE images of the fuel kernels in plate U7MV8021 reveal IL’s having uneven thicknesses and jagged edges.

X-ray maps recorded in the meat of plate U7MV8011 (0.3%Si) clearly show the formation of a U-Mo-Al interaction layer (Figure 118). From the quantitative linescans (eg. Figure 118) a ratio Al/U+Mo of 6 is found for the IL. Even though only 0.3wt% of Si is added to the matrix, the linescan in Figure 118 indicates some presence of Si in the interaction layer but there is no noticeable interaction of Si with the U(Mo) fuel.
In the meat of fuel plate U7MV8021 (2.1wt%Si) hardly any voids are observed (Figure 117b). The SE images show an in-homogenous thickness of the IL around the fuel kernels and at certain locations on the fuel particles there is almost no IL present (pointed out in Figure 117b by arrows). As will be shown later, this is related to the presence of Si rich phases close to the fuel kernel.
From several quantitative linescans the composition of the IL that forms (eg. Figure 119 between point a and b is calculated. At positions at the fuel kernel periphery that are not close to an Si particle, it appears that a near to "normal" \((\text{U,Mo})(\text{Al,Si})_4\) (based on several quantifications) IL has grown. No large concentrations of Si in the layer are measured which is different from the result found in the out of pile experiments [7]. A possible explanation for this difference could be the temperature at which both processes take place.

1.3.2.3 Si addition
The application of silicide layers on a uranium surface is an effective means of counteracting the interaction of the metallic U(Mo) and the aluminum cladding or the aluminum matrix. It is the affinity of U for Si that allows Si to stop the interaction between U and Al [8,9]. The most straightforward method of adding Si to the Al matrix for plate production is to use an Al-Si alloy powder. During hot rolling and blister anneal, the fuel plate is submitted to higher temperatures inducing a thermally driven diffusion of Si atoms from the matrix towards the U(Mo) fuel particles leading to the formation of Si rich preformed layers (PFL) around the kernels.

![Figure 120 Secondary electron and Al, Si, Mo, U and Xe X-ray maps of a fuel kernel in plate U7MV8021. The position of the two measured quantitative linescans L1,L2 are indicated in the SE image.](image)
The effect resulting from the addition of Si to the Al matrix is best seen in the EPMA measurements. The Al, U and Mo X-ray maps obtained by EPMA (Figure 120) show that the uneven growth of the IL is related to the presence of Si at the interface with the U(Mo) fuel kernel. It appears that only at those positions where a Si rich phase was near to the fuel at the start of the irradiation, little IL has grown (Figure 120 point e), supporting the fact that the affinity of U for Si is larger than for Al. This results in the formation of a U(Mo)-Al(Si) interaction layer away from Si rich areas (between point a and b in Figure 120) or the formation of a U - Si layer close to those areas (beyond point e in Figure 120). In case a U-Si layer has formed, no growth of an U-Al IL is observed, supporting the notion of a U-Si layer as an anti-diffusion barrier [8,9]. This can also be measured in quantitative linescans. In the linescan L2 over a fuel particle at point e, very limited U-Al IL can be measured but an increase in the Si concentration is observed. The linescan L1 over the ‘normal’ IL shows that it does not contain large quantities of Si. A gradual decrease of Si content from approx. 1.5 wt% to nearly 0 over the IL (between point a and b) is seen.

In case a Si particle is reached by the IL, at first the IL will incorporate the particle (grow around it). This causes part of the jagged appearance of the outer periphery of the IL (Figure 121).

![Figure 121 SE image combined with the Si X-ray map (white) of the same area. Encircled are some of the Si particles that get incorporated into the growing interaction layer.](image)

1.3.2.4 Swelling
The obtained SEM images were used to quantify, by image analysis, the volume fraction occupied by the different phases, i.e. the U(Mo) fuel particles, the interaction layer (IL) and the matrix (see chapter 4). It should be noted that the values obtained for the volume fraction occupied by the U(Mo) fuel also include the fission gas bubbles. Image analysis on the backscattered electron pictures shows that the bubbles occupy approximately 1% of the volume of the fuel particle.

A direct comparison of the measured volume fractions to their initial values would be biased as the total volume (or meat thickness) can locally vary significantly. However by multiplying
the measured volume fractions with the measured meat thickness the evolution of the volume of the different phases in function of the burn-up can be calculated.

<table>
<thead>
<tr>
<th></th>
<th>Fission density</th>
<th>Volume fraction (%) × Meat thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Matrix</td>
</tr>
<tr>
<td>Initial fresh</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>U7MV8011 (0.3wt%Si)</td>
<td>3.0×10^21</td>
<td>153</td>
</tr>
<tr>
<td>U7MV8021 (2.1wt%Si)</td>
<td>4.2×10^21</td>
<td>147</td>
</tr>
</tbody>
</table>

Table 14 Evolution of the matrix, IL and fuel volume based on the measured meat thickness and volume fractions occupied by the different phases.

Similar to the FUTURE experiment (chapter 4), an increase in volume of the IL at the expense of the matrix is observed. For fuel plate U7MV8021 a lower volume of IL is measured, indicating the positive effect of adding Si to the matrix. The fuel volume evolution shows a slight increase at higher burn-up.

Due to the limited number of data points no further analysis is made on the contribution of the different phases to the overall swelling of the fuel plate.

1.3.2.5 Fission products

Images from the meat of fuel plate U7MV8011 (0.3wt%Si) locally irradiated up to a fission density of 3.1×10^21, show the formation of a fuel-matrix interaction layer. The growth of the IL will result in the creation of a fission product halo around the fuel kernels by snowplowing (Figure 122).

The quantitative linescan of Xe and Nd (Figure 118) reveals that these elements are rather homogenously distributed inside the fuel kernel. The occasional slight decrease in Xe concentration follows the Mo concentration, indicating that the Xe is still contained as nanobubbles inside the fuel cells but is starting to precipitate at the cells boundaries which are slightly less rich in Mo [10,11,12]. The larger bubbles are more likely to get opened.
during sample preparation. Since the analyzed volume of an electron probe is about $1 \times 1 \times 1$ µm$^3$, an apparent lower amount of xenon is measured. An increased concentration of Xe and Nd is seen at the interface IL and matrix (halo), but also inside the IL, a significant amount of fission product is measured (linescan in Figure 118).

Furthermore, at certain locations on the IL/matrix interface in particular where two IL meet, already the formation of large Xe bubbles can be witnessed (pointed out by white arrow in Figure 122).

![Figure 123 SE image, Xe, Nd and Si X-ray map of the meat in fuel plate U7MV8021 (2.1wt% Si).](image)

In the fuel particles of fuel plate U7MV8021 (2.1 wt% Si) locally irradiated up to a fission density of $4.4 \times 10^{21}$, xenon has precipitated out into bubbles but also still patches of homogenously distributed Xe are observed (Figure 123) and measured (linescan in Figure 120 between point c and d). These Xe patches reflect the nanosized bubbles ordered on a superlattice as observed by TEM which are not resolved by EPMA.

In Figure 123 (indicated by the white arrows) it is also seen that at those location where a Si rich layer has formed, no sweeping of the fission products has occurred as no IL has grown. The typical FP halo at this location is therefore absent and a more diffuse scattered image of the FP is seen.

1.3.2.6 Recrystallization

Despite the large deformation, the U(Mo) in plate U7MV8011 (0.3Wt% Si) has behaved in a very stable way (Figure 124 top). The formation of fission gas bubbles on the cell boundaries indicates that grain refinement starts there at a fission density of approximately $3.1 \times 10^{21}$ f/cc. The continuation of the recrystallization throughout the entire cell is seen in fuel plate U7MV8021 which has been irradiated up to $4.4 \times 10^{21}$ f/cc (Figure 124 bottom). It seems that at this burn-up the recrystallization (RC) is almost complete but still cells optically free from bubbles are observed (Figure 124 bottom, indicated by an arrow). The assumption that in these cells the xenon is still contained within the nanobubbles is supported by the EPMA measurements (e.g. Figure 120, Figure 123).
1.4 Conclusion

The non-destructive testing of fuel plate U7MV8011 (0.3 wt% Si) irradiated up to $3.1 \times 10^{21}$ f/cc shows excessive swelling. Microstructural characterization of the fuel reveals that, similar to the FUTURE experiment, an amorphous interaction layer is formed. The accumulation of fission products by this growing interaction layer leads to weakening of the matrix at the interface between the IL and the matrix. This is an initiation point for mechanical failure when the swelling rates become high and creep can no longer accommodate the fast swelling. The benefits of adding Si to the system and as such limit the formation of an IL is proven by the PIE on fuel plate U7MV8021 (2.1 wt% Si). The NDT shows an almost linear increase of the swelling with increasing fission density. A slight acceleration of the swelling can be seen around $3 \times 10^{21}$ f/cc. The destructive analysis has shown that this occurs at the same time as the onset of grain refinement of the fuel. As is shown in chapter 3, recrystallization namely leads to acceleration of the swelling, as the bubbles that result from it, form effective sinks for the fission gas generated in the recrystallized parts of the kernels. Since the local grain sizes (order of few hundred nm) in the fuel after RC are of the same order as the athermal diffusion length of the fission products, the fission gases can now directly reach the gas bubbles. As the kernel gradually evolves to complete recrystallization, the swelling rate increases accordingly. The swelling profile of fuel plate
U7MV8021 can thus be divided into two areas: below a fission density of $3 \times 10^{21}$ f/cc the fuel swelling should be attributed to solid state swelling (incorporation of fission products) while above this limit an acceleration of the swelling is due to the start of refinement of the U(Mo) fuel grains.

IRIS-TUM plates (ANNEX 1), irradiated at moderate power up to higher burn-up (up to respectively 56 and 88% $^{235}$U LEU equivalent for the plates with a 0.3 and 2.1 wt% Si/Al matrix) also show increased swelling rates, but without direct evidence of pillowing. Although it is qualitative, there appears to be a better mechanical resistance to pillowing for the ground UMo based fuel, possibly because the anchoring of the irregularly shaped fuel particles to the matrix is better than for the spherical atomized kernels. Nevertheless, based on the microstructural evolution observed it is believed that eventually the ground fuel will also not be able to resist the internal stresses and yield, certainly at the higher powers at which this fuel needs to operate. As far as the evolution of the fuel microstructure with burn-up is concerned, the UMo material itself shows a very predictable and stable evolution under irradiation as a sizeable fission product inventory is built up inside it. The fission gases were shown to initially precipitate in nanobubbles, which were found to be ordered in a superlattice.

Similarities between atomized and ground fuel are:

- Formation of an interaction layer. The positive effect of Si to as diffusion barrier is shown in both cases.
- The fuel remains crystalline, while the interaction layer becomes amorphous
- Formation of an ordered nanobubble fission gas lattice in the fuel grains

The most striking differences between atomized and ground fuel are:

1. recrystallization: probably due to the higher initial defect concentration in ground fuel, grain refinement will start at a much lower burn-up ($\sim 1.5 \times 10^{21}$ f/cm$^3$) compared to atomized fuel ($3.1 \times 10^{21}$ f/cm$^3$).
2. the swelling behavior: especially at low burn-up the swelling of fuel will be accommodated by the larger as fabricated porosity which is typical for ground powder. Similar to atomized fuel (compared to the IRIS-3 U7MV8021 plate) the swelling curve can be divided into two areas: solid state swelling and swelling resulting from grain refinement. The difference between ground and atomized U(Mo) fuel is at which fission density the accelerated swelling can be witnessed. For ground fuel this is at much lower burn-up.
2 LEONIDAS E-FUTURE plates

2.1 Introduction

Based on the positive results of the low power IRIS-3 [13], IRIS-TUM [14] or the RERTR-6, 7A, 9A-9B experiments [3, 2, 15], the U(Mo) fuel development focused on the addition of Si to the Al matrix of the fuel [4, 15, 16, 5]. In 2009, a European initiative, led by SCK•CEN, ILL, CEA and AREVA-CERCA, initiated the qualification of dispersed U(Mo) for high power reactors, resulting in the startup of the LEONIDAS program [17, 18]. The LEONIDAS program aimed at the qualification of the U(Mo)-Al(Si) dispersion fuel for the use in high power conditions. The first experiment of the program, designated E-FUTURE, was performed to select a Si concentration and fuel plate heat treatment parameters for further qualification. It consisted of the irradiation of 4 full size, flat U(Mo) fuel plates having an Al-Si matrix.

The IRIS3 experiment has demonstrated in mild operating conditions (max heat flux ~200 W/cm²) that 2.1wt%Si was sufficient to improve significantly the in-pile fuel behavior, since no abnormal swelling was observed. One of the conclusions drawn from RERTR experiments [2, 15] is that a minimum of 4wt% Si should be considered necessary to sustain the positive in-pile Si effect under more severe irradiation conditions. As a good compromise between a sufficiently high Si concentration in the Al to sustain its beneficial effect and the lowest possible Si content for fuel back-end (reprocessing) issues, E-FUTURE was designed with two matrix Si concentrations of 4wt% and 6wt% [5].

2.2 Fuel plate fabrication and fresh fuel characterization

The 4 full-size fuel plates in the E-FUTURE experiment consist of 8gU/cc atomized U7wt%Mo particles dispersed in an Al-Si matrix. The manufacturing details and plate identification are shown in Table 15.

The matrix is a mixture of Al powder with either 4 or 6 wt% Si powder and two different cladding types were used (AlFeNi or AG3NE). Granulometric analysis shows that 10% of the Si particles have a diameter less than 1.0 µm, 50% has a d<4.3 µm and 90 % has a d< 13.1 µm. The plates were heat treated under different time/temperature conditions during manufacturing by AREVA-CERCA (Table 16) promoting the Si diffusion from the matrix towards the fuel kernels. Three different thermal treatments were selected to enhance this further:

- at relatively low annealing temperature of 425 °C during 2h : similar to the IRIS-3 fabrication conditions
- at annealing temperature of 475 °C during 2h : effect of higher temperature on enhancement of Si diffusion towards U(Mo)
- at annealing temperature of 475 °C during 4h: varying the pre-irradiation layer thickness and composition.

Next to the plates to be irradiated in BR2, several other fuel plates (submitted to the same heat treatment) were available for fresh fuel examination (Table 15). Fuel plates U7MC4201,
U7MC6101 and U7MC6311 were characterized by SCK•CEN (Table 15, emphasized in yellow) while the others were analyzed by CEA [5].

Two samples were cut from each plate: one cross section classically embedded and polished (down to 1 µm) and one sample embedded and polished parallel to the cladding down to the meat (plan view).

<table>
<thead>
<tr>
<th>Si content in Al matrix</th>
<th>Thermal treatment</th>
<th>cladding</th>
<th>Plate Id.</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 wt%</td>
<td>425 °C 2h</td>
<td>AlFeNi</td>
<td>U7MC4111</td>
<td>Irradiation BR2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlFeNi</td>
<td>U7MC4112</td>
<td>Fresh fuel exam.</td>
</tr>
<tr>
<td></td>
<td>475 °C 2h</td>
<td>Ag3NE</td>
<td>U7MC4201</td>
<td>Fresh fuel exam.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag3NE</td>
<td>U7MC4202</td>
<td>Irradiation BR2</td>
</tr>
<tr>
<td>6 wt%</td>
<td>425 °C 2h</td>
<td>Ag3NE</td>
<td>U7MC6101</td>
<td>Fresh fuel exam.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlFeNi</td>
<td>U7MC6111</td>
<td>Irradiation BR2</td>
</tr>
<tr>
<td></td>
<td>475 °C 4h</td>
<td>Ag3NE</td>
<td>U7MC6301</td>
<td>Fresh fuel exam.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlFeNi</td>
<td>U7MC6311</td>
<td>Fresh fuel exam.</td>
</tr>
</tbody>
</table>

Table 15 E-FUTURE fabrication matrix.

The optical micrographs in Figure 125 of the cross section samples show:
- in all samples a homogenous distribution of the U(Mo) particles in the meat
- sample 4201: decomposition of the fuel (speckled feature of the fuel particles)
- sample 6101: precipitation at the meat/ cladding interface
- sample 6301: increased porosity in meat and some decomposition of the fuel

![Optical microscopy of the cross section samples of fuel plates U7MC4201, U7MC6101 and U7MC6311.](image)

2.2.1 Precipitation

From the detailed images it is observed that not only in sample 6101 precipitation at the interface meat cladding is seen but also in sample 4201, however to a lesser extent (Figure 126 encircled in red).
It is assumed that these precipitates are the result of the interaction between the Si in the matrix and Mg in the cladding forming Mg$_2$Si. That this string of precipitates at the interface meat/cladding is seen in fuel samples 4201 and 6101 and not in sample 6311 is related to the cladding. The cladding of plate 6311 is AlFeNi which contains less than 1% Mg while for the AG3NE cladded plates (4201 and 6101), the cladding contains 2.8 wt% Mg. It is therefore more likely that in the latter case Mg$_2$Si precipitates will get formed. Furthermore, as the matrix of sample 6101 contains more silicon (6 wt%), it is also expected that the Mg$_2$Si precipitate get more easily formed in fuel plate 6101 compared to 4201.

Figure 126 Detailed micrographs of the cross section samples of fuel plates U7MC4201 and U7MC6101. The Mg$_2$Si precipitates at the meat-cladding interface are encircles in red, while the unreacted Si particles in the matrix are pointed out by a blue circle.

The interaction between the Si from the matrix with the Mg of the cladding is confirmed by X-ray maps obtained with EPMA (Figure 127 left image) showing a string of Mg$_2$Si precipitates at the meat-cladding interface. The OM images of the plan view image\(^8\) indicate that these precipitates are located at the boundary of the Al grains of the cladding (Figure 127 right image).

\(^8\) A sample of the fuel plate is embedded with the cladding parallel to the surface of the mount. Next the sample is grinded and polished until the cladding is removed and a plan view of the meat/cladding interface can be observed.
2.2.2 Decomposition

The thermal treatment of the fuel plates was kept below 500 °C to avoid massive transformation of the fuel from $\gamma$ to $\alpha$ phase (see chapter 2).

However, the OM examination in Figure 125, Figure 126 clearly evidences signs of $\gamma$ U(Mo) phase decomposition in fuel plate 4201 and 6311, which is not surprising as these plates were submitted to the highest heat treatment (475 °C). The X-ray diffraction measurements in Figure 128 confirm that a partial $\gamma$-U(Mo) phase decomposition has occurred in all plates but with a more pronounced effect in fuel plates U7MC4201 and U7MC6311. The volume fraction of the interaction phases formed during annealing is expected to be too low to measure but an U(Al, Si)$_3$ phase was observed slightly above the background, especially for plate U7MC6311 (green line Figure 128) annealed at 475 °C and containing 6 wt% Si.
2.2.3 Si distribution

When comparing the 4 wt% Si to the 6 wt% Si samples, it is seen that the matrix of fuel plates 6101 and 6311 still contain a lot of unreacted Si particles (Figure 126 encircled in blue, red particles in Figure 127 and Figure 129).

Only relatively large (~ 5 – 20 µm [5]) unreacted Si particles can be found which tends to indicate that only the smallest Si particles fully dissolve and interact with the U(Mo) kernel surface leading to the formation of the Si rich preformed layers (PFL).

The combined X-ray maps in Figure 129 clearly illustrate the different annealing conditions: In all maps the formation of Si-rich preformed layers is seen but the layer is discontinuous and has varying thicknesses. In addition :

- U7MC4202 : almost no Si particles are seen in the matrix which is in accordance with the lower Si content.
• U7MC6111: similar coverage rate as U7MC4202 but more unreacted Si is observed in the matrix
• U7MC6311: higher coverage rate, thicker Si rich PFL and only a few unreacted Si particles in the matrix.

Several quantitative linescans were defined and measured on fuel samples 4201 and 6101 (for example: Figure 130).

• linescan 1: illustrates clearly that there is no strict correlation between the presence of a Si particle close to the U(Mo) kernel and the formation of a Si rich PFL.
• linescan 2: a thin Si rich PFL in sample 4201 contains approximately 11 wt% Si with some Al.
• linescan 3: the thickness of the PFL in sample 6101 is slightly thicker and contains up to 14 wt% of Si and does not contain significant amounts of Al.
• linescan 4: measurement over a U(Mo) matrix interface with no Si rich PFL.

From all recorded linescans it can be concluded that the Si enrichment of the PFL varies and appears to depend on the layer thickness. For the thick layers, for which the concentration can be measured more accurately as there is less contribution from the Al matrix, the Si content varies between 8 and 14 wt% and very low quantities of Al (<10 wt%). These values correspond to a 30-45 at% Si or the formation of a USi or USi$_2$ PFL. Similar values are found in the annealing test performed by D.D. Keiser et al. [19].

2.3 Irradiation history

The E-FUTURE plates were irradiated in the FUTURE irradiation device at the BR2 reactor of SCK•CEN for three cycles: two cycles of 28 effective full power days (EFPD) and one final cycle of 21 EFPD.

All plates were subjected to very similar power profiles. The maximum power at BOL for plate 6301 was >470 W/cm$^2$ as shown in Table 16. Due to the absence of burnable poisons, there is a gradual reduction in power with irradiation time, reaching a value of around 250 W/cm$^2$ at EOL, attaining a local maximum burn-up of 70% $^{235}$U. In between cycles the plates were visually inspected under water. Before the start of the last irradiation cycle a (dark) discoloration of the surface of plate 6111 was observed. Fearing that this could be an onset to pillowing, it was decided to turn the plate 180° around its long axis. Since the hottest position is located at one of the edges of the fuel plates, this effectively put the high power position during the last cycle at the opposite edge for this plate (Figure 131). It furthermore caused the average and peak power of that plate to be higher during the last cycle compared to the other plates, but the maximum burn-up reached was also ~70%.
<table>
<thead>
<tr>
<th>Plate Id.</th>
<th>U7MC4111</th>
<th>U7MC4202</th>
<th>U7MC6111</th>
<th>U7MC6301</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fabrication data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cladding</td>
<td>AlFeNi</td>
<td>AG3NE</td>
<td>AlFeNi</td>
<td>AG3NE</td>
</tr>
<tr>
<td>Matrix</td>
<td>Al - 4%Si</td>
<td>Al - 4%Si</td>
<td>Al - 6%Si</td>
<td>Al - 6%Si</td>
</tr>
<tr>
<td>Thermal treatment</td>
<td>425 °C – 2h</td>
<td>475 °C – 2h</td>
<td>425 °C – 2h</td>
<td>475 °C – 4h</td>
</tr>
<tr>
<td>Loading (gU/cm³)</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Enrichment (%²³⁵U)</td>
<td>19.75</td>
<td>19.75</td>
<td>19.75</td>
<td>19.75</td>
</tr>
<tr>
<td>wt% Mo</td>
<td>7.3</td>
<td>7.3</td>
<td>7.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

| **Irradiation data** |          |          |          |          |
| EFPD         | 77       | 77       | 77       | 77       |
| Mean BU (%²³⁵U) (f/cm³ U(Mo)) | 48.3 3.63E+21 | 48.1 3.62E+21 | 47.1 3.53E+21 | 47.5 3.57E+21 |
| Max BU (%²³⁵U) (f/cm³ U(Mo)) | 71.3 5.53E+21 | 71.3 5.53E+21 | 68.7 5.31E+21 | 71.4 5.54E+21 |
| Peak Heat Flux (W.cm⁻²) | 457       | 453       | 465       | 472       |

Table 16 Fabrication and irradiation data of the fuel plates of the E-FUTURE experiment

### 2.4 Post Irradiation Examination

#### 2.4.1 Calculated burn-up profile

![Figure 131](image1.png)

Figure 131 Calculated burn-up profile for fuel plates U7MC4111, U7MC4202, U7MC6111 and U7MC6301.
Each of the U7Mo plates has its own burn-up distribution despite of the nearly identical irradiation conditions inside the basket (Figure 131). Especially fuel plate 6111 shows a different distribution as it has been turned 180° around its long axis before the last cycle. Calculations were performed using the MCNP-4C, and the SCALE-4.4A codes.

2.4.2 Non-destructive analysis
The NDT of the fuel plates included visual inspection, plate thickness profiles and oxide thickness profiles. Other analyses performed but not reported in this thesis include gamma spectrometric mapping of the plates (without quantification) and radiochemical burn-up determination.

2.4.2.1 Visual examination

![Visual inspection of the fuel plates through the hot cell windows (plate number on the left).](image)

All four E-FUTURE plates show important swelling in the highest burn-up region and a clear pillowing in the swollen area (inside circles in Figure 132) with plate 6301 (6% Si–475 °C–4 h) the least affected.

2.4.2.2 Thickness measurements
A similar measurement grid of 5 x 1 mm² with measurements every 1 mm in the longitudinal plate direction as in the FUTURE-UMO-1 experiment (chapter 4) has been defined (Figure 133). In addition detailed scans, using a 1*1mm² grid were recorded in the pillowed areas of each fuel plate.
The oxide layer thicknesses on the front and the back of the fuel plates were recorded and corrected for their systematic bias (see FUTURE experiment chapter 4).

Oxide thicknesses close to the pillowed location of the individual fuel plates, amount up to 25 to 30 μm. The oxide thicknesses in the pillowed areas (indicated by red dotted line segments in Figure 134) are topped off at 35-40 μm with a flat profile in the high power zone, indicating incipient spalling. Due to stress build up in the layer (caused by e.g. the pillowing) the oxide layer may become unstable. This may lead to cracking and spalling of the oxide. One should not interpret the oxide thickness measured in the pillowed area.

As was discussed in the FUTURE experiment (chapter 4), the burn-up shows little variation over the plate width. This justifies a width averaging of the measurements (Figure 135), improving statistics of the individual datapoints. For the four plates, the thickness increases gradually over the plate but the deformed areas as visually observed are characterized by a steep increase in plate thickness. The maximum width averaged plate thickness found for fuel plate 4111, 4202, 6111 and 6301 are respectively 1729, 1841, 1551 and 1437 μm. That fuel plate 4202 is the most affected one and 6301 the least deformed is also seen from the inset in Figure 135. The two peaked maximum of fuel plate 6301 is probably due to the 180° rotation with respect to its long axis before the start of the last irradiation cycle. This causes a shift in the location of the high power position on the fuel plate during the last cycle.
2.4.2.3 Plate swelling

The as-measured plate thicknesses of the plates are corrected for the oxide formation and by dividing the corrected plate thickness increase by the initial thickness a value for the plate swelling is obtained (chapter 4).

Figure 135 Width average plate thickness (corrected for oxide layer). The inset shows the details in the pillowed area.

Figure 136 Plate swelling contour plots after correction for oxide contribution to the thickness. The burn-up distribution as calculated by neutronics is overlaid (in %$^{235}\text{U}$).
The initial plate thickness $T_i$ for each of the plates is measured in the out-of-fuel zone. This number is corrected for spring back and the oxide layer outside the fuel zone. The measured plate swelling of each E-FUTURE plates is visualized as 2D contour plots in Figure 136 and is overlaid with the calculated burn-up distributions.

### 2.4.2.4 Fuel swelling

The fuel swelling can be calculated using:

$$S_F = \frac{S_p \times T_i}{T_i} = \frac{T_{corr} - T_i}{V \times t_i} = \frac{\Delta T_{corr}}{V \times t_i} \quad \text{Eq. 39}$$

with $S_F$ and $S_p$ the fuel and plate swelling respectively and $V$ the volumetric U(Mo) loading. $T_i$ is the average measured thickness of the plate outside the meat zone corrected for oxide formation and spring-back. For the meat thickness $t$, the initial value of 510 µm is used. The formula neglects meat porosity and the effect of interaction phase formation on the swelling. It furthermore assumes a uniform meat thickness and fully homogenous U(Mo) dispersion.

Averaging fuel swelling values at positions with similar burn-up allows plotting the fuel swelling in function of the burn-up. By converting the calculated burn-up given in %$^{235}$U consumed to fission density (chapter 4), the fuel swelling can be more appropriately visualized in function of local fission density. In Figure 138 this is done for each of the fuel plates and it can be seen that the swelling profile for all plates is almost linear up to a fission density of $4.8 \times 10^{21}$ f/cc. Above that fission density an increased swelling is observed and the spread on the data points becomes larger.

![Figure 137](image.png)

**Figure 137** Calculated fuel swelling profile including the 1σ spread of the datapoints of the E-FUTURE plates as function of the fission density.

Compared to the swelling profile of the fuel plates from the FUTURE and IRIS-3 experiment (Figure 138), the E-FUTURE plates show a similar swelling rate.
The swelling of fuel plate U7MC6301 is lower compared to the other E-FUTURE plates. The exact origin is not known but this difference may result from small differences in the initial plate thickness or the spring back correction.

As can be seen in Figure 139 a small change in e.g. spring back (18 µm instead of 21 µm) results in a better fit. This is only shown to illustrate the sensitivity to this parameter. The spring back correction is not adjusted in the remainder of the data treatment.

For all E-FUTURE plates and fuel plate U7MV8021 from the IRIS-3 experiment, it was found that the fuel swelling profile consist of two parts. Below a threshold of \( \sim 3 \times 10^{21} \text{ f/cc} \) the swelling rate is slower than above that burn-up. As was shown in the previous sections, this threshold is related to the onset of recrystallization. Fitting of 2 linear trends to the available FUTURE, IRIS-3 and E-FUTURE fuel swelling data in the 2 fission density ‘domains’ (FD < \( 3 \times 10^{21} \text{ f/cc} \) and \( 3 \times 10^{21} \text{ f/cc} < \text{FD} < 4.5 \times 10^{21} \text{ f/cc} \)) yields the following expression for fuel swelling (FSw) evolution (Figure 140):

\[
\begin{align*}
\text{FSw} (%) &= 5.1 \times \text{FD} & [R^2 = 0.97] \ (0.5 < \text{FD} < 3) \\
\text{FSw} (%) &= 7.3 \times \text{FD} - 6.9 & [R^2 = 0.97] \ (3 < \text{FD} < 4.5)
\end{align*}
\]

with fission density (FD expressed in \( 10^{21} \text{ f/cm}^3 \)). These expressions correlate very well with the ones obtained by Kim et al. (see chapter 3, [20]).
2.4.3 Destructive analysis

From the fuel plates, slices over the complete width of the plate are cut. To limit the forces applied on the samples during cutting and as such avoid damage to the fuel, each slice is put in a stainless steel envelope and fixated with epoxy resin.

Several samples per fuel plate (Figure 141), revealing the microstructure at different burn-ups, have been examined with optical microscopy (OM), scanning electron microscopy (SEM)
and electron probe micro-analysis (EPMA). Only the most illustrative images and results are summarized in this thesis, but, unless noted differently, the results described apply for all fuel plates.

2.4.3.1 Fuel behavior

In Figure 142, a composite optical microscopy image across the deformed area of fuel plate 6111 shows a cross-section of the formed pillow. This image is comparable to the observation made on a fuel plate of the FUTURE experiment in which U7wt%Mo dispersed in a pure Al matrix was irradiated for 40 EFPD’s at a maximum heat flux of 340 W/cm$^3$ leading to a BU of $1.4\times10^{21}$ f/cm$^3$ (chapter 3). In the E-FUTURE experiment (U7wt%Mo dispersed in an Al(Si) matrix) the pillowing occurs only after the fuel plates have reached a burn-up of $3.6 \times10^{21}$ f/cm$^3$ and were irradiated at a significantly higher maximum heat flux (470 W/cm$^3$), which clearly indicates the positive effect of adding Si to the matrix. However, the current fuel plates still show pillowing and from the more detailed examinations, it was found that the underlying failing mechanism leading to pillowing seems to be similar to all other U(Mo)/Al(Si) and U(Mo)/Al irradiation experiments.

From the optical micrographs, the plate thickness (without the oxide layer) is measured over the width of the fuel plate U7MC6111 at the highest burn-up position (longitudinal position 580 mm Figure 131) and compared to the plate thickness measurements (corrected for oxide formation) obtained from NDT on an identical location.

Figure 143 Plate thickness measured in NDT and DT on fuel plate U7MC6111 at the max flux plane.

Figure 143 shows the good correlation between the DT and NDT data.
The gradual increase in fuel swelling up to a fission density of $4.9 \times 10^{21} \text{ f/cm}^3_{\text{U(Mo)}}$ as measured in the NDT (Figure 144), is reflected in the SE images across the meat (Figure 145 a,b,c and d). The excessive swelling measured above $5 \times 10^{21} \text{ f/cm}^3$ is consistent with the microstructural image of the fuel sample showing severe deformation of the fuel meat (Figure 145 e).

Looking in more detail (Figure 146a) on fuel plate 6111, it can be observed that, at a relatively low burn-up of $3.2 \times 10^{21} \text{ f/cm}^3$, a thin interaction layer with an irregular thickness has grown around the fuel kernels. The fresh fuel characterization (2.2) showed that a Si rich layer had formed around the particles but that the coverage is not always complete. The
incomplete coverage of the particles is partly due to the inefficient transport of Si towards the fuel but also due to the high loading of the fuel plate. This latter cause is apparent as a clustering of fuel particles with little or no matrix between them.

This clustering is still visible after irradiation (Figure 146). No Si rich preformed layer or U-Mo-Al-Si interaction layer has formed where the kernels touch. At the interface between touching kernels, larger fission gas bubbles (Figure 146b) develop at higher burn-up ($4.9 \times 10^{21}$ f/cm$^3$). However, these do not appear to form the weakest points when observing where the fuel has separated in the pillows.

![Figure 146 Detailed optical images at locations on fuel plate 6111 representing a burn-up of a) $3.2 \times 10^{21}$ f/cm$^3$ U(Mo) b) $4.9 \times 10^{21}$ f/cm$^3$ U(Mo) c) $4.9 \times 10^{21}$ f/cm$^3$ U(Mo) and d) $5.2 \times 10^{21}$ f/cm$^3$ U(Mo).](image)

At this burn-up, also the formation of crescent shaped voids at the interface between the interaction layer and the matrix is observed. These voids are the result of the accumulation of fission products at the interface between the kernels and the matrix. The fission products ejected from the fuel kernel are snowplowed. The pile-up of fission products at this interface will severely weaken the mechanical strength of the fuel plate. A decohesion of the fuel particles from the matrix can be expected and is observed in fuel plate 6111 (Figure 146c). If accumulated local stresses, for example related to the gradual swelling of the fuel with burn-up, cannot be dissipated by creep and exceed the yield strength of the weakened interfaces, cracks start to develop and thermal conductivity deteriorates. This mechanism can subsequently lead to pillowing of the fuel plate.

Even though the fuel in Figure 146b has accumulated the same BU as the fuel in Figure 146c ($4.9 \times 10^{21}$ f/cm$^3$), the microstructure of the latter suggests a difference in irradiation history for that fuel (e.g. larger fission gas bubbles and detachment of the fuel from the matrix). This is indeed the case since, before the start of the last irradiation cycle, plate 6111 was turned
180° with respect to its long axis. This caused a positional shift of the peak power on the plate resulting in the observed differences of microstructure. The image in Figure 146d represents the fuel plate microstructure at a burn-up of $5.2 \times 10^{21}$ f/cm$^3$. Even at this high burn-up the microstructure of the U(Mo) fuel particles is not adversely affected, and only shows the formation of fission gas bubbles, but the voids and fission gas bubbles in-between the fuel kernels and between the IL and matrix have grown even further as a consequence of the mechanical deformation of the meat.

In Table 17 the measured Vickers hardness of the different phases (cladding, fuel, matrix and interaction layer) is listed in function of the acquired burn-up. The hardness of the cladding is fairly constant in all fuel plates, while for the matrix a slightly higher hardness is found in the fuel plates having a higher Si content (6111 plate = 6% Si, 4111 = 4% Si).

<table>
<thead>
<tr>
<th>Sample</th>
<th>FD ($\times 10^{21}$)</th>
<th>Cladding (20HV) (1σ)</th>
<th>Matrix (20HV) (1σ)</th>
<th>IL (20HV) (1σ)</th>
<th>Fuel (20HV) (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6111M1</td>
<td>3.3</td>
<td>81 (3)</td>
<td>153 (24)</td>
<td>504 (81)</td>
<td>335 (11)</td>
</tr>
<tr>
<td>6111M2</td>
<td>4.9</td>
<td>79 (2)</td>
<td>165 (30)</td>
<td>534 (43)</td>
<td>225 (2)</td>
</tr>
<tr>
<td>4111M1</td>
<td>5.1</td>
<td>79 (2)</td>
<td>118 (14)</td>
<td>550 (22)</td>
<td>255 (27)</td>
</tr>
</tbody>
</table>

Table 17 Hardness measurements of the different phases present in a fuel plate.

As expected, for the interaction layer an increase in hardness with increasing fission density occurs since more fission fragment induced defects will be acquired at higher burn-up. For the fuel a decrease in hardness is measured.

### 2.4.3.2 Interaction layer

![Figure 147](image)

Figure 147 Combined U Mα (blue), Si Kα (green) and Al Kα (red) X-ray map obtained at locations on fuel plate 6301 having received a burn-up of $4.1, 5.1$ and $5.5 \times 10^{21}$ f/cm$^3$ U(Mo).

Figure 147 represents the combined large area Al Kα X-ray map (red), Si Kα X-ray map (green) and U Mα map (blue) at different burn-up positions (respectively 4.1, 5.2 and 5.5 $\times 10^{21}$ f/cm$^3$) on fuel plate 6301 recorded with EPMA. An increase in thickness of the
interaction layer (purple) as well as the formation of voids (black) is noticed with increasing burn-up. This observation can be made even clearer by plotting the intensity of the U Mα X-ray map versus the Al Kα X-ray map.

Each point in the diagram (Figure 148) represents a pixel in the mappings plotted in function of the intensity of the U or Al. The color of the points in the diagram is related to the number of pixels which are plotted at the same point: the more intense the point, the higher the number of pixels represented by this point. Four distinct areas can be identified on the diagram: the remaining fuel kernel material (close to the Y axis), the matrix (close to the X axis), the interaction layer (on a tie line between the matrix and the fuel), and the voids (close to the origin).

![Figure 148 Binary intensity diagram that is based on the measured U and Al X-ray intensity (fuel plate 6301).](image)

From Figure 149 it is seen that with increasing burn-up, the size and intensity of the area representing the IL increases, indicating its growth.

Furthermore a shift of this area towards the Y axis on the tie line connecting the fuel and matrix at higher burn-ups (represented by the black dashed line and arrows in Figure 149), is indicative for the dilution of the interaction layer by reaction with the fuel kernel without the presence of more matrix (the IL is growing at the expense of the U(Mo) fuel).
To obtain the composition of the formed interaction layer and Si rich layers, quantitative linescans have been made with EPMA. The results are summarized in Table 18.

<table>
<thead>
<tr>
<th></th>
<th>Local burn-up ×10^{21} f/cm³</th>
<th>Al (wt%)</th>
<th>Si (wt%)</th>
<th>U (wt%)</th>
<th>Mo (wt%)</th>
<th>FP (wt%)</th>
<th>Al+Si U+Mo</th>
<th>at% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL1</td>
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<td>52</td>
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<td>4</td>
</tr>
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<td>63</td>
<td>6</td>
<td>3.7</td>
<td>2.4</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 18 The composition of the formed interaction and Si rich layers. The position of the linescans can be found: for IL1 in Figure 150, IL2 and SiRL1 in Figure 151 and IL3 and SiRL2 in Figure 152.

The scan in Figure 150 starts in the pure Al matrix, traverses the fission product halo and the interaction layer, and ends inside the fuel kernel. The burn-up of the fuel at this position is about 4.1×10^{21} f/cm³. In the fission products graph, the halo is seen as a peak in the Xe, Zr and Nd signals. Quantitatively, the interaction layer (IL1) contains little Si (< 1 wt%) but large
amounts of Al and U (respectively ~44 wt% and ~52 wt%) are measured. Based on the composition in at%, this implies an (Al+Si)/(U+Mo) ratio of approximately 6.

![Image](image1.png)

Figure 150 Combined U (blue), Si (green), Al (red) and Xe (red), Nd (green), Zr (blue) X-ray maps with an open block arrow indication the position of the quantitative linescan. The measured interaction layer is denoted IL1 in the thesis.

At a slightly higher burn-up position (5.1×10^{21} f/cm^3) a similar composition of the IL is measured (Figure 151).

![Image](image2.png)

Figure 151 Combined U (blue) - Si (green)-Al (red) and Xe (red)-Nd (green)-Zr (blue) X-ray maps with an open block arrow indicating the position of the quantitative linescan. The measured interaction layer is denoted IL2 and the Si rich layer SiRL1.
The points of the linescan marked 2 in Figure 151 were averaged and show that the IL(IL2), contains only small amounts of Si (~1.6 wt%) but large quantities of Al and U (~39 wt% Al, ~46 wt% U). The composition of this IL can thus also be written as U(Mo)(Al, Si)6. A second linescan (marked 1) was performed on the other side of the fuel kernel, where a Si rich layer (SiRL1) was identified on the X-ray mappings. Approximately 5 wt% of Si is found as well as a large amount of U (~61 wt%), although it is difficult to avoid surrounding matrix contributions when quantifying such thin layers with EPMA. The (Al+Si)/(U+Mo) ratio is calculated to be approximately 3.

In Figure 152 the linescan runs over a Si rich layer touching a U-Mo-Al-Si interaction layer (burn-up 5.5×10^{21} f/cm^3). Again, it is seen that the Si rich layer (SiRL2) contains large amounts of Si and U and less Al which gives an (Al+Si)/(U+Mo) ratio of ~2. For the thicker U-Mo-Al-Si interaction layers (IL3) at this burn-up an (Al+Si)/(U+Mo) ratio of ~5 is found.

![Figure 152 Combined U (blue)-Si (green)-Al (red) and Xe (red)-Nd (green)-Zr (blue) X-ray maps with an open block arrow indicating the position of the quantitative linescan. The measured interaction layer is denoted IL3 and the Si rich layer SiRL2.](image)

From the X-ray maps and quantitative analyses, it is seen that, surrounding the fuel kernels, there are locations with either a very thin Si-rich interaction/preformed layer or a thick Al-rich U-Mo-Al(-Si) interaction layer. Si-rich layers were formed during plate production and are characterized by their high silicon and uranium content. The layers found after irradiation look very similar to those observed before, but they are less numerous. It seems that only those Si-rich layers that contain more than 5 wt% Si (Figure 151 linescan 1) can limit the Al diffusion as almost no increase in their layer thickness after irradiation is observed (Figure 153).
If the Si rich preformed layer contains more than 5 wt% Si, a U-Si layer is found on the surface of the fuel kernel. Otherwise the formation of a ‘classical’ U-Mo-Al-Si IL is observed. This is consistent with the results of atomistic simulations performed (Figure 155). The simulation analysis shows that an optimum Si content of 5–7wt% in the IL is required to meet the goal of reducing the interlayer growth kinetics and the formation of undesirable uranium compounds [21].

In the thick U-Mo-Al-(Si) interaction layers, hardly any silicon is found and their composition is on average U(Mo)Al₅ to U(Mo)Al₆. When looking in more detail (Figure 154) it is noticed that the composition of such an IL close to the fuel kernel is U(Mo)Al₄. A few microns away from the surface of the fuel kernel, the composition increases to U(Mo)₀.₉Al₄ and at the most outer part of the interaction layer a steep increase in the Al content is measured. Such a profile indicates that the IL gets diluted with Al as long as Al is available. Once the fuel plate runs out of matrix, a dilution of the IL by U(Mo) will occur as the IL continues to grow, as was established from the binary diagrams in Figure 148.

Figure 154 The Al+Si/U+Mo ratio calculated from the measured composition of the interaction layer measured along a line across the layer (left) and a line in the middle of the layer (right).
2.4.3.3 Si distribution
By creating a Si rich layer around the fuel kernels prior to irradiation, the diffusion rate of Al will be reduced, restraining the growth of the interaction layer [22]. Atomistic simulations [21] have shown that in U, Al prefers to occupy sites far from Si atoms, a behavior that explains the power of Si for limiting Al diffusion (Figure 155).

![Figure 155](image1.png)

Figure 155 Equilibrium state of the computational cell at \( T = 450 \) K for a U7wt%Mo dispersed in (from left to right) 3, 5, and 7wt% Si-Al matrix. Al, Si, U, and Mo atoms are denoted with yellow, red, blue, and grey circles, respectively. The simulations show the Si stopping power is optimum for a content of 7wt% Si. The original location of the interface (at the onset of the simulation) corresponds to the middle of each figure (extracted from [21]).

This effect is illustrated in Figure 156: at the position on the U(Mo) fuel kernel surface where a Si rich preformed layer is located (indicated by the open block arrows) no Al rich interaction layer has formed and hence no sweeping of the fission products has occurred (no halo or snowplowing front in the Xe and Zr X-ray map).

![Figure 156](image2.png)

Figure 156 Local X-ray maps obtain on fuel plate 6301: the open block arrows point to location where a Si rich preformed layer is present while the striped arrows indicate the formation of an U-Mo-Al interaction layer.
At those location on the surface where the U(Mo) and the matrix were in direct contact, an Al-rich interaction layer has grown (indicated in Figure 156 by the striped block arrows) and a fission product halo has been produced clearly delineating the interface between interaction layer and matrix.

In the Xe map, also large fission gas bubbles at the interface IL – matrix and in-between touching fuel kernels, are shown to have formed.

![X-ray maps](image)

**Figure 157** Combined U (blue), Si (green) and Al (red) X-ray maps measured at positions on fuel plate 6301 having a burn-up of respectively 3.4, 4.1, 5.1 and 5.5 \( \times 10^{21} \) f/cm\(^3\). The growth of the interaction layer (colored purple) is observed with increasing burn-up while the thickness of the Si rich preformed layers (green) remain unaltered up to 5.1 \( \times 10^{21} \) f/cm\(^3\).

X-ray maps recorded at different burn-ups (Figure 157) illustrate that with increasing burn-up, the thickness of the interaction layer increases (as expected), while the Si preformed layer seems to be unaltered up to a very high burn-up of approximately 5.1 \( \times 10^{21} \) f/cm\(^3\). After that point, it seems that the preformed layers also get diluted with Al and U(Mo) and slowly increase in thickness.

### 2.4.3.4 Fission products

The large area Xe X-ray maps in Figure 158 clearly illustrate the effect of increasing accumulation of fission gas (and therefore also other fission products) with burn-up at the interface of the interaction layer and matrix. An interlinking of these weakened interfaces starts to show at higher burn-up and with the growing number of fission gas bubbles, the formation of a crack pattern is easily imagined.

The Xe, Nd and Zr X-ray maps in Figure 159 show the evolution of the fission products with increasing burn-up. At low fission density (3.4\( \times 10^{21} \) f/cm\(^3\)) the xenon fission gas is largely still contained within the nanobubble lattice, while Nd and Zr are in solid solution.
Figure 158 The Xe X-ray map recorded on fuel plate 6301 at respectively 3.4, 4.8 and $5.5 \times 10^{21}$ f/cm$^3$ U(Mo) reveals the increase in number of fission gas bubbles located at the interface IL-matrix.

At those locations in the meat where an IL has grown also the typical fission product halo is observed at the interface IL and matrix.

Figure 159 Xe, Nd and Zr X-ray maps recorded on samples from fuel plate U7MC6301.

With increasing burn-up, recrystallization that starts at the cell boundaries will progress further in the grains/cells, destroying the nanobubble lattice and creating large bubbles. At
a fission density of $4.1 \times 10^{21} \text{ f/cm}^3$ only a few Xe patches (reflecting the nanobubble lattice) are still observed (Figure 159), all other fission gases have been released to the bubbles formed by RC. Nd and Zr are still in solid solution, with higher concentrations at the interface of the IL and matrix (halo). Recrystallization seems to be complete at a fission density of $5.5 \times 10^{21} \text{ f/cm}^3$ (Figure 159). No more Xe patches are observed and the bubbles have increased in size. The speckled appearance of the Nd X-ray maps indicates that at this fission density Nd start to precipitate. Zr remains in solid solution.

2.4.3.5 Swelling
As was mentioned in 2.4.3.1 the gradual increase in fuel swelling up to a fission density of $4.9 \times 10^{21} \text{ f/cm}^3$ as measured in the NDT (Figure 144), is reflected in the SE images across the meat (Figure 145 a,b,c and d).

![Figure 160 Plate (red lines) and meat thickness (green lines) measurement on position 5 of sample M2 cut from fuel plate U7MC6301.](image)

This can be made more quantitative by measuring the meat thickness. On several positions on each sample 5 thickness measurements were taken and averaged (Figure 160). In Figure 161 the meat thicknesses obtained on all samples (except those showing severe deformation) are plotted as function of their burn-up.

![Figure 161 The thickness of the meat at different burn-up positions as measured on the SE images.](image)

Despite the large scatter (indicating the inhomogeneity of the meat thickness), a steady increase similar to the fuel swelling measured with NDT is seen. The meat swelling profile in Figure 161 seems similar for all fuel plates, which leads to the conclusion that the swelling of
the meat is not to be related to the Si content in the matrix. In further data treatment no distinction will be made between the different fuel plates.

On the SE images Figure 160 also the plate thicknesses of all E-FUTURE samples are measured (black dots in Figure 162). These should be comparable to

- the calculated plate thickness based on the measured meat thickness (Figure 161) increased with the theoretical thickness of the cladding (in total 760 µm) (green dots in Figure 162).
- the plate thickness as measured by non-destructive testing (NDT) at the same location on the plate where the samples originate from (red dots in Figure 162).

The good correlation between the plate thickness DT and the meat thickness DT increased with a fixed cladding thickness shows that (as expected) the cladding does not contribute to the swelling. Furthermore, a good correspondence is again found between the NDT and DT measurements. This confirms the reliability of the NDT results.

The SE images are also used to calculate the volume fraction occupied by the different phases in the meat (matrix, interaction layer and fuel) (see also chapter 4). Plotting the volume fraction in function of fission density would give a biased view as the total volume (or meat thickness) varies with the burn-up (Figure 161).

![Figure 162](image)

*Figure 162* The thickness of all E-FUTURE plates measured at different burn-up position: based on the measured meat thickness (Figure 161) increased with the theoretical cladding thickness (760 µm) (green) or directly measured on the SE images (black) or from non-destructive analysis (red).

However by multiplying the measured volume fractions with the measured meat thickness the evolution of the volume of the different phases in function of the burn-up can be displayed (Figure 163).

The graph in Figure 163 clearly shows that the interaction layer grows mostly at the expense of the matrix. Compared to the initial value, only a slight deviation in the fuel volume is observed.
Figure 163 The volume evolution of the matrix, interaction layer and fuel in function of the fission density.

From the NDT measurements a fuel swelling profile in function of the burn-up was calculated based on the assumption that there is no contribution from the interaction layer and matrix to the overall swelling of the fuel plate. If the IL has no influence on the swelling that would mean that the volume fraction of the IL measured in the DT consists of a proportional volume U(Mo) and Al. From the quantitative analysis (EPMA) it was found that on average a $\text{UAl}_4$ has formed from the interaction between the fuel and the matrix. As described in chapter 3, we can calculate the fuel and matrix swelling based on the volume fractions and meat thickness measurements obtained during DT.

Figure 164 Swelling of the fuel and matrix as obtained by microstructural analysis compared to the swelling measured with non-destructive analysis.

The results of those calculations are plotted in function of the fission density together with the fuel swelling data obtained by NDT. For the left graph the assumption of a $(\text{U,Mo})\text{Al}_3$ layer (corresponding to a volume ratio of 80% Al and 20% UMo) was made while for the right graph a $(\text{U,Mo})\text{Al}_4$ layer (corresponding to a volume ratio of 83% Al and 17% UMo) is assumed. It can be seen that this results in minor differences.

More importantly, with the assumption that the IL does not contribute to the overall swelling the results clearly show that there is no swelling of the matrix and the fuel swelling obtained from the DT measurements correlate very good with the FSw obtained by NDT analysis (Figure 164). The large scatter on the DT derived data points result from the
inhomogeneity of the meat thickness (Figure 161). It should be noted that in Figure 164 measurement on 3 different scales are merged and found to correlate very well:

- on macroscopic scale: fuel swelling measured by NDT
- on microscopic scale: measurement of volume fractions on SEM images
- on mesoscopic scale: meat thickness measurements on SEM images

2.4.3.6 Recrystallization

The detailed secondary electron images in Figure 165 show the evolution of grain refinement in the E-FUTURE plates in function of the fission density. At low BU (~3x10^{21} f/cc) recrystallization has started at the cell boundaries which are low in Mo content. As the BU increase, the grain refinement will progress into the cell interior and create large intragranular bubbles (see also Figure 159).

![Figure 165](image)

Figure 165 Grain refinement is starting at the cell boundaries at low BU and progressing in the cells with increasing fission density. At high burn-up an increase in bubble size is seen.

At high BU, the recrystallization of the whole fuel kernel is complete (above 4.3x10^{21} f/cc). At this point, the diffusion length for the newly generated fission gas becomes smaller than the size of the new grains. As a consequence, the fission gas will go directly to the large bubbles resulting from recrystallization. This is identical to the observations made in the IRIS-3 and FUTURE experiment.

Since the recrystallization started at the cell boundaries, the growth of the fission gas bubbles will be observed there first.
2.5 Conclusion

Four distinct (in Si content and heat treatments) full size, flat fuel plates irradiated in the BR2 reactor up to a burn-up of 70%^{235}U (5.5×10^{21} f/cc) are found to have all pillowed in the highest burn-up positions. From the non-destructive post-irradiation examination, the swelling of the fuel was calculated and plotted as function of the fission density. A linear increase of the swelling is seen up to a fission density of ~3×10^{21} f/cc. Above that burn-up a slight increase in swelling rate is seen but it remains close to linear. Around ~4.5×10^{21} f/cc excessive swelling typical for pillowing of the fuel plate is measured. The fission rates at which the swelling accelerates (3 and 4.5×10^{21} f/cc) are independent of the Si content in the matrix and heat treatment the plates received during fabrication. It can be concluded that they are intrinsic to the U(Mo) fuel.

This is confirmed by the analysis of the microstructure at the different fission densities. At low burn-up (<3×10^{21} f/cc), the U(Mo) fuel will show its typical linear solid state swelling by accumulation of solid fission products and fission gases that form a nanobubble lattice. Around 3×10^{21} f/cc recrystallization is observed at the cell boundaries. As recrystallization causes the release of over-pressurized nanobubbles, microsized bubbles appear on the cell boundaries. The grain refinement slowly progresses into the cell until it is completely recrystallized (around 4.5×10^{21} f/cc). This is reflected in the microstructure by the disappearing of the nanobubble patches and the formation of micrometer sized bubbles in the cells. Above 4.5×10^{21} f/cc, the newly formed fission gas does not form a nanobubbles lattice but will go directed to the large bubbles. This will cause an increased swelling of the fuel (see chapter 3).

Such an increase in fuel swelling can however not be the direct source of pillowing of the fuel plate. From the destructive testing it was also found that even though Si was added to the matrix, an interaction between the matrix and the fuel occurred.

Due to the (required) high fuel loading, clustering of the U(Mo) fuel kernels occurs, leading to insufficient coverage of the fuel particle surface with Si during the thermal treatment prior to irradiation. The PIE results also reveal that in-between the touching fuel particles, larger fission gas bubbles form, their size is much larger that the fission gas bubbles inside the fuel kernel and increasing with burn-up.

From the calculation of the volume fractions occupied by the different phases (fuel, interaction layer and matrix), the positive effect of a higher Si amount added to the matrix and the higher annealing temperature can be derived. Si-rich layers found at some locations around the fuel particles that contain at least 5 wt% Si show no IL growth during the irradiation. These layers appear to be the (unevolved) Si-rich preformed layers that contained sufficient Si. For layers containing less Si, a limited growth caused by diffusion of Al into the layer is seen.
The interaction between uncovered U(Mo) particle surfaces (or those that do not possess the protection of a sufficiently Si-rich preformed layer) and the Al matrix leads to the formation of an U(Mo)Al\(_x\) layer with \(x\) between 4 (close to the fuel kernel) and 6 (close to the matrix). The ejected fission products are snowplowed by this growing interaction layer to the interface of the IL with the matrix. It is this accumulation of fission products at interface that leads to weakening of the core structure of the fuel plate. It is most probable that the interplay between an already weakened core structure of the meat and the increased swelling of the fuel will eventually cause the pillowing of the plate.
3 AlSi matrices for U(Mo) dispersion fuel plates [23]

The E-FUTURE irradiation experiment was intended to identify the best combination of added Si concentration and heat treatments during plate production. Although the experiment has shown a good behavior of the U(Mo) fuel up to a burn-up of ~60% $^{235}$U and a positive influence of a higher Si content (6%Si), an abnormal swelling has been measured in the highest burn-up region [24,25].

Analysis has shown that, in a matrix made of an Al and Si powder mixture, the transport of the larger Si particles to the fuel kernels is inefficient and the formation of a Si rich preformed layer (PFL) with an inhomogeneous thickness is observed.

In this chapter we will show that the use of a heat treated AlSi alloy instead of a mixture, allows obtaining a better spatial dispersion and finer size distribution of the Si precipitates in the matrix. Such a matrix microstructure can be expected to enhance the Si effect since the Si availability is expected to be more efficient during the fabrication but also during irradiation by fission induced diffusion.

However, the mechanical properties of AlSi powders did not allow direct use of it in the fuel plate fabrication (compacting was poor). As such a more detailed study of the properties of heat treated AlSi alloys has been performed.

The term AlSi ‘alloy’ is used to describe an Al rich matrix supersaturated with silicon. Such a structure is obtained by liquid or solid quenching of an Al-Si mixture.

3.1 Properties of AlSi alloys

The starting materials are inert gas atomized Al, Al5Si, Al7Si and Al12Si powder (composition see Table 19), supplied by Alpoco - The Aluminium Powder Co Ltd.

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<th>Fe</th>
<th>Cu</th>
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<td>0.082</td>
<td>0.263</td>
</tr>
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<td>Al12wt%Si</td>
<td>87.06</td>
<td>12.43</td>
<td>0.335</td>
<td>0.072</td>
</tr>
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</table>

Table 19 Chemical composition (main elements) of commercial Al alloys provided by Alpoco - The Aluminium Powder Co Ltd.

The Al–Si system is an eutectic system in which the eutectic composition contains 12.6 wt% silicon and has a melting temperature of 577.6 °C (850.7 K). The maximum equilibrium solid solubility of silicon in aluminum is 1.58 at% at the eutectic temperature. By rapid quenching of the melt, the maximum solid solubility can be exceeded leading to an Al matrix supersaturated with silicon.
Depending on their composition, the AlSi alloys are known as hypoeutectic alloys (Si content < 11 wt%), eutectic (Si content 11–13 wt%) and hypereutectic alloys (Si content > 13 wt%). For this study, only hypoeutectic alloys Al 5wt% Si (Al5Si) and Al 7wt% Si (Al7Si) and eutectic Al 12 wt% Si (Al12Si) are used. The microstructure of the Al–Si alloys depends on the amount of Si, i.e. for hypoeutectic alloys Al7Si it consists of primary aluminum plus eutectic (Figure 166a) and for Al12Si alloy a typical eutectic structure (Figure 166b) is observed.

Figure 166 Microstructure of compacted, as received Al 7wt% Si alloy (a) and Al 12 wt% Si alloy (b).

The microstructure, amount of alloying element dissolved and the retained defects depend on the production route of the powder. Liquid quenching yields a larger dissolved fraction of silicon, a higher excess vacancy concentration and smaller grain sizes compared to solid quenching [26]. Ageing of quenched alloys will lead to precipitation of Si resulting in a uniform dispersion of coherent precipitates in a softer matrix. The resulting properties of the treated alloys are depending on the applied temperature and time. Typically the hardness and strength of the alloy increases initially with time and particle size until it reaches the peak where maximum strength is obtained. Further aging will decrease the strength and hardness.

In literature not much is found on the properties of atomized AlSi powder. Considering that the starting point in the atomization process is a melt of AlSi, the liquid quenched alloys (usually in the form of ribbons) described in the literature will be used as reference.

The Al7Si and Al12Si powders were annealed at 150, 250, 350, 450 and 550 °C (423, 523, 623, 723 and 823 K), for times ranging between 5 and 240 minutes. To perform hardness measurements and microscopy and to simulate part of the fuel plate manufacturing process (compacting of the matrix), the powders were pressed into pellets (Ø 8mm, height ~5 mm) using a manual hydraulic press, applying a force of 5 tons/inch. The pellets were subsequently embedded in resin (hot mounting) and polished.

The Al12Si powders annealed at lower temperatures were difficult to compact. An intact pellet could only be achieved by grinding the broken compact and pressing it again.
3.1.1 **Microstructure and hardness measurements**

Vickers microhardness measurements were carried out on the polished pellets by applying a 20 g load for 2 seconds using a diamond indenter. Each microhardness value reported is an average of 10 measurements. The results have been summarized in Figure 167.

![Figure 167](image)

*Figure 167* The hardness measurements performed on pressed powder pellets show the decrease of the hardness with increasing annealing time and temperature.

The main effect that causes the high hardness before annealing may be dispersion strengthening due to the extremely fine silicon particles. The solution hardening due to the supersaturation of silicon and work hardening due to the cold compacting may be additional effects. The steep decrease at the beginning of the annealing seen at all temperatures is due to the reduction of those effects [27]. Annealing at 550 °C for 30 minutes results in a maximum softening of the alloy. The difference in final hardness, depending on the annealing temperature and time, is due to the dispersion strengthening mechanism based on the growing silicon particles.

As can be seen in optical micrographs in Figure 166, the microstructure of an as-received AlSi7 atomized particle consists of fine-scale α-Al(Si) dendrites and interdendritic Al–Si eutectic, while the Al12Si alloy shows the typical eutectic structure.

The optical images of the Al7Si and Al12Si powders after annealing at 550 °C for respectively 5, 15, 30 and 60 minutes are shown in Figure 168. As already observed with the hardness measurements, after annealing at 550 °C for 30 minutes a fine dispersion of Si particles is obtained. The micrograph obtained after 60 minutes annealing shows that the increase of the Vickers hardness with increasing annealing time can be clearly attributed to the growth of the Si precipitates.
From the optical microscopy performed on the annealed alloys at 550 °C, the precipitation of Si from the Al phase is clearly seen. The size of the Si precipitates increase with increasing annealing time.

3.1.2 X-ray diffraction analysis

The annealed and as received Al7Si and Al12Si powders were also analyzed with X-ray diffraction. The analysis was performed on a Panalytical X’Pert pro system equipped with a Cu tube (Cu Kα1,2=0.1541 nm). The diffraction pattern of the as received Al7Si material (Figure 169) shows, next to an Al phase pattern, diffraction lines belonging to a pure Si phase, indicating crystallization/precipitation of Si. The increasing intensity of the Si line with increasing annealing temperature/time is due to additional precipitation of silicon. The inset of Figure 169 shows that the Si peaks from the as-received atomized powder, are broad. The Si peaks of the annealed powder do not only become more intense with increasing annealing temperature/time but also sharper, confirming coarsening of the Si grains [28].
The position and shape of measured diffraction peaks, can be used to determine microstructural properties such as the concentration of the alloying element dissolved in the matrix, the crystallite size of the precipitating phase, concentration of lattice defects and/or the macro- and microstrain.

In this study, Rietveld analysis is performed to obtain the Si and Al lattice parameter and the evolution of the amount of precipitated crystalline Si. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile (X’Pert HighScore Plus, PANalytical). The Si crystallite size and the microstrain in Si precipitates and Al matrix are determined.

<table>
<thead>
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<th>Lattice parameter (Å)</th>
<th>wt% Si precipitated</th>
<th>wt% Si in solid solution</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>4.04940</td>
<td>-</td>
</tr>
<tr>
<td>Atomized Al</td>
<td>4.04848</td>
<td>-</td>
</tr>
<tr>
<td>Al7wt%Si</td>
<td>4.04694</td>
<td>3.4</td>
</tr>
<tr>
<td>Al12wt%Si</td>
<td>4.04467</td>
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</table>

Table 20 Lattice parameters of pure Al, atomized Al and Al7Si, Al12Si alloys. Both quantification of the amount of Si precipitated and lattice parameters are obtained through Rietveld analysis. The amount Si in solid solution is calculated from the initial amount added and the amount Si precipitated.

The lattice parameter of the atomized alloy powder is smaller than that of pure (cast) Al. Formation of a substitution solid solution by dissolving Si atoms in the Al matrix is considered to be the reason the lattice parameter decreases because the atomic diameter of Si (111 pm) is smaller than that of Al (143 pm). The measured lattice parameters of the as received Al, Al7Si and Al12Si powders in Table 20 show a decrease with increasing Si content of the alloy.

It can also be observed in Table 20 that the lattice parameter of the atomized Al powder is lower than that of cast Al. In case the quenching rate is sufficiently high (>10^4 K sec^{-1}) nearly all vacancies present in the melt at high temperature will be retained at room temperature as excess vacancies. The presence of such vacancies is noticed by the contractions of the lattice. The cooling rate of powder prepared by gas atomization is calculated to be in the range of 10^4 – 10^5 K sec^{-1} [29,30], which is much higher than the quenching rate of normal casting. The lower lattice parameter of atomized Al compared to cast Al is believed to result from the high concentration of excess vacancies in atomized powders.

In the presence of dissolved alloying elements, the amount of excess vacancies can be even higher than in pure (atomized) aluminum and their concentration correlates with the amount of dissolved alloying element. Table 20 shows that the lattice parameters of as received Al7Si and Al12Si are indeed lower than the lattice parameter of atomized Al and since the amount of dissolved Si for the Al7Si is lower than that of Al12Si, the latter alloy contains the highest concentration of excess vacancies and hence has the smallest lattice parameter.
Excess vacancies play an important role in the precipitation process as they can enhance Si diffusion during low temperature (<200 °C) aging. In high temperature aging however, dislocations, stacking faults and grain boundaries are known to act as nucleation sites for precipitates [31]. No enhancement of solute Si diffusion is to be expected as excess vacancies disappear within a very short time at high temperatures.

Considering the differences in the nucleation kinetics at low/high temperature aging and as only a limited amount of data at low temperature (150 °C) is available, only the high temperature results will be discussed further.

In Figure 170 a,b, the change in lattice parameter of the Al rich phase and the amount of precipitated Si (Figure 170 c,d) of Al7Si and Al12Si are plotted as function of the annealing time.

![Image](image.png)

**Figure 170** The variation resulting the heat treatment of the Al lattice parameter (a,b) and the amount of precipitated Si (c,d) as measured by XRD and extracted from the scans by Rietveld analysis.

The observed increase of the Al lattice parameter is considered due to the transformation stresses induced by silicon precipitation. As the ageing proceeds, less transformation stress in the matrix is introduced as less Si will precipitate or precipitation has been complete (see also Figure 170 c,d). At this point, the recovery process can catch up and a maximum in the lattice parameter value is reached [32].
The variation resulting the heat treatment of the Si lattice parameter as measured by XRD and extracted from the scans by Rietveld analysis.

The equilibrium solid solubility of Al in silicon is very low and a lot of uncertainty exists on the absolute value. In [33], a maximum solubility of 0.016 ± 0.003 at% Al in Si at 1190 °C (1463 K) is given. The dissolution of Al in Si would enlarge the Si lattice parameter. The decrease of a_{Si} observed on ageing in Figure 171 may thus be interpreted as the result of precipitation of Al from the Si rich phase.

In hypo-eutectic alloys, the Al-rich phase solidifies primarily during quenching whereas in the hypereutectic alloys the Si-rich phase will solidify primarily [32]. It might therefore be expected that the Si-rich phase of the Al12Si alloy after quenching will contain more aluminum than the Si rich phase of the Al7Si alloy. The Si lattice parameter of the quenched Al12Si alloy will thus be larger that of the Al7Si alloy, as observed.

There are two sources that contribute to peak broadening observed in X-ray diffraction patterns: crystallite size and inhomogeneous strain. Even if both are present simultaneously it is still possible to calculate them separately from the measured XRD pattern. Values for the strain and crystallite size can be obtained through various methods. In this study, the Williamson-Hall method is used, which relies on the principle that size and strain broadening can be formulated respectively as

\[ \beta_L = \frac{KL}{L \cos \theta} \]

\[ \beta_e = C \varepsilon \tan \theta \]

with \( \theta \) the Bragg angle, \( \lambda \) the radiation wavelength, \( K \) a constant which depends on the peak shape and the crystal type (usually \( K=0.9 \)), \( C \) a constant which relies on the nature of the strains (typically \( C \sim 4 \) or \( 5 \)), \( L \) the crystallite size and \( \varepsilon \) the inhomogeneous strain.

The total peak broadening will be the sum of both contributions and can be written as

\[ \beta_{tot} \cos \theta = C \varepsilon \sin \theta + \frac{KL}{L} \]
By plotting $\beta_{\text{tot}} \cos \Theta$ as function of $\sin \Theta$, the strain component $C \varepsilon$ can be obtained from the slope and the size component $K \lambda / L$ from the intercept. It should be noted that most of these size-strain analysis methods (including Williamson-Hall), depend on a lot of assumptions. The found numbers should therefore be treated in a relative sense and not as absolute.

Figure 172 The measured microstrain in the Si and Al phase after annealing of Al7Si.

The evolution of the inhomogeneous strain in Si and Al and the Si crystallite size after annealing of Al7Si alloy are plotted in respectively Figure 172 and Figure 173. It should be noted that for Al12Si, similar results are found.

Figure 173 Growth of the Si crystallite resulting from the heat treatments of Al7Si.

At the start of Si precipitation, the quenched-in stress will disappear (reducing the strain) but transformation stresses are being introduced (increasing the strain) which are not dissipated readily. However the transformation stresses will affect the Si phase more than the Al rich phase [32]. As such, the strain of the Al phase decreases and that of the Si phase will increase, as observed in Figure 172. With increasing annealing time, the amount of Si precipitating reduces or precipitation is complete. From then on less or no further precipitation stresses are induced and relaxation becomes more dominant. The microstrain
that remains after ageing is due to the thermal misfit induced by cooling from the annealing temperature to room temperature at which the diffraction measurements were performed [32].

The crystallite size of the Si particles (Figure 173) increase with increasing annealing time and temperature. At the adopted ageing temperatures, the excess vacancies are almost instantly transformed into clusters (dislocation loops or voids), which will act as preferential nucleation sites for silicon precipitation (heterogeneous nucleation) [31]. In a second stage, critical Si nuclei are formed that result in silicon precipitation. During the subsequent coarsening stage the Si precipitates will grow by dissolving and diffusion of small particles in favor of the larger ones (Ostwald ripening).

The evolution of the strain in the Al matrix (Figure 172) is consistent with the hardness measurements (Figure 167). Annealing of the AlSi powders for 30 min at a temperature of 550 °C, will result in a soft, strain free Al matrix in which fine Si particles are homogenously dispersed. Compaction, which is required for fuel plate fabrication, of such pre-annealed powders will be more successful than untreated or low temperature annealed powders.

To show that the presence of the fine Si dispersion in the matrix will be beneficial for the formation of homogeneously thick Si rich preformed layers on the surface of the U(Mo) kernels, an annealing study of U(Mo) fuel kernels dispersed in various matrices is performed.

3.1.3 Annealing study of U(Mo) dispersed in an Al, Al-Si mixed or AlSi alloy matrix

U(Mo) kernels were mixed with pure Al powder, atomized Al5Si or a mixture of pure Al (size ~125 µm) and pure, fine (<25 µm) Si powder (5wt%). Although a 5% Si content was used, similar microstructure as the Al7Si and Al12Si alloy can be found as illustrated above and as such the results allow illustration of the differences in microstructure between alloy and mixture and the evolution of the U(Mo)-Al(Si) interaction. To study the separate effects, the U loading was kept low so individual particles can be considered to behave independently. It can therefore be assumed that the Si concentration (5% or 7%, 12%) is less important in this case, where a sufficient reservoir of Si is available in the matrix surrounding each kernel. It may become more important as the volume fraction of kernels increases. The mixtures are subsequently pressed into pellets using a manual hydraulic press, applying a force of 5 tons.

Annealing tests of the dispersion fuel samples were carried out in vacuum sealed quartz capsules. The annealing temperatures are chosen to simulate to some degree

1) the thermal component of the in-pile diffusion (340°C)
2) the fabrication behavior (450°C).
3) the enhanced diffusion due to fission product recoils (550°C)

At the same time, they have been chosen at values where literature data exists for comparison [7]. Although only the true in-reactor behavior can provide final conclusions, the results of these out-of-pile tests may provide indications on the expected relative behavior. Table 3 provides an overview of the experiment.
<table>
<thead>
<tr>
<th>Anneal T</th>
<th>U(Mo) + Al</th>
<th>U(Mo)+Al5wt%Si</th>
<th>U(Mo)+Al+(5wt%)Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>340 °C</td>
<td>130 d</td>
<td>130 d</td>
<td>130 d</td>
</tr>
<tr>
<td>450 °C</td>
<td>4 h</td>
<td>4 h</td>
<td>4 h</td>
</tr>
<tr>
<td>550 °C</td>
<td>4 h</td>
<td>4 h</td>
<td>4 h</td>
</tr>
<tr>
<td>550 °C</td>
<td>2 h</td>
<td>2 h</td>
<td>2 h</td>
</tr>
</tbody>
</table>

Table 21 Summary of the annealing experiment of U(Mo) particles dispersed in an Al, AlSi alloy or Al-Si mixture matrix

After the thermal treatment, the pellets are removed from the capsules and cut in their longitudinal direction. One half of the pellet is embedded in epoxy resin and polished on successively finer grid finishing on cloth using 1µm diamond paste.

The samples have been investigated by Electronprobe Microanalysis (Cameca SX100).

In Figure 174 the composition X-ray images (Al Kα in blue, U Mα in green and Si Kα in red) are shown for all the systems annealed at different temperature and times.

### 3.1.3.1 U(Mo) dispersed in an Al Matrix

The X-ray maps in Figure 174 of the U(Mo) fuel kernels dispersed in Al and annealed at 340 °C for 130 days (Figure 174.1) or at 450 °C for 4h (Figure 174.2), show that no noticeable interaction occurred between the fuel and the matrix. However, after being submitted to a temperature of 550 °C for 2h (Figure 174.3) most of the U(Mo) fuel particles have reacted with the Al matrix. This interaction is even more extensive after annealing at 550 °C for 4h (Figure 174.4). Looking at a more detailed image of a reacted fuel particle (Fig. 10), it can be assumed that the interaction between U(Mo) and Al has started uniformly around the kernel, creating a thick U-Mo-Al interaction layer. The formation of the IL is followed by penetration of the interaction into the kernel. It appears that the cell boundaries, which are depleted in Mo (typical for atomized U(Mo) and resulting from rapid solidification during cooling), are the preferred diffusion pathways for Al. It has been shown [34] that, in the ternary system U-Mo/Al, the regions rich in Mo show a slower diffusion of Al.
Quantitative analysis (linescans and point analyses) of the interaction layer (e.g. Figure 175) formed after annealing at 550 °C for 2h gives an average composition of 53 at% Al, 41 at% U and 6 at% Mo. Similar results are found after annealing at 550 °C for 4h: 55 at% Al, 38 at% U and 7 at% Mo. In general an Al/U+Mo ratio of ~ 1.1 to 1.2 is found (Table 22) which is rather low and most probably related to the bad contact between the fuel kernels and the matrix or the surface condition of the particle.

340°C – 130 days  
450°C – 4 hours  
550°C – 2 hours  
550°C – 4 hours

U(Mo) in Al matrix

U(Mo) in Al – Si (mixture) matrix containing 5wt% Si

U(Mo) in AlSi (alloy) matrix containing 5wt% Si

Figure 174 X-ray maps (Al Kα in red, Si Kα in green and U Mo in blue) of U(Mo) dispersed in a pure Al matrix, Al – 5wt%Si mixture or in an Al5wt% alloy. The systems were annealed at 340 °C for 130 days, 450 °C for 4 hours, 550 °C for 2 hours and 550 °C for 4 hours. Please note the different magnifications.
Figure 175 Al, Mo and U X-ray map of U(Mo) dispersed in a pure Al matrix, annealed at 550 °C for 2 hours. A quantitative linescan is taken to measure the interaction product. The position of the linescan is indicated by the red arrow in the Al X-ray map.

<table>
<thead>
<tr>
<th></th>
<th>At% Al</th>
<th>At% U</th>
<th>At% Mo</th>
<th>Al/U+Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 °C - 2 h</td>
<td>53</td>
<td>41</td>
<td>6</td>
<td>1.1</td>
</tr>
<tr>
<td>550 °C - 4 h</td>
<td>55</td>
<td>38</td>
<td>7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 22 Composition of the interaction layer formed between U(Mo) particles and a pure Al matrix at annealing temperature of 550 °C.

3.1.3.2 U(Mo) dispersed in a mixture of Al and Si (5wt%) matrix.

The X-ray maps of the U(Mo) fuel particles dispersed in a mixture of Si (5wt%) and Al, annealed at 340 °C for 130 days (Figure 174.5) or at 450 °C for 4h (Figure 174.6), show that almost no interaction of the fuel with the matrix has occurred. Only a very small, discontinuous Si rich layer around some of the fuel kernels can be seen (Figure 176). After the heat treatment at 340 °C and 450 °C, still larger and smaller Si particles remain in the matrix and no clear precipitate free zone (PFZ) has formed [35]. Annealing at 550 °C for 2 hours causes the number of small Si particles to diminish and after 4 hours at 550 °C only large Si particles, some close to or even touching the fuel kernels, are still observed in the matrix. The interaction of the fuel particles with the (smaller) Si particles and the Al matrix results in the formation of a thick interaction layer (Figure 174.7 and Figure 174.8)
The X-ray maps in Figure 177 show that the reacted kernels consist of two layers, one located in the kernel center having a high Si concentration and an outer layer containing a higher Al concentration.

The formation of two interaction layers is confirmed by a quantitative linescan (Figure 178) indicating an increased Si concentration towards the fuel kernel center, while the Al concentration is high at the interface of fuel kernel and matrix and low at the center. From several linescans and local point analyses, an average composition of the (Al rich) outer layer and inner (Si rich) layer is obtained (Table 23).

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>Layer</th>
<th>At% Si</th>
<th>At% Al</th>
<th>At% U</th>
<th>At% Mo</th>
<th>Al/Si</th>
<th>Al+Si/U+Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 °C - 2 h</td>
<td>Outer layer</td>
<td>29</td>
<td>24</td>
<td>41</td>
<td>6</td>
<td>0.83</td>
<td>1.1</td>
</tr>
<tr>
<td>550 °C - 2 h</td>
<td>Inner layer</td>
<td>42</td>
<td>13</td>
<td>40</td>
<td>5</td>
<td>0.31</td>
<td>1.2</td>
</tr>
<tr>
<td>550 °C - 4 h</td>
<td>Outer layer</td>
<td>13</td>
<td>46</td>
<td>35</td>
<td>6</td>
<td>3.54</td>
<td>1.4</td>
</tr>
<tr>
<td>550 °C - 4 h</td>
<td>Inner layer</td>
<td>22</td>
<td>11</td>
<td>57</td>
<td>10</td>
<td>0.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 23 Composition of the interaction layer formed between U(Mo) particles and an Al-Si mixed matrix at annealing temperature of 550 °C.

These results show that even at lower annealing temperature a Si rich layer is formed at the interface between the fuel kernel and the matrix. At higher heating temperatures, the Si diffuses more rapidly than Al into the kernel, forming an almost stoichiometric USi layer. However with time, Al will also penetrate into the fuel kernel, diluting the Si rich layer.

Similar observations have been made on Al cladded natural U slugs described in Chapter 5 [36].
Figure 178  X-ray maps of completely reacted fuel kernel dispersed in an Al-Si mixture matrix, after annealing at 550 °C for 2 hours.

3.1.3.3  U(Mo) dispersed in an atomized Al5wt%Si Matrix.
The AlSi alloy quenched during atomization forms a metastable solution (Figure 179) in which Si precipitates in a finely dispersed way during thermal treatment (Figure 180 and Figure 181).

Figure 179  Al, U and Si X-ray map of a U(Mo) particles dispersed in an AlSi alloy matrix, as received.

Figure 180  Al, U and Si X-ray map of a fuel particle dispersed in an AlSi alloy matrix at an annealing temperature of 450°C for 4 hours.

Thermal transport of the fine Si precipitates from the matrix to the fuel kernel occurs even at annealing temperatures as low as 340 °C (Figure 174.9) and at 450 °C (Figure 174.10). On the
fuel kernel surface a Si-U-Mo interaction layer forms while a Si precipitate free zone (PFZ) is seen in the matrix [35]. It is noticed that a thin Si rich layer is formed at the surface of the fuel particle and that the Si further penetrates the kernel through the U-rich cell boundaries (Figure 180).

At low annealing temperatures, the PFZ and the Si-U-Mo interaction layers are not homogeneous in width/thickness. As expected, the PFZ becomes more pronounced at higher temperatures (Figure 181) and the interaction between the fuel and the Si is extensive (Figure 174.11, Figure 174.12).

Quantitative analysis (Figure 182) reveals the interaction of the fuel with Si and Al. From the linescan, the higher chemical affinity of Si for U, compared to Al, is clear. The composition of the layers is found in Table 24.

Composition measurements of the interaction layers are plotted in a pseudo ternary (U+Mo)-Al-Si diagram (Figure 183) and compared to the composition of interaction layers
found in literature [37,19,38,39]. It should be noted that the out of pile experiments in [37,19,38,39] were performed using AlSi alloys with different Si content (in [39,38]: Al 6061 (0.6 wt% Si), Al 356 (7.1 wt% Si), in [37]: Al 4343 (7.4 wt% Si) or Al-Si mixtures with 4 or 6 wt% Si [40].

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Type</th>
<th>At% Si</th>
<th>At% Al</th>
<th>At% U</th>
<th>At% Mo</th>
<th>Al/Si</th>
<th>Al+Si/U+Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 °C - 2 h</td>
<td>Outer layer</td>
<td>22</td>
<td>42</td>
<td>31</td>
<td>5</td>
<td>0.52</td>
<td>1.8</td>
</tr>
<tr>
<td>550 °C - 2 h</td>
<td>Inner layer</td>
<td>33</td>
<td>2</td>
<td>56</td>
<td>9</td>
<td>0.06</td>
<td>0.5</td>
</tr>
<tr>
<td>550 °C - 4 h</td>
<td>Outer layer</td>
<td>13</td>
<td>46</td>
<td>36</td>
<td>5</td>
<td>3.53</td>
<td>1.4</td>
</tr>
<tr>
<td>550 °C - 4 h</td>
<td>Inner layer</td>
<td>19</td>
<td>22</td>
<td>51</td>
<td>8</td>
<td>1.16</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 24 Composition of the interaction layer formed between U(Mo) particles and an AlSi alloy matrix at annealing temperature of 550 °C.

Regardless of the annealing temperature, the type of matrix or the Si content of the matrix, the composition of the resulting interaction layer seems to be lying in-between the tie-lines USi$_2$-Al and U$_3$Si-Al. In situ XRD measurements to study the interaction of Si thin layers with U(Mo) substrate [41] have shown that in an annealing experiment the first crystalline phase formed due to the interaction of U(Mo) with a limited amount of Si is USi$_2$. With increasing temperature and time and still supply of Si this phase will eventually transform into U$_3$Si.

Figure 183 Pseudo ternary (U+Mo)-Al-Si diagram containing the composition of the IL formed in this study and in [10,29,30,31]

Due to the higher affinity of Si (compared to Al) for U, the interaction between the matrix and the fuel in the current investigated systems, will be between the U(Mo) particle/substrate and the Si diffusing through the Al matrix. It can thus be expected that a USi$_2$ layer is formed on the outer surface of the fuel kernel. Since the Si particles closest to
the fuel kernel will diffuse first, a small PFZ zone is created exposing the formed USi$_2$ layer to a nearly pure Al matrix (dashed tie-line USi$_2$-Al in Figure 183). Considering the limited supply of Si particles to U(Mo) and depending on the annealing temperature, the expected end phase of the interaction between U and Si is U$_3$Si. Exposure of that phase to a pure Al matrix (free of Si particles) defines the second (dashed) tie-line in Figure 183. Drawing the (dotted) tie lines between other uranium silicide crystalline phases (U$_3$Si$_5$, USi, U$_3$Si$_2$) and Al, shows that nearly all found compositions of the interaction layer can be found on one of those tie lines.

Dependent on the annealing time and temperature as well as the amount of available Si, it seems that at first a thin crystalline uranium silicide layer is formed. In the following steps of the annealing process, this layer is exposed to pure Al and Al will start to diffuse and dilute the uranium silicide layer.

### 3.2 E-FUTURE-II

Heat treated AlSi alloys were used to manufacture full size fuel plates for the E-FUTURE-II experiment. The experiment was aimed to test higher Si concentrations in the matrix with an improved availability of the Si. The fuel plates in the E-FUTURE-II experiment consist of a dispersion of 8g$_U$/cc atomized U-7w%Mo particles in an Al-Si (7 and 12 w% Si) matrix. The plates were irradiated in the BR2 reactor with a goal to achieve a similar irradiation history as the E-FUTURE-I plates. 2 of the 4 fuel plates were found stuck in the irradiation basket after 1 cycle, with 2 more becoming stuck after the second cycle. It was found the plates had become seriously deformed.

More information on the E-FUTURE-II experiment can be found in ANNEX 2

### 3.3 Conclusion

Addition of Si to the Al matrix of a MTR U(Mo) based fuel plate has been proven by several irradiation experiments to be beneficial in reducing or delaying the formation of the typical U-Mo-Al interaction layer, which, due to its properties, is a key contribution to excessive swelling of the fuel plate.

Out-of-pile studies have been performed to determine the optimum amount of Si to effectively delay the IL growth, in which form the Si (Al-Si powder mixture or AlSi alloy) is most efficient and how to optimize the powder properties for fabrication. The annealing studies reveal that, at high temperature, there is basically no difference between an Al-Si powder mixtures or an AlSi alloy, as far as the formation of U-Mo-Al-Si layers is concerned. However, it should be noted that these annealing studies cannot be considered fully representative for the in-pile behavior. In anneals at temperatures typically used during fabrication, more uniform Si rich preformed layers are formed using the alloy.

Aging studies on AlSi alloys show that annealing of the alloy at 550 °C for 30 minutes results in a soft and strain free Al rich matrix, making it easier to make a compact (one of the first
steps in the production process of the fuel plate) of the mixture of pretreated AlSi matrix with U(Mo) particles. Annealing of the AlSi powders will also result in an Al matrix in which fine Si particles are homogenously dispersed. With such a microstructure, the Si atoms will get transported more efficiently to the surface of the U(Mo) particle, during the production of the fuel plate.

However, the irradiation of fuel plates containing a high Si Al-Si mixture or AlSi alloy matrix has failed as the plates got severely deformed (E-FUTURE-II).

4 General conclusion

Several irradiation experiments with high density atomized U(Mo) dispersion plates have been performed based on adding Si to the Al matrix in order to obtain a stable in pile behavior of this low enriched fuel system. As described in chapter 5, the principle of adding Si to the meat relies on the high affinity of Si for uranium. During hot rolling and blister anneal, the fuel plate is submitted to higher temperatures inducing a thermally driven diffusion of Si atoms from the matrix towards the U(Mo) fuel particles leading to the formation of Si rich preformed layers around the kernels. The diffusion behavior will depend on the rolling and annealing temperatures. During the irradiation, both these preformed layers and the residual Si in the matrix are expected to impede the formation of a U-Mo-Al interaction layer and change its properties, which are known to lead to undesired pillowing of the fuel plate.

Irradiation of the IRIS-3, IRIS-TUM and E-FUTURE U(Mo) fuel plates containing various Si amounts added to the Al matrix, have been performed. However, after irradiation most of the full size plates still exhibited local unacceptable swelling and/or almost complete consumption of the matrix as result of extensive growth of the interaction layer with ensuing reduction of the mechanical integrity of the fuel plate.

Examination of the fabricated fuel plates prior to irradiation, revealed that diffusion of Si takes place, but that the coverage of the U(Mo) particles with a Si rich layer is not complete, leaving large areas on the U(Mo) surface still exposed to a nearly pure Al matrix. Increasing the Si amount will result in thicker Si rich preformed layers but not per se in a higher coverage fraction of the U(Mo) particles. The diffusion of Si towards U(Mo) is hindered by the high loading required (8g\textsubscript{U}/cc or close to 50 vol%). Furthermore, it was found that small Si particles (< few \textmu m) dissolve more efficient than the larger particles. Out of pile studies showed that the use of a heat treated Al-Si ‘alloy’ (i.e. an Al rich matrix supersaturated with silicon) instead of a mixture, allows to obtain a better spatial dispersion and finer size distribution of the Si precipitates in the matrix. Such a matrix microstructure can be expected to lead to an enhanced Si effect since the Si availability is expected to be more efficient during the fabrication but also during irradiation by fission induced diffusion. Unfortunately, fuel plates containing Al-Si alloys are harder to fabricate due to the mechanical properties of the Al-Si powder and the irradiation causes severe deformation of the plates (E-FUTURE-II irradiation experiment)
An alternative to cover the U(Mo) particles with a Si layer would be to directly apply Si on the surface of the fuel particles by coating them. In that case, one can either apply a coating such that a more favorable interaction layer will be formed through selective compound formation (e.g. Si coating [42]) or a chemically inert coating (e.g. ZrN [43]) can be used to form a barrier for fission induced ion mixing between the fuel and the matrix.
References

International Meeting On Reduced Enrichment For Research And Test Reactors (RERTR), Beijing, China (2009).


Chapter 7 SELENIUM

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Summary

In several irradiation experiments, Si was added to the matrix to reduce the interaction layer formation and improve the properties of the interaction phase in an attempt to allow a U(Mo) based dispersion fuel plate to be irradiated up to very high burn-ups with a sufficient quantity of matrix left at the end of irradiation. By thermally annealing some of the fuel plates in the E-FUTURE and E-FUTURE-II experiments, it was attempted to optimize the Si-rich pre-formed layers around the fuel particles during fabrication. The experiments however clearly showed that just adding Si to the matrix is not sufficient to prevent the pillowing of the U(Mo) based dispersion fuel plates irradiated at high power and at elevated burn-up. Important quantities of interaction layer still form, causing weakened IL-matrix interfaces.

As the IL formation occurs at the U(Mo)-matrix interface, it is logical to attempt to solve the problem by introducing a barrier at that interface which prevents the interaction between U(Mo) and the matrix. For the Surface Engineering of Low ENriched Uranium-Molybdenum (SELENIUM) project, TRIM calculations were performed to estimate the required diffusion barrier thicknesses, based on a ballistic approach. The conclusion was that a layer of ~0.6µm Si or ~1µm ZrN should be sufficient to avoid the recoiled Al and U atoms from interacting, thus effectively preventing IL formation. A PVD magnetron-sputtering device for the coating of particles was constructed and used to produce U(Mo) atomized powder with such coatings. In a next step, two full size flat fuel plates were produced with these particles and irradiated in the BR-2 reactor. The irradiation conditions were selected to mimic the E-FUTURE campaign. Even with a maximum local burn-up of 5.3x10^{21} f/cm³ (nearly 70%^{235}U) in the highest power positions, none of the SELENIUM plates showed signs of pillowing or excessive swelling at the end of irradiation.

Non-destructive analysis of the plates showed that the fuel swelling profiles of both plates were very similar to each other and to the evolution of the E-FUTURE plates. At the fission densities >4.5x10^{21} f/cm³, where pillowing was observed in the E-FUTURE plates, an acceleration of the fuel swelling evolution with burn-up was noticed for both SELENIUM plates. The overall fuel swelling progress, as well as its acceleration at high burn-up, was found to be highly comparable for all E-FUTURE and SELENIUM plates, notwithstanding the fact that no Si was present in the SELENIUM plate with the ZrN coated particles.

In addition, the microstructural evolution of the SELENIUM fuel shows an improved behavior over the E-FUTURE plates. The Si coated fuel has less interaction phase formation at low burn-up but at the highest burn-up positions, defects start to develop on the coating/IL-matrix interface. The largest difference in microstructure is observed in the ZrN coated fuel, which shows a virtual absence of reaction between the U(Mo) and the Al, up to fission densities of 4.5x10^{21} f/cm³, after which the IL formation starts and defects develop in the matrix near the U(Mo) particles. The defects are different from the ones observed in the Si-based systems and show a tearing of the matrix in the areas directly surrounding the U(Mo) particles.
From both the non-destructive and the microstructural analyses, a clear onset of different phenomena is observed at $4.5 \times 10^{21}$ f/cm$^3$. The commonality of the fission density level at which these phenomena start to occur, appears to indicate an intrinsic cause related to the U(Mo) itself. Fuel behavior modelling indicates that recrystallization may be an important factor in this behavior.
1 Introduction

From the irradiation experiments described in the previous chapters (FUTURE [1] (chapter 4), IRIS3 [2] (chapter 6), E-FUTURE-I [3] (chapter 6),.. ) it has become clear that the growing interaction layer contributes to the mechanical destabilization of the fuel plate by the formation of weakened interfaces. As irradiation progresses and fission density accumulates, the growing interaction layer (IL) sweeps up (‘snowplowing’) the ejected fission products piling them up at the IL / matrix interface, creating a fission product halo around the fuel kernels with their interaction layers. It is believed that at this interface, fission gas bubbles will coalesce and grow into the observed crescent moon shaped voids under mechanical strain. The fission product halos cause decohesion of the matrix from the fuel, severely weakening the structure of the meat and hindering thermal conductivity. If local stresses, for example related to the normal gradual swelling of the fuel with burn-up accumulation, can no longer be relieved by creep and exceed the yield strength of the weakened interfaces, cracks start to develop. This mechanism will eventually lead to pillowing of the fuel plate. The exact order of fission gas accumulation and decohesion of the interface is yet unclear.

Any solution to stabilize the in-pile behavior of U(Mo) dispersion fuel therefore needs to inhibit the formation of an interaction layer, limit its growth or accommodate for it by providing more matrix.

The option to limit the excessive growth of the interaction layer by adding silicon to the system, was explored in several irradiation experiments. It was found that the use of Al-Si matrices could work if not for the inefficient diffusion of Si combined with the high U loadings, resulting in an incomplete coverage of the kernels with a Si-rich preformed layer (see chapter 6, fresh fuel characterization), which in itself might already contain important amounts of Al.

Applying a pure Si coating directly on the fuel kernel surface, not only brings the fuel in close contact with silicon but also assures that a complete coverage of the U(Mo) surface is achieved and that the coating does not contain significant amounts of Al. As the supply of Si to the U(Mo) is readily available throughout the heat treatment during plate production, the formation of a pure uranium silicide layer is expected. From experiments with model systems (chapter 5) it was found that out of all possible uranium silicide phases, the $U_3Si_5$ phase is most likely to form during fuel plate fabrication. Such high Si content in the preformed layer is expected to be very efficient in preventing Al diffusion.

In the IRIS-3 and E-FUTURE experiment (chapter 6) Si is added to the matrix to reduce the formation and improve the properties of the interaction layer, in an attempt to irradiate U(Mo) based dispersion fuel plates up to high burn-ups with a sufficient quantity of matrix left at the end of irradiation.

The formation of an interaction layer between the fuel and the matrix is an ion driving diffusion process (ballistic effect). Any solution to avoid the formation of such a layer needs
to prevent the recoiled Al and U atoms to interact. The introduction of a diffusion barrier at the U(Mo)-matrix interface would serve that purpose [4].

2 Surface Engineered Low ENrIched Uranium-Molybdenum fuel

The SELENIUM (Surface Engineering of Low ENrIched Uranium-Molybdenum) fuel development project of SCK•CEN [5] was initiated to investigate coatings as a way to inhibit interaction layer formation (Patented IPN WO 2011/051447 A1). The project consists of the production, irradiation and post-irradiation examination of two flat, full size plates containing coated U(Mo) atomized powders dispersed in a pure Al matrix.

As coating material, silicon was chosen as it forms a uranium silicide layer (chapter 5) which has a stabilizing effect on the fuel-matrix interaction because of the limiting power of Si for Al diffusion. However, the presence of Si in a fuel plate is not a preferred element in the back end of the fuel cycle (reprocessing). As such, a second type of coating was chosen based on its ability to prevent direct contact between uranium and aluminum. Such a coating should be of a substance that is metallurgical inert towards the U(Mo) and the Al matrix. ZrN, W, Nb, .. are examples of substances that do not readily interact with the U(Mo) or Al. Initially pure Zr was chosen but it turned out that sputtering of a Zr layer is not possible as during deposition the coated fuel kernels start to coagulate. Based on the experience of the Russian MIR irradiated mini rods containing ZrN coated U(Mo) [6], also in this study, a ZrN coating was sputtered on the surface of the U(Mo) particles.

2.1 STEPS&DRUMS

Surface engineering of the U(Mo) particles in SELENIUM is performed using magnetron sputter deposition in the most common configuration, i.e. the planar one with parallel target and anode electrode surfaces. Small permanent magnets are arranged on the back of the circular target (Figure 184) in circular rings.

![Figure 184 Configuration and principle of magnetron sputtering.](image)

A magnetic field is superposed on the cathode and glow discharge, parallel to the cathode surface. The electrons in the glow discharge will show cycloidal motion and the center of the orbit drifts in a direction of $ExB$ with the drift velocity of $E/B$, where $E$ and $B$ denote the electric field in the discharge and the applied magnetic field respectively.
The magnetic field is oriented such that these drift paths for electrons form a closed loop, the so-called "racetrack." This electron trapping effect increases the collision rate between the electrons and the sputtering gas molecules enabling a stable plasma discharge at sputtering gas pressures as low as $10^{-3}$ to $10^{-5}$ Torr. The sputtered atoms fly off in ballistic fashion to impinge on substrates and form a film. PVD offers a fairly low cost and high flexibility for target material choice, co-deposition and multi-layer deposition capability and avoids heating of the material/substrate.

The additional difficulty in coating powders compared to flat surfaces is the need to continuously agitate the powder so that the particles receive a homogeneous coating with even thickness. This can be accomplished by the use of a rotating drum in the vacuum chamber. The technique is known as barrel sputter deposition [7] and is shown schematically in Figure 185.

![Figure 185 Schematic representation of a barrel sputter deposition setup (from [7])](image)

In 2009, SCK•CEN and the University of Ghent developed a Sputtering Tool for Engineering Powder Surfaces and Deposition Reactor for Uranium based Model Systems (STEPS&DRUMS) to coat U(Mo) powder (Figure 186). The reactor is a vacuum vessel with at one end a rotating drum to coat particles (STEPS) and at the other end a sample holder to sputter (uranium) films on flat surfaces (DRUMS). The reactor is pumped down to the $10^{-6}$ mbar range and high-purity Ar gas is admitted in the chamber at a rate of 80 cc per minute. In the case of ZrN deposition [8], high purity nitrogen is added at a rate of 6 cc per minute. Deposition of Si or Zr from ultra-high purity metallic targets is performed using two sources operated simultaneously at powers of 1kW (for Si) or 800W (Zr) each, gradually decreasing due to thinning of the targets. To obtain a homogeneous coating of the U(Mo) particles, the powder is kept in motion by rotation of the drum at roughly 2-5 rotations per minute. Because the STEPS&DRUMS setup is a research tool, sputter geometries are optimized for flexibility, rather than for production,
which leads to relatively long sputter times, up to 7 hours to obtain the desired coating thicknesses.

Figure 186 Image of the STEPS&DRUMS (“Sputtering Tool for Engineering Powder Surfaces” & “Deposition Reactor for Uranium based Model Systems”) and a schematic view of the drum and sputter targets.

2.2 Coating requirements and production

TRIM calculations were performed to estimate the required diffusion barrier thicknesses, based on a ballistic approach (chapter 3) and it was concluded that a diffusion barrier of ~1µm ZrN should be capable of avoiding the recoiled Al and U atoms from interacting, thus effectively preventing IL formation.

Figure 187 Evolution of the equivalent Si matrix concentration with coating thickness (8g_U/cc) (from [9]).

It was chosen that the SELENIUM plate with the Si coated particles should contain a similar total Si quantity as the E-FUTURE plates in order to make a fair comparison. In such a case, it
can be calculated that for a kernel size of 70 µm diameter and a loading of $8g_{U/cc}$, a coating thickness in the range 400-600 nm is needed (Figure 187).

Sputter speed calibrations were performed by sputter depositing the desired material on stainless steel atomized powder and taking samples of the coated powder every hour. As such, the gradual increase in coating thickness could be used to calibrate the deposition speed on powders and determine the sputtering time required to achieve the desired coating thickness on the U(Mo) powders, as shown in Figure 188. The determined sputter times were then used to deposit coatings on natural uranium based U(Mo) atomized powder to verify their validity.

![ZrN deposition speed calibration](image)

Figure 188 Typical deposition speed calibration line obtained on stainless steel atomized powder, in this case for deposition of ZrN.

After a successful preparation of two batches (a batch corresponds to the amount required for one full size fuel plate) of coated U(Mo) powders with acceptable thicknesses, 2 batches of LEU(Mo) powder (mean kernel size = 70 µm) purchased from KAERI, were coated under the established conditions. The coatings on the LEU were always performed in a single run, so the coating process was never interrupted.

The coatings are characterized using X-ray reflectometry (XRR [10]), scanning electron microscopy (SEM [11]), electron microprobe analysis (EPMA [11]) and high energy X-ray diffraction (HE-XRD [12])

2.3 Properties of the coatings

2.3.1 Si coating

SEM was performed on a polished mount containing Si coated particles embedded in an Ag matrix to obtain a good density contrast (Figure 189). Of 50 randomly chosen fuel particles, the thickness of the coating was obtained at four positions. A homogeneous coating with an average thickness of $815 \pm 183$ (s.d.) nm is measured (Figure 190).
The high standard deviation is expected due to the absence of stereographic corrections. The thickness of the coating layer for large fuel kernels will of course be smaller than on those particles having a small diameter. No uncovered particles have been observed.

X-ray diffraction (XRD) and X-ray reflectivity measurements (XRR) were performed on a comparable Si coating deposited on a flat surface (Si wafer) to assess respectively the crystallography and density of the layer. XRD showed that as expected the Si coating is amorphous. From the critical angle in an XRR measurement the density of the layer can be determined (Figure 191, [10]). It is found that the density of the deposited Si layer is slightly lower (2.1 g/cm$^3$) than bulk Si (2.33 g/cm$^3$), which is typical for sputter deposited layers.
Figure 191 X-ray reflectivity measurement of Si layer resulting from the deposition of ~300 nm thick Si layer on a Si wafer.

Synchrotron high energy X-ray diffraction (HE-XRD) has been carried out on the ID15B beamline using a 87 keV X-ray beam [12] on the coated powder in as received state [13,14]. The analysis revealed that no interaction between Si and U(Mo) during deposition has occurred. The absence of crystalline Si peaks in the diffraction pattern indicates that the deposited film is indeed in an amorphous state, as can be expected in sputter deposited layers (Figure 192).

2.3.2 ZrN coating

Similar as for the Si coated particles, the thickness of the ZrN coating was measured from the SEM images at four positions on 50 randomly chosen fuel particles.
A very smooth and homogeneous ZrN coating (Figure 193) with an average thickness of 1157 ± 308 (s.d.) nm (no stereoscopic correction) (Figure 194), was deposited on the U(Mo) particles. The large kernels have, similar to the Si coating, a smaller coating thickness and the rate of covered particles is almost 100%.

XRR and XRD were performed on a comparable ZrN coating deposited on a flat surface (Si wafer) to assess respectively the crystallography and density of the layer. It was found that the crystalline ZrN coating has a density of 6.82 g/cm$^3$ is found, which is a little lower than the theoretical density of 7.09 g/cm$^3$. 

Figure 193 Secondary electron image of a ZrN coated U(Mo) particle.

Figure 194 Result of ZrN coating thickness measurements with SEM.

3 Fuel plate fabrication and fresh fuel characterization

The fuel plates in the SELENIUM experiment consist of an 8g/U/cc dispersion of coated, atomized LEU (19.7% $^{235}$U) based U-7w%Mo alloy particles in a pure Al matrix and were fabricated by AREVA-CERCA using the standard plate production process. The plates selected for irradiation were identified as U7MD1221 (600 nm Si coating) and U7MD1231 (1 μm ZrN coating).

Next to the plates for irradiation, also sister plates containing NU(Mo) were produced to be characterized in as received state.

3.1 As received fuel plates

3.1.1 Si coated

The microstructure of the as received fuel plates reveals that the Si coating has been damaged during the production process, especially those particles located at the meat / cladding interface (Figure 197).
Figure 197 The combined EPMA X-ray color map (Al Kα blue, U Mα red and Si Kα green) shows the microstructure of the as received fuel plate. It is observed that the coatings are damaged but no interaction occurred between the matrix and the fuel.

This indicates that the largest effect on the coating does not come from the increased temperature during plate fabrication but from the mechanical wear imposed during rolling of the plates. Large areas on the U(Mo) particle surface are as such exposed to the matrix. The matrix also contains pure Si particles, part broken coating layers, part Si flakes mixed in with the coated powder. The latter are resulting from the coating process, as silicon will also be deposited on the rotating drum. The tumbling U(Mo) powder pulverizes the fragments that have flaked off after the deposited Si film on the drum has reached a certain thickness. From the SEM measurements it seems that almost no interaction has taken place during the thermal treatment of the plates at production stage (hot rolling and blister test), even though there was direct contact between U(Mo) and Al. HE-XRD of the as received fuel plate however, identifies the growth of two crystalline phases: a distorted form of U₃Si₅ and U(Al,Si)₃ [13] (Figure 192).

Figure 198 The HE-XRD measurements show that no interaction occurred between the U(Mo) fuel and the deposited Si coating but that the heat treatment during plate production caused the formation of a distorted U₃Si₅ and U(Al,Si)₃ phase. (Figure adapted from [13])

Quantification of the (intact) coating with EPMA, particularly to ascertain the Al content, is inaccurate since the electron beam interaction volume and coating thickness are of comparable size. Nevertheless it is likely that the pure Si coating in contact with the pure
U(Mo) kernels has mainly transformed into a pure U$_3$Si$_5$ layer during the plate production process (as predicted in chapter 5) and that those locations where the coating was damaged, layers of U(Mo)(Al, Si)$_3$ have formed.

3.1.2 ZrN coated

As can be seen in Figure 199, cracks in the coating, perpendicular to the U(Mo) surface, have formed. This is most probably the result of a thermal expansion mismatch between the fuel and the coating (thermal expansion coefficient for U10Mo (similar to the U7Mo used) is 11.5×10$^{-6}$ m/m K [15] and for ZrN is 7.24×10$^{-6}$ m/m K [16]).

![Figure 199](image)

Figure 199 The combined EPMA X-ray color maps (Al Kα blue, U Mα red and Zr Lα green) of the as received fuel plates containing ZrN coated fuel, show that the coatings are damaged.

This thermal expansion mismatch between coating and substrate results in tensile stress on the coatings in the radial direction and compressive strain in the tangential direction, and opposite stresses during the cooling phase. It is the tensile stresses in the films that could cause through thickness microcracking [17]. However, the cracks may also result from mechanical forces acting (rolling) on the brittle, ceramic ZrN.

3.2 Annealing study of coated U(Mo)

To simulate the influence of plate production (hot rolling, blister test) and, to some extent, the enhanced diffusion due to fission product recoil, the coated powders were mixed with Al powder, pressed (manual hydraulic press) into pellets and annealed at 450°C for 4 hours and 550 °C for 2 and 4 hours. To study the separate effects, the U loading was kept low so the individual particles can be considered to behave independently in these model systems. Heat treatments were also performed on samples of the as received plates fabricated with NU U(Mo). Only an additional anneal at 550 °C for 2 and 4 hours has been applied to samples of the as received fuel plates for comparison with the pressed samples since the fuel has already been submitted to a heat treatment during plate production.
3.2.1 Si coated U(Mo)

In the model systems with the Si coating, the coating stays relatively intact during pressing and annealing and only a minor penetration of silicon into the fuel kernel was observed for some selected particles, even at higher temperatures (Figure 200).

![Figure 200](image1)

The combined EPMA X-ray color maps (Al Kα blue, U Mα red and Si Kα green) show that in the model systems at higher annealing temperature, an interaction between the Si coating and the U(Mo) fuel kernel occurs.

On the other hand, submitting the as received Si coated fuel plates to an anneal at 550 °C for 2 and 4 hours causes substantial interaction between the matrix and the fuel particles. This interaction is quite extensive at the interface of the meat and the cladding (Figure 201) where most particles with damaged coatings are located (Figure 197).

![Figure 201](image2)

The damage to the Si coatings is most extensive at the meat/cladding interface after annealing of the as received fuel plate at 550 °C for 4 h.

Local point quantitative X-ray analysis (EPMA) of the interaction layer formed in this anneal shows that the ratio Al+Si/U+Mo is ~3 (Al >70at%, Si <5 at%), indicating the growth of the U(Al,Si)₃ layer as also identified with HE-XRD in the as received plate.

3.2.2 ZrN coated U(Mo)

Analysis of the model system containing an Al matrix embedded ZrN coated powder annealed at 450°C for 4 hours and 550 °C at 2 and 4 hours, reveals that at no temperature and time an interaction between the coating and the fuel or Al matrix has occurred.
The combined EPMA X-ray color maps (Al Kα blue, U Mα red and Zr Lα green) show that in the model systems no interaction between the fuel and ZrN coating or matrix is observed in the annealing experiment of the coated powder.

As can be seen from Figure 199, also no interaction between Al and U(Mo) has occurred during plate production with these coatings. However, submitting the ZrN/U(Mo) fuel plate to an additional anneal at 550 °C for respectively 2 and 4 hours, results in the formation of an interaction layer as Al can reach the U(Mo) surface through the microcracks. Contrary to the Si coating, the damage to the ZrN film seems to be randomly distributed throughout the meat (Figure 203), which is a further indication for the role of the thermal expansion mismatch in the cracking.

However, thermal anneals are not a very good simulation of the in-pile behavior. It has been shown (chapter 3 and 5) that in-pile the formation of an interaction layer is not thermally driven but rather the result of a ballistic effect. As such would heavy ion irradiations give a more realistic prediction of the in-pile behavior.

### 3.3 Ion irradiations [18]

The samples have been irradiated with iodine at 80 MeV perpendicular to the surface at the Maier-Leibnitz tandem accelerator in Garching, Germany, until an integral fluency of \( F = 1 \times 10^{17} \) ions/cm\(^2\) has been reached. The total energy \( E \) of the incoming ion is deposited within the penetration depth \( p \) inside the respective material, where \( p = 14 \) µm for Al and \( p = 6 \) µm for UMo. The sample temperature was around 200 °C during heavy ion irradiation (sample...
holder temperature 5 mm beside the irradiated area). It has been shown before that such irradiation conditions cause effects comparable to in-pile irradiation.

![Cross section through the irradiated surface of the samples with Si (a) and with ZrN (b) coating. In case of a sufficiently thick and intact coating (green) no UMo/Al interaction occurs. Otherwise (red), a conventional interaction layer forms during irradiation.](image)

It was found that no U(Mo)/Al interdiffusion occurred at spots that were sufficiently protected by a coating layer, while fuel matrix interdiffusion occurred at those locations where the fuel kernel was not protected by a Si or ZrN layer (Figure 204). The Si coating of the UMo particles is attacked during ion irradiation but it is not entirely dissolved. The results obtained on the samples coated with 1000 nm ZrN are divided: on the one hand, the IL formation is completely suppressed in case of undamaged ZrN layers. On the other hand, a significant IL grows at positions where the ZrN layer shows cracks. The formation of an IL at positions where the ZrN layer reveals cracks can be regarded as expected and confirms the annealing tests (3.2.2).

### 4 Irradiation history

<table>
<thead>
<tr>
<th>Plate Id.</th>
<th>U7MD1221</th>
<th>U7MD1231</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabrication data</td>
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<td></td>
</tr>
<tr>
<td>Cladding</td>
<td>AG3NE</td>
<td>AG3NE</td>
</tr>
<tr>
<td>Matrix</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>coating</td>
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<td>1000nm ZrN</td>
</tr>
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<td>Loading (gU/cm³)</td>
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<td>8</td>
</tr>
<tr>
<td>Enrichment (%²³⁵U)</td>
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<td>19.75</td>
</tr>
<tr>
<td>wt% Mo</td>
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<td>7</td>
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<td>Irradiation data</td>
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<td></td>
</tr>
<tr>
<td>EFPD</td>
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<td>69</td>
</tr>
<tr>
<td>Mean BU (%²³⁵U) (f/cm³ U(Mo))</td>
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<td>47.5 (3.5x10²¹)</td>
</tr>
<tr>
<td>Max BU %²³⁵U (f/cm³ U(Mo))</td>
<td>69.2 (5.3x10²¹)</td>
<td>69.6 (5.3x10²¹)</td>
</tr>
<tr>
<td>Peak Heat Flux (W.cm⁻²)</td>
<td>466</td>
<td>466</td>
</tr>
</tbody>
</table>

Table 25 Fabrication and irradiation history of the SELENIUM fuel plates.
The SELENIUM plates were irradiated in the BR2 reactor of SCK•CEN for 1 cycle of 27 EFPD and 2 cycles of 21 EFPD. The plates were loaded on April 24th, 2012 and discharged after the last cycle on October 23rd, 2012. The irradiation history was, to the maximum extent possible, aligned with the E-FUTURE irradiation (chapter 6) to allow a direct comparison between the experiments. Both SELENIUM plates were subjected to a maximum power at BOL close to 470W/cm². Due to the absence of burnable neutron absorbers, there is a gradual reduction in power with irradiation time, reaching a value of around 250 W/cm² at EOL, attaining a plate average burn-up of ~48% 235U and a local maximum burn-up just below 70% 235U. The fabrication characteristics and irradiation conditions are summarized in Table 25.

5 Post-irradiation examination

5.1 Calculated burn-up profile

The 3-D spatial distribution of the fuel burn-up in the plates is calculated using the MCNP code linked with the burn-up module ORIGEN-S in the SCALE code [19].

![Figure 205 Calculated burn-up profile of fuel plates U7MD1221 and U7MD1231.](image)

Both fuel plates show a similar profile with a maximum burn-up (maximum heat flux) located around 580 mm from top and close to one side of the plate (Figure 205).

5.2 Non-destructive analysis

The NDT of the fuel plates included visual inspection, plate thickness profiles, oxide thickness profiles and gamma spectrometric mapping of the plates.

5.2.1 Visual examination

The photographs of the fuel plates after irradiation show clearly the delineation of the meat. Again, a gradient in the color of the meat is observed indicating a difference in oxide layer thickness. At the max flux position, it appears that the oxide layer has spalled off and that the bare cladding is observed (greyish color).

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9 The results of the gamma spectrometry were not available in time to be included in this thesis.
5.2.2 Thickness measurements

Plate and oxide thickness profiles of each plate were recorded in 20 line scans along the length of each plate with measurement values every 1 mm (~875 points per scan). Line scans were taken at 2.5 mm intervals along the plate width, from 6 mm to 51 mm from the edges of the plate, simultaneously recording the plate and oxide thicknesses (Figure 207).

The corrected oxide profiles of each SELENIUM plate are visualized in Figure 208. Oxide thicknesses close to the peak power location amount to ~35 µm for both plates. The oxide
thicknesses in the highest power areas (around 600 mm from top and close to one side of the plate) are topped off at 35-40 µm with a flat profile in the high power zone, indicating incipient spalling.

The oxide thickness profiles look similar to the profiles obtained on the E-FUTURE plates [20], which were afterwards confirmed by destructive measurements. The oxide profiles measured on the FUTURE-U(Mo) plate U7MTBR07 are also similar, but the oxide thicknesses are lower, which is consistent with the lower burn-up acquired.

During the measurements, it was observed that the SELENIUM plates had quite an important quantity of loose particles on their surfaces, which sometimes cause artefacts in the measurements as particles are stuck on the measurement probes. Some of these measurements were rejected as outliers, while others were kept in the dataset. It was verified that the end results were not significantly affected by the remaining measurement artefacts or the removal of outliers thanks to the large dataset. The origin of the loose particles is believed to lie in the incipient oxide spallation.

The burn-up shows little variation over the plate width. As was discussed in the FUTURE (chapter 4) and E-FUTURE (chapter 6) experiments this justifies a width averaging of the measurements.

![Figure 209 Plate thickness measurements average over the width of the plate.](image)

For both fuel plates a thickness profile that follows the BU profile, is measured (Figure 209). For the ZrN coated fuel plate (U7MD1231), a slight increase is observed at the highest burn-up position but compared to the E-FUTURE plates this is only a minor increase (Figure 210).

Except for the high burn-up area, the increases in plate thickness in the E-FUTURE and SELENIUM irradiation experiment are in agreement, which is expected in view of the similar irradiation histories (burn-up and power).
5.2.3 Swelling

5.2.3.1 Plate swelling
The as-measured plate thicknesses of the plates are corrected for the oxide formation and by dividing the corrected plate thickness by the initial thickness a value for the plate swelling is obtained. The initial plate thickness $T_i$ for each of the plates is measured in the out-of-fuel zone and equals $\sim 1274 \, \mu m$ for fuel plate 1221 (Si) and $\sim 1278 \, \mu m$ for fuel plate 1231 (ZrN). This value is corrected for spring back and the thickness of the oxide layer outside the fuel zone. The calculated plate swellings are visualized in a 2D contour plot and are overlaid with the calculated burn-up distributions (Figure 211). As can be seen, the maximum swelling is recorded in the highest burn-up location and reaches an absolute maximum of 8% for the 1221 plate (Si) and 10% for the 1231 plate (ZrN).

The swellings of the plates measured in the SELENIUM experiment are much smaller compared to the fuel plates from E-FUTURE, where an absolute maximum swelling of 108, 147, 69 and 36 % was measured in respectively fuel plate 4111, 4202, 6111 and 6301.
5.2.3.2 Fuel swelling

The plate thickness profiles can be converted to the fuel swelling ($S_f$) distributions using the volumetric fraction $V$ of U(Mo) in the fuel meat (48.6%) and the meat thickness $t_i$ (510µm). The fuel swellings recorded in points with similar burn-ups (interval of 0.5%) are averaged and the evolution of the fuel swelling with burn-up or fission density is plotted (Figure 212). The calculated burn-up is used, as quantitative $\gamma$-spectrometry results are not available in time.

The swelling of U(Mo) is previously described in chapter 3 and evolves linearly with fission density if it originates strictly from solid state swelling due to fission product accumulation.

![Figure 212 Calculated fuel swelling profile including the 1σ spread of the data points of the SELENIUM plates as function of the fission density.](image)

For both plates, a fairly linear swelling caused by accumulation of fission products is observed up to a fission density of $4.5 \times 10^{21}$ f/cc. Above that burn-up an acceleration in the swelling rate can be seen (Figure 212). For the U7MD1221 (Si) data, the spread is identical throughout the complete burn-up range, while the spread increases somewhat in the high burn-up portion of the U7MD1231 (ZrN) data. This can be interpreted as an indication of a process taking place inside the fuel plate, which is not depending on the burn-up.

It should be noted that fuel plate U7MD1231 (ZrN) contains no Si and yet shows the same swelling profile as plate U7MD1221 (Si). Furthermore, both SELENIUM plates do not show excessive swelling at high fission density as observed in the E-FUTURE plates.

In Figure 213 the fuel swelling profiles measured on the fuel plates of the FUTURE, IRIS-3, E-FUTURE and SELENIUM experiment are plotted in function of the fission density. The graph shows a very good correlation between the results obtained on all plates, independent of power, loading, composition, microstructure etc. All data points actually have different power histories (each point has reached its BU through a different heat flux path) and the
fuel meat microstructure will show varying amounts of U(Mo)-matrix interaction. This indicates that the observed swelling is not a fission rate effect but that the behavior is most likely strictly dictated by the solid state swelling due to fission product accumulation at low burn-up and enhanced by recrystallization at higher burn-up.

The lower burn-up portion of the SELENIUM data (especially SELENIUM 1231 (ZrN)) shows some deviations from linearity, which are currently unexplained. They may be due to some local inhomogeneity in the loading of these prototype plates changing actual local burn-up values. Quantitative gamma spectrometry should allow clarifying these deviations. For this reason, the low burn-up SELENIUM1231 (ZrN) data is not taken into account in the derivation of the swelling trend at low burn-up shown in Figure 214.

Also for the interpretation of the swelling behavior of the SELENIUM plates we start from the notion that the linear evolution law of the fuel swelling consists of two parts: one linear part below ~3×10^{21} f/cm³ and the other quasi linear between 3×10^{21} f/cm³ and 4.5×10^{21} f/cm³. In the previous chapter this threshold is explained as the fission density at which fuel restructuring starts taking place. Microstructurally, this is translated as the breakdown of
the fission gas nanobubble lattice leading to the formation of micron size fission gas bubbles as visible by scanning electron microscopy. Restructuring is caused by damage accumulation in the lattice of the U(Mo) fuel as an effect from the fission product bombardment. Above a certain threshold, this damage leads to an athermal restructuring of the fuel, effectively 'resetting' the lattice damage. After grain refinement, the local grain sizes (order of few hundred nm) in the fuel are of the same order as the athermal diffusion length of the fission products. The micron sized fission gas bubbles formed due to recrystallization will thus act as sinks for the newly formed fission gas. This leads in part to a larger swelling rate of the fuel.

Fitting of 2 linear trends to the available FUTURE, IRIS-3, E-FUTURE fuel and SELENIUM swelling data in the 2 fission density ‘domains’ (FD < 3×10\(^{21}\) f/cc and 3×10\(^{21}\) f/cc < FD < 4.5×10\(^{21}\) f/cc) yields the following expressions for fuel swelling (FSw) evolution (Figure 214):

\[
\text{FSw(\%)} = 5.2 \times \text{FD} - 0.1 \quad [R^2 = 0.96] \quad (0.5 < \text{FD} < 3) \quad \text{Eq. 40}
\]
\[
\text{FSw(\%)} = 6.6 \times \text{FD} - 5 \quad [R^2 = 0.89] \quad (3 < \text{FD} < 4.5) \quad \text{Eq. 41}
\]

with fission density (FD expressed in 10\(^{21}\) f/cm\(^3\)).

Comparing to the swelling expressions derived in previous chapter (only data from the FUTURE, IRIS-3, E-FUTURE plates):

\[
\text{FSw(\%)} = 5.0 \times \text{FD} - 0.1 \quad [R^2 = 0.96] \quad (0.5 < \text{FD} < 3) \quad \text{Eq. 42}
\]
\[
\text{FSw(\%)} = 7.3 \times \text{FD} - 7.2 \quad [R^2 = 0.91] \quad (3 < \text{FD} < 4.5) \quad \text{Eq. 43}
\]
a good agreement is found for the low burn-up region (Eq. 40 and Eq. 42). For the high BU region (Eq. 41 and Eq. 43) when taking all the data from all plates into account, the slope has become smaller. This is mainly due to the low swelling rate of the SELENIUM U7MD1221 (Si) plate. Leaving those data out of the fitting procedure results in a swelling law at high BU of:

\[
\text{FSw(\%)} = 7.1 \times \text{FD} - 6.6 \quad [R^2 = 0.92] \quad (3 < \text{FD} < 4.5) \quad \text{Eq. 44}
\]

The lower swelling rate of fuel plate U7MD1221 (Si) is atypical and more detailed analysis is needed to offer an explanation.

5.3 Destructive analysis

5.3.1 Fuel behavior

5.3.1.1 Fuel plate U7MD1221 (Si coated)

Several samples, all having received a different burn-up, were cut from each fuel plate (Figure 215). The samples were embedded and prepared for SEM and EPMA analysis.
The burn-up locations of the samples on the fuel swelling curve measured during NDT, is indicated in Figure 216.

The gradual increase in fuel swelling up to a fission density of \(~4.9\times10^{21}\) f/cm³ as measured in the NDT (Figure 216), is reflected in the SE images of the plate cross sections at various fission densities (Figure 217).
Figure 217 Secondary electron images of the cross sections of samples M5B \((2.2 \times 10^{21} \text{ f/cm}^3)\), M5B \((2.2 \times 10^{21} \text{ f/cm}^3)\), M4B \((2.9 \times 10^{21} \text{ f/cm}^3)\), M3B \((3.7 \times 10^{21} \text{ f/cm}^3)\), M2A \((4.4 \times 10^{21} \text{ f/cm}^3)\), M7A \((4.9 \times 10^{21} \text{ f/cm}^3)\) and M1A \((5.2 \times 10^{21} \text{ f/cm}^3)\).

The overview of the cross sections of the plate that have been submitted to different fission densities shows that the cladding thickness remains fairly constant but it is the thickness of the meat that increases above \(3.7 \times 10^{21} \text{ f/cm}^3\).

Figure 218 Detailed SE images of the fuel obtained at the various fission densities/samples as shown in Figure 217.

Looking in more detail at the fuel (Figure 218), it is seen that below this burn-up a Si rich layer surrounds the fuel kernels while at increasing fission density on some locations on the surface of the fuel kernels an outer layer grows. The combined X-ray map in Figure 219 shows that it concerns a U(Mo)-Al-Si interaction layer (purple color).
Figure 219 Combined X-ray maps (Si in green, Al in red and U in blue) on the highest BU sample ($5.2 \times 10^{21}$ f/cc) of fuel plate U7MD1221. The interaction between the fuel and matrix colors purple.

It should be noted that at high burn-up, voids between the outer layer and matrix are seen, but most of them do not have that typical crescent moon shape previously seen in other U(Mo) irradiation experiments. Most of these voids are located in the Si-rich layer and in the matrix even cracks can be seen (Figure 219 voids in black).

Except for the formation of some fission gas bubbles (in the fuel interior and in-between touching particles), the fuel does not seem to alter. The fuel behavior in the SELENIUM plate containing silicon coated U(Mo) particles is similar to the U(Mo) fuel dispersed in an Al/Si matrix in the E-FUTURE irradiation (Figure 218, Figure 220).

Figure 220 Comparing the microstructure of the meat on several positions on the max flux plane of fuel plate U7MD1221 (Si coated) and U7MC6111 (Al-6wt%Si matrix).
However, when comparing the microstructure of the meat in the SELENIUM plate to that of the E-FUTURE plates, several differences can be observed (Figure 220):

- at the lowest burn-up side of the max flux plane (MFP) (right side in Figure 220) the Si coating on the surface of the fuel kernels in the SELENIUM plate is still intact while in the meat of the E-FUTURE plate, the interaction layer surrounding the fuel kernel has substantially grown. This difference in IL growth can also clearly be seen in combined X-ray mapping (Figure 221) where the interaction between the fuel (blue) and the matrix (red) results in numerous IL’s (purple) in the E-FUTURE sample.

- at the higher burn-up region of the max flux plane (MFP) (left side in Figure 220) also in the SELENIUM plate a growth of the coating / interaction layer is seen as well as the formation of large fission gas bubbles in-between fuel kernels and the appearance of voids/cracks in the matrix (Figure 219) or at interface matrix/IL (Figure 220). For the E-FUTURE plate the bubbles in-between touching fuel particles are very large as well as the crescent shaped voids at the IL-matrix interface.

The most striking difference between the SELENIUM and the E-FUTURE fuel however, is the size of the fuel particles and the distribution of Si (Figure 221). In the E-FUTURE plates, the fuel particles are small (<~50 µm) and only ‘patches’ of Si are randomly surrounding the fuel kernels. As a result more U(Mo)-Al interaction has occurred. What was also already shown in the previous chapter 6, wherever clustering of the E-FUTURE fuel particles appeared, no Si was present in-between the touching particles. The fuel particles in the SELENIUM plate are nearly double in size (<~100 µm) and also clustering of the fuel kernels is observed in this plate, but here the touching particles are still separated by their Si coating. The Si distribution throughout the meat is much more homogenous and effectively covering the surface of the fuel particles. As a consequence, much less IL growth is observed in the SELENIUM plate.
5.3.1.2 **Fuel plate U7MD1231 (ZrN coated)**

![Fuel plate U7MD1231 (ZrN) diagram](image)

Figure 222 Location of the samples on the plate swelling contour plot overlaid with BU distribution of the U7MD1231 plate.

![Fuel swelling versus fission density curve](image)

Figure 223 Location of some of the examined samples on the fuel swelling versus fission density curve.

Similar as in the fuel plate U7MD1221 containing Si coated fuel particles, the gradual increase in fuel swelling up to a fission density of $\sim 5 \times 10^{21}$ f/cm$^3$ as measured in the NDT (Figure 223), is reflected in the SE images of the plate cross sections at various fission densities (Figure 224).
From the cross section images (Figure 224) and the detailed photographs in Figure 225 it can be stated that the microstructure of the meat (on this scale) does not alter up to a fission density of $\sim 3.7 \times 10^{21} \text{ f/cm}^3$. The U(Mo) fuel particles are dispersed in the matrix that also contains some ZrN flakes (a result from the coating process).

Above $3.7 \times 10^{21} \text{ f/cm}^3$ several changes in the meat microstructure are observed:

- the ZrN coating increases in thickness: the coating seems to swell to a thickness of several micrometers.
• cracks at the coating/matrix interface: it concerns tearing of the matrix at the highest burn-up position and is different from the crescent shaped porosities observed in the other experiments. It should be noted that these cracks run parallel to the surface of the plate.
• visible fission gas bubbles in the fuel kernel
• formation of an interaction layer: in the SE image of Figure 225 these are colored light grey, while in the combined X-ray map of Figure 226 they are colored purple. Further details on the IL will be given later in this chapter.

![](image1.png)

Figure 226 Large area combined X-ray maps (Zr in green, Al in red and U in blue) on the highest BU sample (5.2x10^{21} f/cc) of fuel plate U7MD1231. The interaction between the fuel and matrix colors purple.

• the fuel particles become oval shaped: at low BU the fuel kernels are more circular while at high BU they have an oblong shape. At high BU, the fuel kernels will swell resulting from fission product accumulation and recrystallization. Considering the structure of the fuel plate (picture frame), the fuel particles will swell and deform in the direction that has the least constrains, i.e. the vertical direction when the plate is lying horizontal (Figure 227).

![](image2.png)

Figure 227 cross section of the fuel plate showing the direction of fuel kernel deformation.
This can also be quantified by calculating the shape factor: a perfect circle has a shape factor of 1 while for a line the shape factor approaches 0. As can be seen in Figure 228 the shape factor of the fuel kernels in the lower burn-up sample approaches 1 while at a high fission density they have a shape factor of ~0.5.

When comparing both plates from the SELENIUM experiment (Figure 229), it can be stated that they show a comparable evolution of their microstructure for many, but not all aspects.
At the lower BU side of the max flux plane (MFP), the coatings are still intact (except for an increase in thickness of the ZrN coating) and no visible changes to the fuel or matrix are observed except the formation of visible fission gas bubbles. At higher BU, in both plates the formation of an interaction layer is seen as well as void formation / tearing of the matrix. The most distinct difference between the meat containing ZrN coated U(Mo) and the meat with the Si coated fuel is the appearance of bubbles in-between touching fuel particles. These are totally absent in fuel plate U7MD1231 (ZrN).

5.3.1.3 Hardness measurements
Accurate Vickers hardness measurements have been performed on the fuel in both plates of the SELENIUM experiment. They are performed with identical measurement settings as for the in de E-FUTURE plate (force: 100 gF), making a comparison possible.

Plotting the U(Mo) Vickers hardness as function of the fission density, a nearly constant hardness is measured up to a FD of 3 to 3.5 $\times 10^{21}$ f/cm$^3$. Above this burn-up, a steady decrease is seen, which is probably related the increase of the porosity in the fuel caused by the recrystallization process. The grain refinement will destroy the fission gas nanobubble lattice, releasing the xenon gas (contained in overpressurized nanobubbles) to larger bubbles visible with scanning electron microscopy (Figure 225).

A more detailed description on the recrystallization is given later in this chapter.
Vickers hardness of the fuel measured in fuel plates U7MD1221 (SELENIUM), U7MD1231 (SELENIUM), U7MC4202 (E-FUTURE), U7MC6111 (E-FUTURE) and U7MC6301 (E-FUTURE).

5.3.2 Interaction layer

5.3.2.1 Fuel plate U7MD1221 (Si coated)

As already stipulated above, at locations with higher fission density the formation of interaction layers is observed (Figure 231 indicated by black arrows). To obtain information on the composition of the interaction layer and coating, EPMA has been performed. When analyzing the data, one should keep in mind that the size of the measurement volume of the probe (electron beam) is comparable to the size of the coating, which means that in many cases no absolute values can be extracted for the composition of the IL or coating.

The combined Si, Al and U X-ray maps recorded on the max BU sample near the fuel extremity (picture frame), reveal that most of the damage caused to the coatings during the plate production process (3.1.1), has disappeared. This healing effect would only be possible if the Si particles of the damaged coating were still in the proximity of the fuel. The presence of Si dust particles in the matrix (an inevitable result from the coating process 3.1.1) will also add substantially to the Si availability.
The EPMA X-ray maps show almost no growth of interaction layers (Figure 232, colored purple). However it should be noted that at this location we do not expect much IL growth since the thermo-physical conditions near the picture frame are different due to the prevailing constrains. A good indication if an IL has grown is to search for the accompanying fission gas halo (Figure 232 white arrows). For a fuel kernel lying at the interface of the meat with the cladding, an mixture of coating layer (green) and IL (purple) can be seen (Figure 232 encircled). This does indicate that the coating at this location was probably partially damaged, putting the fuel in direct contact with the matrix/cladding. Damage of coating layers and subsequent IL growth during irradiation at this location is to be expected, since the fresh fuel characterization (3.1.1) showed that the Si coating on the particles located at the meat / cladding interface has been damaged by the mechanical wear imposed during rolling of the plates (Figure 197).

The quantitative linescan over a Si coating (Figure 233) shows that indeed an intermixing of the Si coating with U(Mo) and Al happened, but no interaction between the fuel and matrix occurred. At this location, the typical fission product halo created by the sweeping IL as it grows, is absent and a more diffuse pattern for the fission products is observed.
Figure 233 Combined U (blue), Si (green), Al (red) and Xe (red), Nd (green), Ba (blue) X-ray maps with an open block arrow indicating the position of the quantitative linescan.

More extensive growth of an interaction layer is seen on the same sample but at a location more towards the center of the fuel plate (Figure 234). It is however interesting to see that most IL’s are still covered with a Si coating (fine green line covering the purple layer). This could not be distinguished in the SE images (Figure 231) due to lack of contrast between the Si coating and the Al matrix but it can be measured in the quantitative linescan over an interaction layer (Figure 235). From the analysis of several linescans the composition of the IL can be identified as an U(Mo)Al₃. It is clearly seen (Figure 235) that the IL does not contain silicon.

By the snowplowing effect the growth of the interaction layer has created a fission product halo. As the halo is located at the interface between coating layer (covering the IL) and matrix, this may be an indication that the IL must have started to form already early in the irradiation experiment.
Figure 234 Collage of combined X-ray maps recorded on sample U7MD1221 M1A (5.2 ×10^{21} f/cm^3)(top Si = green, Al = red and U = blue Bottom : Xe = red, Nd = green and Ba = blue).

Figure 235 Combined U (blue), Si (green), Al (red) and Xe (red), Nd (green), Ba (blue) X-ray maps with an open block arrow indicating the position of the quantitative linescan.
5.3.2.2 Fuel plate U7MD1231 (ZrN coated)

Figure 236 Different types of layers surrounding the fuel kernels in fuel plate U7MD1231 sample M10A (a) double coating layer (b) IL formation at crack (c) IL formation under coating layer through a crack located in another plane

Higher magnification SE images of the layers surrounding the irradiated fuel kernels in fuel plate U7MD1231, show three types of layers:

- Figure 236 a: double coating layer (most common).
- Figure 236 b: interaction layer ‘bursting’ through the coating layer.
- Figure 236 c: interaction layer inside the fuel kernel covered by an intact coating layer (only at highest burn-up positions).

For the double coating layer, the layer closest to the fuel could be the original ZrN coating while the outer layer could be a mixture of ZrN and Al induced by fission fragment intermixing. In Figure 236 b and c the growth of an U(Mo)-Al interaction layer is seen. It appears that the cracks in the ZrN coating observed in the fresh fuel examinations (3.1.2) form pathways for the Al to penetrate the kernel and interact with the fuel. However in Figure 236 c the coating layer is still intact which could point to healing of the cracks. Figure 236 b gives an indication for fuel swelling pressing the formed interaction layer through the coating layer (note the curled up coating layer at the edges of the IL). As seen in chapter 3, accelerated fuel swelling occurs when recrystallization takes place. As this occurs at very high burn-up it can again be derived that formation of the IL’s already happens very early in the irradiation experiment.

The combined U, Al and Zr X-ray distribution maps (Figure 237) clearly show that even at the highest burn-up position, the ZrN coating is still intact for most U(Mo) kernels. The linescan over two touching fuel kernels confirms the presence of Zr in the coating (N is very hard to map or quantify with EPMA especially with a high radiation background present) but also some Al can be measured (Figure 238).
Figure 237 Collage of combined X-ray maps recorded on sample U7MD1231 M10A \((5.2 \times 10^{21} \text{ f/cm}^2)\) (top: Zr = green, Al = red and U = blue Bottom: Xe = red, Nd = green and Ba = blue).

It is not completely clear if the Al is incorporated in the coatings or if some Al matrix was squeezed in-between the layers. However the fission products are clearly contained within the coatings.
The linescans as well as the X-ray mappings (Figure 239) show (similar to the Si coatings) that the formed interaction layers are still covered with a ZrN coating. A substantial amount of Al (~45 wt%) is measured in the (thin) ZrN coating layer, but this might well be related to the size of the measuring volume which is comparable to the coating thickness. Hence a large contribution from the matrix can be expected. The composition of the interaction layer varies between U(Mo)Al$_3$ (fuel side) to U(Mo)Al$_4$ (coating/matrix side).
5.3.3 Fission products

5.3.3.1 Fuel plate U7MD1221 (Si coated)

Figure 240 U, Mo, Al, Si, XE, Nd, Zr and Ba X-ray distribution maps recorded with EPMA on sample U7MD1221 M1A (5.2 ×10^{21} f/cm^3).

Figure 240 shows the X-ray distribution maps of several elements covering fuel particles that have received the highest burn-up (5.2 ×10^{21} f/cm^3). The central fuel particle shows at one side the interaction of Si with uranium (Figure 240 a), while on the rest of the surface an interaction between Al and U occurred (Figure 240 b). The complete kernel (including the IL) is still covered with the Si coating.

For the measured fission products following observations can be made:

- Xenon: inside the fuel kernel no Xe filled patches are observed but numerous microsized bubbles are present. This indicates that the Xe nanobubble lattice has been destroyed during grain refinement. At the interface of the fuel and the IL, larger Xe bubbles are recorded (Figure 240 c). Located in-between touching particles are several large fission gas bubbles (which were opened during sample preparation).
- Neodymium: the Nd X-ray map has a speckled appearance inside the fuel kernel meaning that Nd is no longer in solid solution but has precipitated (as a consequence of recrystallization).
- Zirconium: The X-ray map shows a homogenous distribution of Zr inside the fuel kernel meaning that Zr remains in solid solution even at this high BU (as expected).
- Barium: similar to Nd, the Ba X-ray map covering the fuel particles is speckled meaning that also this fission product has precipitated out.
At those location where an interaction layer has grown the fission product halo can be seen (Figure 240d).

As can be seen in Figure 241, the distribution of Xe is quite different in the E-FUTURE plates where numerous large Xe filled bubbles have formed at the interface of the IL and matrix. Those crescent shaped bubbles in combination with the fission product halo (both resulting from a growing IL) are the underlying cause of the fuel core structure weakening resulting in pillowing of the plate. The Xe large area map recorded on the SELENIUM plate shows a more diffuse distribution of the fission products. The absence of large amounts of crescent shaped bubbles and FP halo’s is consistent with the observation of only little IL growth.

5.3.3.2 Fuel plate U7MD1231 (ZrN coated)

The fission product behavior in function of the fission density is best seen from the X-ray mappings recorded on a low (Figure 242) and on a high BU sample (Figure 243).

The Xe X-ray map of the low BU samples (Figure 242) clearly show the Xe patches (representing the nanobubble lattices) inside the fuel kernel. The formation of such a lattice inside the U(Mo) cells is seen from the good correlation between the Mo and Xe X-ray map. The homogenous distribution of the other fission products (Nd, Ru and Ba) indicates that they are still in solid solution at this burn-up, at least within the resolution of the EPMA.

Since no IL formation is observed at this burn-up, no fission product halo’s have been formed.
At high fission density, precipitation of Xe, Nd and Ba is measured (at least this appears so at the resolution of the EPMA) while Ru remains in solid solution.

High resolution X-ray mappings (Figure 244) of several fission products (Ba, Nd, Y, Ru, and Ce) confirm that some elements stayed in solid solution (Ru) while all others had precipitated (Ba, Nd, Y and Ce).
Overlaying the X-ray maps of the precipitates with the combined U, Mo X-ray map (Figure 244) shows that the large Ba precipitates can be found mostly on the cell boundaries and near the ZrN coating. In addition, the Y particles are found on the cell boundaries but there is no correlation with the Ba precipitates (Figure 245).

Nd and Ce seem to precipitate near the cell boundaries but in the U(Mo) cells (Figure 244) and a good correlation between the two fission products is measured (Figure 245).

High resolution X-ray mappings at lower burn-up ($3.7 \times 10^{21}$ f/cc) show no sign of solid fission product precipitation. Either the particles are too small to observe with microscopy at that point or they have not yet precipitated and are still contained within the fuel lattice. In that case, the appearance of the solid fission product particles at a fission density of $4.5 \times 10^{21}$ f/cc could indicate that at this burn-up a second recrystallization occurs but it is also possible that the precipitates form after the first recrystallization (which starts at $3 \times 10^{21}$ f/cc) and have grown sufficiently to become visible in the EPMA.
5.3.4 Swelling

Similar as was done for the E-FUTURE plates (chapter 6), the meat thicknesses measured at several locations on each sample is plotted as function of the burn-up (Figure 246). A steady increase in the meat thickness is seen in both plates and when comparing correlates well with the meat swelling of the E-FUTURE plates, this is remarkable for fuel plate U7MD1231 as it contains no Si. This observation indicates that the meat swelling is unrelated to the Si or to the IL formation.

From the SEM images the volume fraction occupied by the different phases in the meat (matrix, IL and fuel) is measured as well as the meat thickness. These two values allow us to evaluate the change in volume of the different phases in function of the fission density. The graph in Figure 247 shows that for both plates up to a burn-up of $4.5 \times 10^{21}$ f/cc there is no formation of an interaction layer and even the volume of the fuel and matrix does not seem
to deviate that much from the initial value. Above 4.5x10^{21} f/cc both plates show a steep increase in the IL volume but also a simultaneous decrease of the matrix volume.

However, the swelling curve obtained with NDT shows for both plates an almost linear increase in the fission density domain between 2x10^{21} f/cc and 4.5x10^{21} f/cc (Figure 212). Since no IL has formed in this burn-up area, the observed swelling is thus the result of a volume increase of the fuel and/or the matrix. The microstructure does not give any indication that there has been a swelling of the matrix and current understanding would also not predict matrix swelling, therefore it is believed that the only contribution to the overall swelling is resulting from the fuel.

As seen in chapter 3 and also calculated in chapter 6 for the E-FUTURE plates, if we assume that the measured volume fraction of the IL consist of a proportional volume U(Mo) and volume Al (assuming 80% Al and 20 % UMo corresponding to a (U,Mo)Al₃ layer), the fuel and matrix swelling can be calculated.

![Figure 248 Swelling of the fuel and matrix as obtained by microstructural analysis compared to the swelling measured with non-destructive analysis.](image)

With this assumption it is seen in Figure 248 that the swelling measured with NDT can be linked solely to the swelling of the fuel as no increase in volume of the matrix is measured and calculated. The slight increase of the matrix volume above 4.5x10^{21} f/cc in fuel plate U7MD1231 should be correlated to the tearing of the matrix (as seen in Figure 225). The image processing software used to obtain the volume fraction from the SEM images will automatically assign the tears to the matrix.
5.3.5 Recrystallization

![Figure 249](image1.png)

Figure 249 Evolution of the fuel microstructure in fuel plate U7MD1221 (Si) with increasing burn-up.

The sequence of the recrystallization process as observed in the IRIS-3, IRIS-TUM and E-FUTURE irradiation experiment can also be found in the SELENIUM plates (Figure 249, Figure 250). At low BU (~3x10^{21} f/cc) recrystallization has started at the cell boundaries that are low in Mo content.

![Figure 250](image2.png)

Figure 250 Evolution of the fuel microstructure in fuel plate U7MD1231 (ZrN) with increasing burn-up.

The delineation of the cell boundaries in Figure 251 is indicative for the ‘recrystallization front’ that will expand into the cell with increasing burn-up. Inside the U(Mo) cells, the grain refinement will gradually destroy the nanobubble lattices releasing the overpressurized fission gas and creating large intragranular bubbles (Figure 249, Figure 250 between 3 and 4.5x10^{21} f/cc).
At high BU, the recrystallization of the whole fuel kernel is complete (around $4.5 \times 10^{21} \text{ f/cc}$). The irradiation enhanced diffusion length for the newly generated fission gas is smaller than the size of the new grains. As a consequence, the fission gas will go directly to the large bubbles resulting from recrystallization (Figure 251). Since the recrystallization started at the cell boundaries, the growth of the fission gas bubbles will be observed there first, giving a bimodal distribution of the bubble size.

Figure 251 Grain refinement start at the cell boundaries at a burn-up of $\sim 3 \times 10^{21} \text{ f/cc}$ and proceeds into the U(Mo) cells until it is completely recrystallised (around $4.5 \times 10^{21} \text{ f/cc}$).

6 Conclusion

The SELENIUM irradiation experiment tested the applicability of coatings on U(Mo) powder to prevent the interaction of the fuel with the matrix. The formation of such an interaction layer can, as has been shown in previous irradiation experiments, lead to pillowing of the fuel plate.

Two fuel plates, one with 600 nm Si coating on the kernels and one with 1 µm ZrN coating, were irradiated in the BR2 reactor and examined. The fuel swelling data obtained by non-destructive testing shows a linear evolution with fission density, very comparable with the data obtained in the E-FUTURE irradiation. The linear evolution shows a slope change around $3 \times 10^{21} \text{ f/cc}$, which is linked to the onset of fuel restructuring as was observed in the microstructure.

At the high burn-up side, the evolution of the swelling shows acceleration for all E-FUTURE and SELENIUM plates at the same point and in the same way, but the pillowing observed in the E-FUTURE plates, producing plate swellings of >100%, is not observed for SELENIUM. The exact origin of the accelerated swelling in the highest burn-up/power zones of the plates is currently not firmly established. The E-FUTURE plates show a large increase in the spread of the plate swelling at points with similar burn-up, indicating the mechanical failure of the plate. For SELENIUM, such an increase of the spread is not recorded for the plate with Si coating and only a limited increase is seen for the plate with ZrN coating.
The destructive analysis clearly shows the positive effect of the coatings. No interaction of the fuel with the matrix occurs up to a fission density of $4.5 \times 10^{21} \text{ f/cc}$. The interaction layer that has formed at high BU is mostly still covered with the coating layer. This is indicative that the IL formed early life prior to the healing of the damaged coating. This healing effect for the Si coating is the result of the close proximity of the scattered coating to the U(Mo) kernel surface combined with the high affinity of Si for U and the fission fragment induced diffusion. The cracks in the ZrN coating perpendicular to the kernel surface form most probably the entrance path for Al to the fuel kernel, resulting in the formation of an IL.

Assuming that the volume increase of the IL is proportional to decrease of the fuel volume and matrix (IL grows at the expense of the fuel and matrix) and that the IL itself does not contribute to the overall swelling, it can be derived that the swelling measured with NDT is solely related to the swelling of the fuel.

Evidence of recrystallization occurring in the fuel is found in several measurements:

1. a decrease of the hardness with increasing fission density at the start of the grain refinement ($\sim 3 \times 10^{21} \text{ f/cc}$) but it should be noted that this might be an artefact from the formation of microsized fission gas bubbles.

2. release of Xe filled nanobubbles and formation of large intragranular bubbles

3. precipitation of solid fission products

The microstructure at high burn-up (above $4.5 \times 10^{21} \text{ f/cc}$) of the meat containing ZrN coated fuel particles shows tearing of the matrix and a change in shape (from circular to oblong) of the fuel particles. This indicates that the creep in the matrix cannot accommodate the swelling of the fuel. Tearing of the matrix is also seen in the meat containing the Si coated U(Mo) particles but to a much lesser extent.

This latter phenomenon combined with the precipitation of the solid fission products resulting from a second recrystallization could be the source of the accelerated swelling observed at $4.5 \times 10^{21} \text{ f/cc}$ but further analysis is required to give a conclusive answer.
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Chapter 8 Are we ready to convert?

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1 State of the art

For nearly 2 decades a worldwide effort has been done to seek an acceptable solution for replacing the high enriched fuel still used in high performance research reactors. Within Europe, the focus was set on the use of low enriched dispersion U(Mo) fuel as replacement. All the irradiation experiments performed confirm that this fuel material can indeed withstand the high irradiation conditions and shows a stable behavior over a large burn-up region. However, during irradiation of the U(Mo) dispersion fuel phenomena are occurring which lead to excessive swelling and subsequent pillowing of the fuel plate.

From the early irradiations of U(Mo) dispersion fuel in Europe (e.g. FUTURE chapter 4 Figure 252) and in the USA (e.g. RERTR-3 Figure 252), it became clear that an interaction occurs between the matrix and the fuel resulting in an interaction layer.

![Image](image_url)

Figure 252 Top: Optical micrographs of test plate R04 from the US RERTR-3 test irradiated to a fission density of $2.9 \times 10^{21}$ f/cm$^3$ (from [1]).

The U(Mo)-matrix interaction is a fission fragment induced diffusion effect making it mainly fission rate (ion-driven mobility) and temperature (thermal mobility) dependent.

The main consequence of the formation and continuous growth of the interaction layer is the snowplowing of the fission products that have been ejected out of the fuel kernel and into the matrix. This effect can be recognized in the microstructure as the halo of fission products that forms at the interface of the IL and matrix. This lead to high concentrations of fission products at the interface of the matrix with the IL, severely weakening the meat structure and possibly leading to mechanical failure when the swelling rate becomes too high.
The excessive IL formation leading to plate pillowing at low burn-up in U(Mo)-Al was first addressed by adding Si to the matrix. The limiting effect of silicon on the formation of the fuel-matrix interaction layer, is based on the higher affinity of Si for U compared to the affinity of Al for U. This means that we expect the Si in the matrix to interact (during plate production) with the U(Mo) leading to Si rich layers around the fuel kernels. It was however observed that the formation of these Si-rich preformed layers (PFLs) on the surface of the U(Mo) kernels cannot be well controlled, leaving large areas on the U(Mo) surface still exposed to a nearly pure Al matrix. Out of pile studies showed that increasing the Si amount results in thicker Si rich PFLs but not per se in a higher coverage fraction of the U(Mo) particles. It was also found that the diffusion of Si towards U(Mo) is hindered by the high loading required (8gU/cc). PIE of the irradiated E-FUTURE full size plates show that they still exhibit local unacceptable swelling and/or an almost complete consumption of the matrix as result of extensive growth of the interaction layer.

The out of pile studies also showed that the use of a heat treated Al–Si ‘alloy’ (i.e. an Al rich matrix supersaturated with silicon) instead of a mixture, allows to obtain a better spatial dispersion and finer size distribution of the Si precipitates in the matrix. Such a matrix microstructure can be expected to lead to an enhanced Si effect since the Si availability is expected to be more efficient during plate fabrication but also during irradiation by fission induced diffusion.

Figure 253 SEM image and Si X-ray map for R3R030 (US RERTR-6 experiment) where interaction layers were relatively thin. The plate consisted of U(Mo) dispersed in an 4043 Al alloy (4.8%Si) and was irradiated with a peak heat flux of 101.5 W/cm$^2$ up to an average fission density of $3.3 \times 10^{21}$ f/cm$^3$. (Figures from [2])

The low power irradiation of U(Mo) dispersed in an AlSi alloy matrix with low Si content, showed promising results (eg. IRIS-3 chap.6, RERTR-6 Figure 253).

However for both mixture and alloy matrix usage, it turns out that a continuous Si supply is needed during irradiation to keep the preformed layers stable. The fission fragment intermixing at the interface of the Si-rich layer with the matrix causes the PFL to get diluted with Al with increasing burn-up, letting the typical U-Mo-Al interdiffusion behavior eventually take over.
The usage of a high Si content alloy was not successful as the fuel plates containing such a matrix are hard to manufacture and irradiation of them led to severe deformation of the plates (E-FUTURE-II). The exact mechanism leading to the buckling is as yet not fully understood, but may be related to the creep properties of an AlSi alloy matrix with high Si content.

Another alternative to prevent the interaction between the U(Mo) fuel and matrix is to apply a diffusion barrier. From the observations made on the ZrN coated in e.g., the ZrN coated SELENIUM plate (chap.7) or Russian MIR irradiated mini rods (Figure 254), the protective potential of a diffusion barrier coating is shown to be superior to the effect of the Si in the matrix or as a coating.

Figure 254 Microstructure of as fabricated and irradiated U9wt%Mo fuel particles coated with ZrN. The results are from the irradiation of mini-rods at the MIR reactor (Russia). (Figures from [3])

The destructive analysis of the SELENIUM plates clearly shows the positive effect of the coatings. For both plates (ZrN and Si coated) no interaction of the fuel with the matrix occurs up to a high fission density (or high fission rate at beginning of life). It is believed that this is the result of one of 2 possible mechanisms:

- The cracks observed in the ZrN coating after plate production acting as entrance ports for diffusion of Al towards U(Mo) and the IL formation occurs during the high fission rate period of the irradiation (BOL). Once the IL formation is started and an initiation point is created, the barrier properties of the coating are broken and IL formation continues in those locations up to the point where the fission rate drops low enough. When the FR remains below a threshold, the coating can continue to protect the kernel and no IL formation occurs in those locations.

- The BOL fission rate is high enough to quickly deteriorate the coating properties and allow it to become transparent to Al. IL formation is started, continuing to form the EOL microstructure observed. At locations where the FR is lower, the coating retains its protective properties. This description can account for the clear difference in location of the IL between the Si bearing fuels and the ZrN coated fuel. For the latter, most of the IL is inside the coating, rather than protruding outward. Where outward IL formation is observed in the case of ZrN, this resembles IL formation due to interruptions in the coating, similar to what was seen in ion irradiation experiments of these fuels. Such outward IL formations are found more throughout the plate and
are not restricted to the high FR zone. Most likely they are the result of the initial microstructure.

No IL formation was seen in the Russian irradiations of ZrN coated fuel (Figure 254), where very high fission densities were reached, but at low fission rate throughout the irradiation.

The formation of interaction layers is only important because of their effect on the mechanical strength of the fuel plate. This is only an issue when the swelling rates become too high for the possible creep rates.

![Figure 255 Fuel swelling in function of fission density of the FUTURE U7MTBR07 plate, the IRIS-3 U7MV8011 and U7MV8021 plates, the E-FUTURE U7MC4111, U7MC4202, U7MC6111 and U7MC6301 plates and the SELENIUM U7MD1221 and U7MD1231 plates.](image)

Both the plates of the E-FUTURE and SELENIUM plates show a similar swelling behavior up to a fission density of \(~4.5\times10^{21}\) f/cm\(^3\) (Figure 255). However, the microstructure of the plates is different in this burn-up area: whereas for the E-FUTURE plate the formation of classic fuel matrix interaction layers is observed, in both SELENIUM plates those are completely absent. The observed swelling is also recognized in the DT analysis as an increase of meat thickness. Plotting the meat thickness of the E-FUTURE and SELENIUM samples, measured on the SEM images as function of the burn-up (Figure 256), the swelling of the meat with increasing fission density is observed.

![Figure 256 The thickness of the meat at different burn-up positions as measured on the SE images.](image)
Again, even with a large scatter on the data points (reflecting the inhomogeneity of the meat thickness), a good correlation is found between the plates from E-FUTURE and from SELENIUM despite the differences in microstructure (i.e. no IL has formed in the SELENIUM plates).

The fuel swelling of the plates calculated from the NDT results are based on the assumption that the interaction layer and matrix do not contribute to the overall swelling. From the SEM images, next to the meat thickness measurements, the volume fraction occupied by the different phases in the meat (matrix, IL and fuel) of all E-FUTURE and SELENIUM was measured. Assuming that the measured volume fraction of the IL consist of a proportional volume $U(Mo)$ and volume $Al$, the calculation of the fuel and matrix swelling based on DT data (volume fractions and meat thickness obtained from SEM images) should result in a fuel swelling profile similar to the one measured with NDT and no matrix swelling.

From the destructive analyses it was found that in most of the experiments, a $UAl_4$ like composition has formed from the interaction between the fuel and the matrix. Taking the atomic volumes (atomic weight over density, i.e $Al=10 \text{ mol/cm}^3$ and $U(Mo)= 12.9 \text{ mol/cm}^3$), this means that 80% of the volume from the IL originates from the matrix and 20% from the fuel. Using these assumptions, the swelling of the fuel ($FSw$) and matrix ($MSw$) can be calculated from the measured volume fractions and meat thickness relative to the initial values (Figure 257).

![Figure 257 Swelling of the fuel and matrix as obtained by microstructural analysis compared to the fuel swelling measured with non-destructive analysis for the E-FUTURE and SELENIUM plates.](image)

For the E-FUTURE and SELENIUM plates no swelling of the matrix was calculated but the fuel swelling occurring in both experiments and calculated from the DT results correlate very well with each other and the NDT measurements. These good correlations indicate that the contribution to the observed swelling solely comes from the U(Mo) fuel.

The $U(Mo)$ swelling profile measured with non-destructive analysis and confirmed by the microstructure consists of two parts (Figure 255)
low burn-up region ($< \sim 3 \times 10^{21} \text{ f/cm}^3$) : This domain is characterized as linear solid state swelling by accumulation of fission products. Van den Berghe et al [4] and later Gan et al [5] found that the fission gas created during irradiation has enough (thermal) mobility to arrange into an ordered nanobubbles lattice (Figure 258) and can be treated as part of the solid state swelling.

![Figure 258 TEM images showing the superlattice of fission gas bubbles observed in a U–7Mo particle of bcc structure orientated at zone [0 1 1]. The selected-area diffraction (SAD) patterns showing rings due to oxides formed at the U–7Mo fuel particle from sample preparation. An enlarged view of the SAD pattern showing the satellite spots due to the bubble superlattice. (from [5])](image)

high burn-up region ($> \sim 3 \times 10^{21} \text{ f/cm}^3 > \sim 4.5 \times 10^{21} \text{ f/cm}^3$) : a burn-up area characterized by an accelerating quasi-linear swelling behavior related to fuel restructuring or recrystallization. Around $\sim 4.5 \times 10^{21} \text{ f/cm}^3$ a more exponential growth in the swelling profile is observed. It is as yet not clear to what it is related but the microstructure show that at this fission density the recrystallization of the fuel is complete and the formation of larger solid fission precipitates is seen.

From the microstructure observation, fuel grain refinement seems to play an important part in the fuel swelling over a large burn-up area. In general, recrystallization starts at the grain boundaries which coincide for U(Mo) fuel (having an inhomogeneous cored structure) with the cells boundaries which are characterized by their lower Mo content (Figure 259a).
With increasing fission density the recrystallization will progress inwards to the cell center. The threshold for recrystallization is thus defined by the Mo content, with earlier and faster recrystallization for lower Mo content. Recrystallization of the complete fuel kernels is seen around a fission density of \( \sim 4.5 \times 10^{21} \text{ f/cm}^3 \) (Figure 259b).

Recrystallization leads to acceleration of the swelling, as the bubbles that result from it, form effective sinks for the fission gas generated in the recrystallized parts of the kernels. Since the local grain sizes (order of few hundred nm) in the fuel after recrystallization are of the same order as the athermal diffusion length of the fission products, the fission gases can now directly reach the gas bubbles. The gas atoms occupy a larger volume when in a bubble then when in solid solution or nanobubbles. As the kernel gradually evolves to complete recrystallization the swelling rate increases accordingly. In principle this swelling rate is non-linear but the first part of curve \( \sim 3 \times 10^{21} \text{ f/cm}^3 > \text{FD} < \sim 4.5 \times 10^{21} \text{ f/cm}^3 \) can be approximated by a linear law. The swelling in the low and high burn-up domain can therefore be fitted with two linear expressions:

\[
\text{low burn-up: } \text{FD} < \sim 3 \times 10^{21} \text{ f/cm}^3:\nF_{\text{Sw}}(\%) = 5.2 \times \text{FD} - 0.1 \quad \text{Eq. 45}
\]

\[
\text{high burn-up: } \sim 3 \times 10^{21} \text{ f/cm}^3 > \text{FD} < \sim 4.5 \times 10^{21} \text{ f/cm}^3:\nF_{\text{Sw}}(\%) = 6.6 \times \text{FD} - 5 \quad \text{Eq. 46}
\]

The excellent correlation with the expressions obtained by Kim et al [7] (described in chapter 3) is remarkable, as their swelling laws are based on measurements performed on monolithic fuel. Since monolithic fuel does not contain a matrix and as such no IL can be formed, this correspondence is another proof that the IL does not contribute to the overall swelling of the fuel plate.

---

Figure 259 Microstructure of the U-9.4%Mo particles in Al matrix at burn-up of (a) ~58.8% and (b) ~85% irradiated in the Russian MIR reactor. The arrows designated by letter A show the pores, arrows designated by letter B show the secondary phase precipitates. (from [6]).
In several experiments the porosity of the fuel (i.e. the precipitation of the gaseous fission products into larger bubbles) at different burn-ups was measured (Figure 260). In the Russian as well as the European experiment (both completely independent of each other) a more or less steady rise in porosity is seen between up to $\sim 4.2 \times 10^{21}$ f/cm$^3$ followed by a steep increase.

![Figure 260 Measured porosity of the fuel plotted in function of the fission density. (a) U9.4%Mo fuel irradiated in the Russian MIR reactor (as full size (IRT-U)and mini-rod) (extracted from [6]) (b) U7Mo from the IRIS-3, E-FUTURE and SELENIUM experiment.

Both dataset can be fitted using [6]:

$$ \frac{\Delta V}{V} = K_1 \times \frac{F}{F_c} \times \frac{1 + \left(\frac{F}{F_c}\right)^{(a+b)}}{1 + \frac{K_1}{K_2} \times \left(\frac{F}{F_c}\right)^{(a)}} $$

Eq. 47

with $F$ the fission density, $F_c$ the critical fission density (4.2), $K_1$, $K_2$, $a$, $b$ constants having a value of respectively 3.58, 12.5, 60, -0.7 [6].

The increase in porosity observed around $4.2 \times 10^{21}$ f/cm$^3$ in Figure 260 coincides with the exponential increase of the fuel swelling (Figure 255). However, the microstructure observed shows that at this fission density the recrystallization of the fuel is almost complete. To account for this further acceleration of the swelling one could postulate the solid fission products start to precipitate. Large solid fission products particles (found in SELENIUM chap.7, RERTR-7 Figure 261, MIR irradiation Figure 259b) are found at high burn-up.
Figure 261 FIB sample obtained from fuel plate R3R050 irradiated in the US RERTR-7 experiment. The accompanying fission density is $\sim 5.2 \times 10^{21}$ f/cm$^3$. (from [8]).

It is however measured and observed that for the E-FUTURE plates the fuel swelling becomes excessive indicating pillowing of the fuel plates while for the SELENIUM plates the swelling rate increases but remains acceptable.

From all the experiments performed so far it has become clear that in order to qualify and replace the HEU fuel currently still used in high power research reactors with LEU U(Mo), very distinct engineering efforts are required. The LEU U(Mo) fuel system needs to cope with high fission rate and irradiation up to high fission density. The first one requires limiting the interaction layer formation. The SELENIUM irradiation has shown that a coating protecting the fuel particles is an effective barrier again the diffusion of Al.

As the UMo swelling is strongly influenced by the recrystallization effect, the most effective engineering of the fuel system to reduce the swelling rate at high fission density will need to address the recrystallization. Grain refinement is known to be influenced by the Mo content of the fuel and its grain size. Working on these 2 parameters, but taking into account the reactor requirements, the proposed engineering consists of a homogenization of the fuel (avoiding Mo concentration gradients) with formation of the largest possible grains (delaying and reducing the rate of recrystallization). This comes down to submitting the fuel kernels to a heat treatment prior to plate production. The effect of such an anneal can be assessed by observing the results of the KOMO-5 irradiation (Figure 262), in which a heat treated fuel was included. In Figure 262, it can be seen that the recrystallized volume fraction, even at high FD, is much lower than in a fuel kernel that was not heat treated (IRIS-3,E-FUTURE,SELENIUM). This provides support that the complete recrystallization can be delayed and reduced making U(Mo) dispersion fuel useable in high power research reactors.
Limited amount of recrystallization is observed in the fuel kernels from the Korean KOMO-5 experiment, irradiated up to fission density >5x10²¹ f/cm³. Prior to the irradiation the fuel kernels had a heat treatment resulting in Mo homogenization and grain size increase.

2  Outlook

In 2013 CEA, ILL, TUM, SCK•CEN representing their current and future research reactor operators (Orphée, JHR and RHF in France, FRM II in Germany and BR2 in Belgium) and the fuel manufacturer AREVA-CERCA, have created HERACLES (High performance European Reactors Action for their Conversion into a Low Enriched Solution) and partnered with the US RERTR program. The HERACLES group aims at preparing the selection of the technical solutions based on due and justified grounds that will be chosen for the qualification of high density LEU fuel.

Currently two irradiation campaigns, designated EMPIrE and SEMPER FI, are planned. EMPIrE is a miniplate test designed for irradiation in ATR (US). The main goals of the test are:

1. Fission rate sensitivity of ZrN:
   - Irradiation of ZrN coated fuel plates with high and low fission rate to different fission densities to identify the mechanism for IL formation with ZrN coated particles (see chapter 7).
   - Confirmation of coated fuel performance in miniplate configuration and extension to higher burn-up (>6.2 x 10²¹ fissions/cm³).
2. Alternative coating processes (ALD, CVD) using prototype fabrication processes
   - Irradiation of (new) coated fuel particles under same conditions as above to allow direct comparison on engineering scale and on detailed scale.
3. First annealing
   - Test irradiation of annealed fuel particles in Al-Si matrix for direct comparison to existing data. This allows separating the effect of the annealing on the fuel swelling from the fission rate effect of the coating.

SEMPER FI is the first irradiation test of HERACLES, planned in BR2 in 2016. It is a subsize platelet test with CERCA production, based on an irradiation device called INSPIRE currently under design. The main goals for the test are:
1. Effect of annealing and importance of IL formation with reduced swelling
   - Irradiation of as-received and annealed UMo (optimized annealing parameters) in Al-Si matrix.
   - Irradiation up to different burn-up (>6.2 × 10^{21} fissions/cm^3) using different fission rates (combined influence of annealing and coating). Confirmation of absence of fuel swelling fission rate effect (for same EOL fission density)

2. ZrN with modified fuel (annealing)
   - Irradiation of ZrN coated fuel particles as-received and after annealing (optimized annealing parameters).
   - Irradiation up to different burn-up (>6.2 × 10^{21} fissions/cm^3) using different fission rates (combined influence of annealing and coating)

The PIE data from EMPIrE will not be available for feeding SEMPER FI due to the timing of the experiments, but both datasets will directly feed the definition of the full size plate testing programmed afterwards to restart the qualification process.

So are we ready to convert? Not yet, but we have made and continue to make important progress.
References

ANNEX 1 The use of ground fuel with and without Si: IRIS-TUM

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1 Introduction [1]

It can be expected that the irradiation behavior of U(Mo) fuel would not depend on the fabrication method of the powder. However, in two irradiation experiments, fuel plates consisting of ground U(Mo) powder dispersed in a pure Al matrix were successfully irradiated to higher burn-up:

- The French IRIS-1 experiment, a collective effort between AREVA subsidiaries and the Commissariat à l’Energie Atomique (CEA), contained full-size flat plates with a uranium loading of 8 g cm\(^{-3}\). The fuel particles consisted of either U7wt%Mo or U9wt%Mo powders dispersed in pure Al matrix. The plates were irradiated between 1999-2001 in the IRIS device in the OSIRIS reactor up to a peak burn-up of 67.5\% 235\(^{\text{U}}\) (5.1\times10^{21} \text{ f/cm}^3) [2].

- In 2002, the Atomic Energy of Canada Limited (AECL) fabricated and irradiated pin type mini-elements containing U7wt%Mo and U10wt%Mo fuel particles dispersed in pure aluminum, with a loading of 4.5 g U/cm\(^3\). These mini-elements were irradiated under nominal conditions in the National Research Universal (NRU) reactor. Discharge burn-ups up to 80 \% 235\(^{\text{U}}\) (6.2\times10^{21} \text{ f/cm}^3) were achieved [3].

The good results obtained from the low power IRIS-1 irradiation experiment or the high temperature pin irradiations do not warrant good behavior at more demanding reactor conditions.

In 2003, the Technische Universität München (TUM) in collaboration with CEA and AREVA-CERCA decided to pursue this direction and investigate if there was indeed a different behavior of ground U(Mo). It was also intended to incorporate the developments from the use of atomized fuel by adding Si to the Al matrix; thus testing if ground fuel with Si also resulted in more stabilized in-pile behavior.

2 Fuel plate fabrication and irradiation history

Fuel plates U8MV8002, U8MV7003, U8MV8503 and U8MV8501 are four of the six full-size, AlFeNi clad fuel plates containing ground U(Mo) powder, that were irradiated in the OSIRIS reactor [4]. The fabrication and irradiation data are summarized in Table 26. The fuel loading of plate U8MV7003 is 7.3 g U\text{tot}/cm\(^3\), while the other plates have a loading of ~8.4 g U\text{tot}/cm\(^3\). All plates have a uranium enrichment of approximately 49.5 \% 235\(^{\text{U}}\). The fuel meat consists of ground U8.1wt%Mo particles dispersed in either a pure (A5) aluminum matrix (plates U8MV8002, U8MV7003) or an Al2.1wt%Si matrix (plates U8MV8503, U8MV8501). The cladding of the fuel plates is AlFeNi alloy (1 \% Fe, 1 \% Ni and 1 \% Mg). Fuel plate U8MV7003 was loaded after the 2\(^{nd}\) irradiation cycle to replace a fuel plate that could not be reinserted due to mechanical deformation (not related to pillowing of the fuel plate I). Therefore, U8MV7003 was irradiated for fewer effective full power days (EFPD).

After five irradiation cycles, fuel plates U8MV8002 and U8MV8503 were unloaded for PIE. At the end-of-life (EOL), these plates had reached a maximum burn-up of 56.3 \% 235\(^{\text{U}}\) LEU (Low Enriched Uranium) equivalent (4.2\times10^{21} \text{ fissions/cm}^3 U(Mo)) and 57.8 \% 235\(^{\text{U}}\) LEU equivalent.
(4.4×10²¹ fissions/cm³ U(Mo)) respectively [4]. The final burn-up was determined after corrections based on the gamma spectrometry results with a 3% error margin.

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</table>

Table 26 Fabrication data and summary of the irradiation history of the IRIS-TUM fuel plates

Because none of the plates showed break-away swelling after the 5th irradiation cycle, it was decided to continue the irradiation, using plates U8MV7003 and U8MV8501. However, after the 8th irradiation cycle, the swelling was such that these plates were also unloaded and subjected to PIE. At their EOL, plates U8MV7003 and U8MV8501 reached a maximum burn-up of 66.5 % ²³⁵U LEU equivalent (5.0×10²¹ fissions/cm³ U(Mo)) and 88.3 % ²³⁵U LEU equivalent (7.2×10²¹ fissions/cm³ U(Mo)) respectively [4].

Please note that throughout this section on ground fuel, if expressed in %²³⁵U, the LEU equivalent will be used as burn-up value, although the enrichment of the plates was almost 50%.

The fuel plates under investigation have been irradiated at the outer corners of the OSIRIS reactor, facing the core sideways. As a consequence, there was a strong anisotropy in the neutron flux in the vertical as well as horizontal direction of the test plates [4]. The resulting burn-up profile of the fuel plates allows a selection and analysis of locations with fuel irradiated to different burn-up. From the gamma spectrometry measured at CEA, the burn-up profile over the fuel plates was fitted and an estimate of each of the measured positions in the PIE could be derived.
3 Fresh fuel characterization

The U(Mo) alloy is produced by arc melting. The cast coupons are heat-treated under vacuum at 900 °C for 72 h and then quenched to preserve the metastable γ-phase. Powders are produced by grinding these bulk alloys under an inert atmosphere (low oxygen content) in a glove box. The resulting powder therefore has an irregular shape and contains oxygen which is assumed to come from the extended time needed to obtain the desired particle size (Figure 263). The oxide layers seen inside the fuel kernel are referred to as oxide stringers. A UO$_x$ layer can also be observed on the outer surface of the fuel kernel, but this observation is made mostly on particles at the interface of the fuel meat and cladding. The formation of such an oxide layer is therefore attributed to the processing of the fuel plate.

![Figure 263 Al, O, U and Mo X-ray maps showing the formation of UO$_x$ layers in the fresh ground fuel kernel.](image)

4 Post-irradiation examination

4.1 Non-destructive testing

Similar to the IRIS-3 experiment, the thickness of the fuel plates$^{10}$ is measured using the in-pool bench located in one of the channels of the OSIRIS reactor. These measurements were done prior to and after each cycle.

Measurement configuration (Figure 264):

- longitudinal scans containing 250 data points measured every 2.5 mm, at Y-position 26, 0, -13, -21 and -26 mm
- transversal measurements comprising 116 data points measured every 0.5 mm, at X-position 307 mm (MFP).

![Measurement configuration](image)
The plates were irradiated at positions 11 & 17 located at the outer corners of the fuel array of OSIRIS. As a consequence a strong anisotropy in neutron flux in vertical as well as horizontal direction of the test plates was expected. This anisotropy is reflected in the plate thickness measurements at MFP (Figure 265).

A continuous increase in plate thickness after each cycle is observed except for the fuel plates having an Al-2.1 wt% Si matrix (8501 and 8503). In those latter ones, the plate thickness increase during the first 3 cycles is almost non-existent.

From Figure 265 it is also seen that the edge of the plate facing the core of the reactor displays the largest increase in plate thickness. This is also observed in the contour plot based on the longitudinal scans recorded on fuel plate U8MV8501 (Figure 266).
The fuel swelling for all fuel plates is calculated based on the corrected (for corrosion of the cladding) average plate thickness at MFP, measured after each cycle. The burn-up after each cycle is calculated and at EOL verified with gamma spectrometry.

Figure 267 Fuel swelling in function of the fission density.

For the fuel plates containing no Si (U8MV8002 and U8MV7003), the swelling curve in Figure 267 is nearly linear, with a slight acceleration around $2.5 \times 10^{21}$ fissions/cc. For fuel plates U8MV8501 and U8MV8503 which have a Al-2.1wt%Si matrix, no swelling seems to occur at low fission density (up to $1.5 \times 10^{21}$ f/cc). The delay should be attributed to the by the (fabrication) porosity in the meat, which is high in ground fuel compared to atomized fuel. For fuel plate U8MV8501 and U8MV8503 an acceleration of the swelling is seen around $\sim 2 \times 10^{21}$ f/cc and a second one around $\sim 4.6 \times 10^{21}$ f/cc.

Compared to the fuel plates containing atomized U(Mo) fuel and no Si in the matrix (FUTURE U7MTBR07 and IRIS-3 U7MV8011), the IRIS-TUM plates with ground powder dispersed in a pure Al matrix do not show breakaway swelling (Figure 268). The IRIS-TUM plates with silicon in the matrix however show an increased but linear swelling behavior compared to the IRIS-3 plate with 2.1% Si in the matrix (U7MV8021).
4.2 Destructive testing

In Figure 269, the relative positions of the samples on the fuel plates are indicated. Several locations on each of the samples have been analyzed.

The microstructure of the U(Mo) fuel was analyzed by optical microscopy (OM), scanning electron microscopy (SEM), and electronprobe microanalysis (EPMA). Sample preparation was similar to the IRIS-3 samples (chapter 6).
4.2.1 Fuel behavior

Figure 270 Collage of micrographs giving an overview of the samples from fuel plates U8MV8002 and U8MV7003. The estimated burn-up at the edges of the samples is also given.

Figure 270 and Figure 271 show collages of micrographs that provide an overview of the different fuel samples. The calculated burn-up at the extremities of these samples are also indicated. These collages give an indication of the swelling of the fuel plates, but no excessive swelling is observed. The horizontal cracks observed in some of the samples (especially in one sample from plate U8MV8002 and one from U8MV8503) are considered to be due to sample preparation.

Figure 271 Collage of micrographs giving an overview of the samples from fuel plates U8MV8503 and U8MV8501. The estimated burn-up at the edges of the samples is also given.
After irradiation, the oxide layer on the metallic fuel kernel surface and the UO\textsubscript{x} stringers inside the fuel particles are still clearly observed (Figure 272). The presence of such an oxygen layer on the fuel kernel could alter the properties of the fuel-matrix interaction layer, but does not appear to inhibit interaction layer growth.

![Figure 272 OM image of fuel particles in fuel plate U8MV8002 with no Si (left) and U8MV8503 with 2.1 wt% Si added to the matrix (right).](image1)

From the O, U and Mo X-ray maps (Figure 273), it can be seen that the oxide stringers appear depleted in Mo. At higher magnification, it can be observed that Mo is found as a metallic precipitate in these oxygen stringers. As Mo is not soluble in UO\textsubscript{x}, one can indeed expect that Mo precipitates during the oxidation of the fuel (grinding process or fuel plate processing). With the presence of Al and U in the meat, the oxygen potential will stay low enough to keep Mo in a metallic form during irradiation.

![Figure 273 Al, O, U and Mo X-ray maps showing the presence of UO\textsubscript{x} layers in the irradiated ground fuel kernels and the formation of an interaction layer between the fuel and the matrix.](image2)

In Figure 274 the measured Vickers hardness of the different phases (cladding, fuel, matrix and interaction layer) is plotted in function of the acquired burn-up. The hardness of the
cladding is fairly constant in all fuel plates, while for the matrix a slightly higher hardness is found in the fuel plates having a Al/Si matrix.

Figure 274 Vickers hardness measurements of fuel plates U8MV7003-U8MV8002 with no Si added to the matrix and fuel plates U8MV8501-U8MV8503 with an Al-2.1wt%Si matrix.

A slight decrease of the hardness of the IL with increasing BU is seen, but for the fuel this decrease is even more apparent and seems to start between 2 and 3 x 10^{21} fissions/cc. A decrease in hardness would be a typical result of grain refinement but it can also be of gas bubble formation.

4.2.2 Interaction layer

As expected, an interaction between the fuel kernels and the surrounding matrix has occurred during irradiation in all fuel plates. In Figure 275, a collage of secondary electron images of the cross sections of fuel plate U8MV8503 and U8MV8501 (both containing 2.1 wt% Si in their matrix) taken at different burn-up positions, shows the evolution of the fuel meat. It is seen that with increasing burn-up, the Al-Si matrix is consumed for the formation of the fuel-matrix interaction layer, up to the point where no more matrix is observed (Figure 275d). Also, the growth of large bubbles outside of U(Mo) and the swelling of the fuel plate are clearly illustrated.
Figure 275 Secondary electron images of the cross sections of the fuel plates U8MV8503 and U8MV8501 at a) $1.4 \times 10^{21}$, b) $3.6 \times 10^{21}$, c) $5.1 \times 10^{21}$ and d) $6.8 \times 10^{21}$ fissions/cm$^3$ burn-up.

At first glance (Figure 272) the fuel plates with and without Si added to the matrix and irradiated to the same burn-up, have similar features. It is only by measuring the thickness of the interaction layer at the various burn-up positions on all plates that a distinct difference between the plates with and without addition of Si is seen. This evolution is depicted in Figure 276.
The measured thickness of the interaction layer in the fuel plates containing an Al matrix with or without Si added to it. The scattered square points are the interaction layer thicknesses measured at the edge area. The standard deviations for the individual measuring points are around 1 µm.

Up to a fission density of $\sim 3.5 \times 10^{21}$ fissions/cm$^3$ U(Mo) ($\sim 48 \% ^{235}$U), the thicknesses of the interaction layer formed in the fuel plates with and without Si added to the matrix, are comparable. However, the thickness of the interaction layer in the plate with the matrix containing 2.1wt% Si is always smaller than the interaction layer thickness in the plate without Si for the same burn-up. An accelerated increase in the interaction layer thickness with increasing burn-up for the fuel plate without Si is observed at a lower fission density ($\sim 3.5 \times 10^{21}$ fissions/cm$^3$ U(Mo)) compared to the fuel plate containing 2.1wt% Si, where an increase is observed only above $4.5 \times 10^{21}$ fissions/cm$^3$ U(Mo).

For the fuel plate U8MV8501 with 2.1wt% Si added and irradiated to a local maximum burn-up of $7.2 \times 10^{21}$ fissions/cm$^3$ U(Mo), the thickness of the interaction layer has reached $\sim 17$ µm at the highest burn-up location. At this burn-up, the interaction layer can only grow further by consuming U(Mo), thus reducing its Al and Si concentration since the Al-Si matrix is completely consumed (Figure 275 d).

The graph in Figure 276 also shows the thicknesses of the interaction layers measured in the edge area (close to the picture frame) of the different samples. These points have not been included in the general profile as they deviate too much from the other observations. This indicates an influence of the constraints on the meat close to the edges, which lead to different local thermo-physical and hydrostatic conditions [5]. The stress caused by the framing forces at the edges of the plate result in high local pressure values inside the fuel. This has an impact on the pore formation and interaction layer thickness at high burn-up. Similar constraints appear in irradiated pin type fuel.
The difference between fuel plates with or without Si added to the matrix is also reflected in the composition of the interaction layer (measured with EPMA). As can be seen in Table 27, the composition is not strictly related to the fission density but rather correlates with the thickness of the interaction layer. As the interaction layer grows its Al concentration will increase. For fuel plate U8MV8501(Al-Si), a compositional change from (U,Mo)Al<sub>3.3</sub> (at a thickness interaction layer of ~5 µm) to (U,Mo)Al<sub>4.2</sub> (at a thickness interaction layer of ~7.5 µm) can be measured. However, when the fuel meat runs out of Al-Si matrix, the interaction layer is diluted by the U(Mo) as the growth of the interaction layer slowly continues. A decrease in the Al concentration towards (U,Mo)Al<sub>3.3</sub> (at an interaction layer thickness of ~16.5 µm) ensues. It should be noted that Si is not included in the composition, as its concentration is negligible compared to the Al concentration.

A similar relation between the interaction layer thickness and its composition can be seen in fuel plate U8MV7003(Al). Due to the absence of Si in the matrix, the fission density at which a certain interaction layer thickness is reached, and hence probably a certain composition of the interaction layer, is lower in fuel plate U8MV7003(Al) than in fuel plate U8MV8501(Al-Si). Of course, there is also an influence of the fission rate, power and temperature, since the kinetics of formation of the interaction layer also influences the composition, but because all fuel plates in the current study were irradiated under similar conditions, this should not be taken into account in the interpretation of these results.

It was observed by TEM that in fuel plates with and without Si, most of the interaction layers are completely amorphous. A dark field image and the corresponding diffraction pattern of such an area are shown in Figure 277. In the diffraction pattern, only diffuse diffraction intensity was found, which is typical for an amorphous material. In a dark field image, obtained by selecting a small section of the diffuse diffraction ring, no features can be distinguished confirming that the interaction layer is amorphous. Taking the most intense part of the diffuse ring as a measure for the nearest neighbor distance \( d_{nn} \), a value of \( d_{nn} \approx 0.24 \) nm for both samples is obtained, similar to what is found in atomized fuel (chapter 4, [6]).

<table>
<thead>
<tr>
<th>Fuel plate U8MV7003</th>
<th>Fuel plate U8MV8501 (with Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fission density ( (f/cm^3) )</td>
<td>IL thickness ( \mu m )</td>
</tr>
<tr>
<td>3.4 ×10&lt;sup&gt;21&lt;/sup&gt;</td>
<td>~8</td>
</tr>
<tr>
<td>4.7 ×10&lt;sup&gt;21&lt;/sup&gt;</td>
<td>~13</td>
</tr>
</tbody>
</table>

Table 27 Interaction layer (IL) thickness and composition at different burn-up in fuel plates U8MV7003(Al) and U8MV8501(Al-Si). Remark: the silicon concentration is negligible compared to the Al concentration and is therefore not included in the composition. The average IL thicknesses are based on 10 measurements and a standard deviation of around 1 µm is found. The given composition of the IL is based on averaging quantitative data obtained from linescans.
4.2.3 Silicon distribution

When Si is added to the Al matrix at room temperature, it will be mainly present in the form of precipitates because of its low solubility in Al. During the manufacturing of the fuel plates, some of the Si is thermally transported from the matrix to the fuel kernel surfaces \([7,8,9]\), producing pre-formed Si-rich layers around the fuel particles (Figure 278). The net transport of Si to the kernel surface is promoted by the U-Si chemical affinity and the mobility generated by the fission product displacement cascades during irradiation.

![Figure 278 Al, U and Si X-ray maps of fresh ground fuel showing the preformed Si rich layers at the fuel kernel surface.](image)

For the samples of the IRIS-TUM plates, the Si distribution maps after irradiation show an inhomogeneous distribution of silicon in the interaction layer at all locations and burn-up (Figure 279). This indicates that the consumption of the Si by the interaction phase through
the fission recoil does not assure a homogeneous distribution of the Si in the interaction layer.

![Figure 279 Backscatter electron images (left) and corresponding Si X-ray map (right), at a,b) 35\% 235\text{U} (2.5\times10^{21} \text{ f/cc}) c,d) 67\% 235\text{U} (5.0\times10^{21} \text{ f/cc}) d,e) 85\% 235\text{U} burn-up (6.7\times10^{21} \text{ f/cc}) .

Several PIE results show the disappearance of Si precipitates around fuel kernels in the recoil zone [10,7]. In out-of-pile tests, in which the mobility is generated by temperature, precipitate free zones are found in diffusion couples [11]. However, in the current study remaining Si precipitates inside the recoil zone around the kernels are still sometimes observed. From the Xe and Nd profiles in the quantitative linescan (Figure 280), the recoil zone around the fuel kernels can be marked out. In the recoil zone of one kernel (bottom left in Figure 280) no silicon is measured, while some is present in the zone of the second kernel (top right in Figure 280). Still, it should be kept in mind that the images are recorded at a ‘random’ cross section in a 3D structure.
4.2.4 Swelling

The large increase of the meat thickness with increasing burn-up as seen in Figure 275 is made quantitative by measuring the thickness at several positions and plotting them against the fission density (Figure 281).

A steady increase in the meat thickness is observed and a similar profile is obtained for the plates with and with Si added to the matrix, indicating that the formation of an IL does not contribute to the overall swelling. In further data treatment no distinction will be made between the two set of plates.

The SE images are also used to calculate the volume fraction occupied by the different phases in the meat (matrix, interaction layer and fuel) (see also chapter 4). Plotting the volume fraction in function of fission density would give a biased view as the total volume (or meat thickness) varies with the burn-up (Figure 281). However by multiplying the
measured volume fractions with the measured meat thickness the evolution of the volume of the different phases in function of the burn-up can be displayed (Figure 282).

![Figure 282 The volume evolution of the matrix, interaction layer and fuel in function of the fission density.](image)

The cross section images in Figure 275 clearly show that even at a low burn-up, most of the matrix is consumed. This is reflected in the graph (Figure 282) showing the changes in volume of the different phases. It is clear that the IL forms at the expense of the matrix, while the volume of the fuel does not deviate much from the initial value and remains nearly constant up to high burn-up.

From the NDT measurements a fuel swelling profile in function of the burn-up was calculated based on the assumption that there is no contribution from the interaction layer and matrix to the overall swelling of the fuel plate. As described in chapter 3 if the IL has no influence on the swelling that would mean that the volume fraction of the IL measured in the DT consists of a proportional volume U(Mo) and Al (80% Al and 20% UMo). Using these assumptions, the swelling of the fuel \( (FSw) \) and matrix \( (MSw) \) can be calculated from the measured volume fractions and meat thickness relative to the initial values.
However if we plot the calculated fuel and matrix swelling using the 80/20 volume ratio) in function of burn-up Figure 283, no correlation is found between the fuel swelling calculated using the DT data and the FSw based on the NDT measurements and an increasing matrix swelling is calculated. If however we would use a 60/40 volume ratio, a better correlation between the DT/NDT FSw is found and no swelling of the matrix is calculated (Figure 284).

It is not clear why a different volume ratio for the IL formed on ground U(Mo) particles should be taken. The 60/40 ratio would mean that the IL formed in ground fuel contains relatively more U that the IL formed in the atomized fuel systems. A possible explanation could be that due to the higher available fuel surface the Al matrix gets very quickly consumed by the formation of the IL. The only way those formed layers can continue to grow with increasing fission density is by dilution of the IL with U(Mo).

From Figure 284 it is seen that the fuel swelling calculated with DT correlates very well with the FSw based on NDT results. The matrix shows no swelling (as expected) but there is a large scatter which should be related to the presence of cracks in the sample which hinders the image processing.
4.2.5 Fission product

TEM was only performed on samples from the medium burn-up fuel plates U8MV8002(Al) and U8MV8503(Al-Si). The TEM examination of the fuel shows that for both samples, the U(Mo) kernels are still crystalline at a rather high burn-up of approximately 32 %\(^{235}\)U (2.3\(\times\)10\(^{21}\) f/cc). In the fuel kernels, fission gas nanobubbles were observed in out-of-focus bright field images. Areas were found in all specimens, where the bubbles align on a regular lattice (Figure 285a). The average size of the bubbles measured in the bright field image equals 2 nm and the lattice parameter is 7 nm for U8MV8002(Al). In fuel plate U8MV8503(Al-Si) the size of the nanobubbles is about 3 nm and they are separated by about 6 nm.

![Figure 285 a) Out-of-focus bright field images showing the U(Mo) grain containing a fission gas bubble lattice. b) The corresponding diffraction pattern. The inset shows an enlarged image of the transmitted beam. The small satellite spots are the result of diffraction at the bubble lattice. c) Out-of-focus bright field image of a U(Mo) grain that does not contain a regular fission gas bubble lattice. d) Diffraction pattern showing no satellite spots. The inset contains an enlarged image of the 00-2 diffraction spot.](image)

The corresponding diffraction pattern in Figure 285b gives additional information about the U(Mo) grain. The sharp, intense spots all agree with the crystal structure of U(Mo) for a grain oriented along the [1-10] axis. Apart from the intense reflection, weaker diffraction rings can be observed, which agree with an UO\(_2\) crystal structure. Due to the exposure to air during the sample preparation and handling, the uranium oxidizes and many small oxide grains are formed.

Thus, from the few superlattice diffraction spots, an estimation of the bubble lattice parameters was obtained, but too few data are available to fully characterize its structure.
Gan et al. [12] suggested that the bubble superlattice has an fcc structure oriented parallel to the U(Mo) bcc lattice. The superlattice reflections observed in the ground fuel kernels of Figure 285b are in agreement with that statement.

In the specimen from plate U8MV8002(Al) also U(Mo) grains were found which do not contain a fission gas bubble lattice (Figure 285c,d). In the specimen from plate U8MV8503(Al-Si), no such areas were observed, but one can expect that they do exist. The fact that some grains did not contain a regular lattice anymore could indicate that at a burn-up of 32 %235U (2.3×10^{21} f/cc) either the lattice cannot form due to the lattice stress or that recrystallization has already started. As TEM investigations did not reveal important concentrations of line defects, it is most probable that grain refinement starts at low burn-up in ground fuel.

This is confirmed by EPMA analysis performed at different burn-up (Figure 286). At low BU (2.3×10^{21} f/cc) only on the grain boundary recrystallization and as such the formation of larger bubbles, has occurred. This is seen in the Xe X-ray map where the grains inside the fuel kernel are delineated giving the fuel particle a speckled appearance. The linescan shows

![Images of EPMA analysis](image-url)
the typical fission product halo at the interface between the matrix and the IL. Inside the kernel, a rather constant quantity of Xe and Nd is measured, showing that the xenon is still contained within nanobubbles inside the grains.

Within increasing burn-up ($3.4 \times 10^{21}$ f/cc), a larger quantity of Xe and Nd is measured. A FP halo is still seen at the interface matrix-IL, but inside the fuel particle the amount of Xe is less than Nd. This indicates that recrystallization is occurring inside the grain and that the overpressurized Xe nanobubbles have precipitated into larger bubbles. With sample preparation these bubbles get opened and as such an apparent lower quantity of Xe is measured. With higher BU ($4.6 \times 10^{21}$ f/cc) the bubbles resulting from RC have grown as they get filled by the newly generated fission gas directly.

4.2.6 Recrystallization

![Figure 287 Evolution in microstructure of ground fuel, with increasing burn-up.](image)

That recrystallization in ground fuel starts at low burn-up is clearly seen in Figure 287. At burn-up of $1.4 \times 10^{21}$ f/cc, fission gas bubbles are already present on the grain boundaries and at a burn-up of $2.9 \times 10^{21}$ f/cc the intragranular bubbles indicate that recrystallization is already progressing in the grain. A complete restructuring of the fuel occurs (based on the images in Figure 287) between $4 \times 10^{21}$ and $5 \times 10^{21}$ f/cc. Once the diffusion length of the fission products is of the same order as the new grain sizes (few 100 nm) all newly generated gas will directly go to the bubbles resulting from recrystallization. As such above $5 \times 10^{21}$ f/cc an increase in bubble size is observed.
5 Conclusion

It is shown that ground U(Mo) fuel dispersed in an Al-2.1wt%Si matrix can be irradiated to a maximum local burn-up of 88.3 % $^{235}$U LEU equivalent ($5.9 \times 10^{21}$ f/cm$^3$ U(Mo)), with a thickness increase of the meat by 323 μm equivalent to a swelling of 66 %, but without resulting in failure of the fuel plate. It is also shown that the observed moderate, but positive effect of Si as inhibitor results from the presence of this element in the interaction layer, although the concentration is very inhomogeneous and appears to be too low to fully inhibit interaction layer growth at any point.
References

ANNEX 2 Adding more Si to the system : E-FUTURE-II

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1 Introduction

Analysis has shown that, in a matrix made of an Al and Si powder mixture, the larger Si particles will get inefficiently transported to the fuel kernels and the formation of a Si rich preformed layer (PFL) with an inhomogeneous thickness is observed. The use of a heat treated AlSi alloy instead of a mixture, allows obtaining a better spatial dispersion and finer size distribution of the Si precipitates in the matrix. Such a matrix microstructure can be expected to enhance the Si effect since the Si availability is expected to be more efficient during the fabrication but also during irradiation by fission induced diffusion. However, the mechanical properties of AlSi powders did not allow direct use of it in the fuel plate fabrication.

Ageing studies on AlSi alloys showed that annealing of the alloy at 550 °C for 30 minutes results in a soft and strain free Al rich matrix, making it easier to create a compact (one of the first steps in the production process of the fuel plate) of the mixture of pretreated AlSi matrix with U(Mo) particles. Annealing of the AlSi powders will also result in an Al matrix in which fine Si particles are homogenously dispersed. With such a microstructure, the Si atoms will get transported more efficiently to the surface of the U(Mo) particle, during the production of the fuel plate.

To see if the an increased Si content and/or a better spatial distributions of Si particles in the Al matrix leads to a better irradiation behavior, the E-FUTURE-II experiment was defined.

2 Plate production and irradiation history

The fuel plates in the E-FUTURE-II experiment consist of a dispersion of 8gU/cc atomized U-7w%Mo particles in an Al-Si (7 and 12 w% Si) matrix. The Al-Si 'alloy' matrix powder was annealed in inert atmosphere at 550 °C for 30 minutes before mixing with the U7Mo particles (see chapter 6). All plates were manufactured with an AG3NE cladding and all plates were given a heat treatment at 425°C for 2h. Plate U7MD1202 was given an additional heat treatment of 2h at 425°C (so 4h in total) Table 28.

<table>
<thead>
<tr>
<th>Plate number</th>
<th>Si content</th>
<th>Matrix type</th>
<th>Thermal Treatment</th>
<th>Cladding Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>U7MD0703</td>
<td>7%</td>
<td>'Alloy'</td>
<td>425°C - 2h</td>
<td></td>
</tr>
<tr>
<td>U7MD 1201</td>
<td></td>
<td>Mixture</td>
<td>425°C – 2h (2x)</td>
<td>AG3</td>
</tr>
<tr>
<td>U7MD 1202</td>
<td>12%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U7MD 1211</td>
<td>Mixture</td>
<td></td>
<td>425°C - 2h</td>
<td></td>
</tr>
</tbody>
</table>

Table 28 Plate production history

After the first irradiation cycle (cycle 01/2012), 2 E-FUTURE-II plates (0703 and 1201) were found to be stuck in the irradiation basket (basket designation EFT-2). The 2 plates that could be removed (1202 and 1211) were inserted in a spare basket (basket designation EFT-1) and their irradiation was continued. After the second cycle (cycle 02/2012), also these plates were found stuck in the basket. The sequence of events is schematically described in the
diagram in Figure 288. Photographs of the plates stuck in the basket under water in the BR2 pool are given in Figure 289.

Figure 288: Sequence in which all 4 E-FUTURE-II fuel plates became stuck in their irradiation baskets in 2 sequential cycles.

The baskets with the stuck plates needed to be partially dismantled in the BR2 hot cell to recover the plates. The E-FUTURE-II plates were subsequently transported from BR2 to the LHMA and subjected to non-destructive analyses.

Figure 289: Underwater photographs of (a): the 2 plates stuck in basket EFT-2 after the first irradiation cycle. The stuck plates 0703 and 1201 are on the left side of the basket in these photographs. (b): the 2 plates stuck in basket EFT-1 after the second irradiation cycle. The stuck plates 1211 and 1202 are on the right side in this photograph. The plates visible on the other side of the divider are the plates of the SELENIUM experiment [1,2]
3 Post-irradiation examination

3.1 Non-destructive analysis

The deformed plates were submitted to visual inspection, thickness and oxide thickness measurement. However, the deformation of the plates was so severe that the oxide thickness measurements were completely invalid and could not be used.

3.1.1 Visual examination

3.1.1.1 Reactor hot cell: dismantling of the E-FUTURE irradiation baskets

To recover the fuel plates, the irradiation devices EFT-2 and EFT-1 needed to be partially dismantled. Before opening the device, an observation of the plates in the device was also done in hot cell, confirming the observations under water. The photographs in Figure 290 show the photographs of the devices through the top of the device.

![Figure 290](image)

Figure 290: View through the top of the irradiation devices EFT-2 (left) and EFT-1 (right) in hot cell before the dismantling of the devices is started. Observations are comparable to the underwater observations (Figure 289)

To recover the plates, it was necessary to separate the 2 'clam-shell'-type halves of the device, effectively opening up the rig. The open basket EFT-2 is shown in Figure 291 and basket EFT-1 is shown in Figure 292. When opening basket EFT-2, both plates were stuck in one half of the basket, clearly showing their approximate configuration in pile. With the opening of basket EFT-1, one plate was stuck in each half. The extraction of the plates immediately revealed that the plates had been severely deformed, resembling a buckling of the plates under compressive forces. The most severely deformed plate is the 0703 plate. It is likely that the 0703 and 1201 plates were in contact at some time. Fission product releases were observed during cycle 01/2012 and wet sipping of the EFT-2 basket after the cycle showed one of the plates to be defective.
It is uncertain if the plate deformations happened simultaneously or if the deformation of one plate led to the deformation of another in the same channel. The divider plate, which is present in the middle of each E-FUTURE device, certainly avoided a cross-over of the influence of the deformations from a thermo-hydraulic point of view, but it is not certain that there were no neutronic effects.

Figure 292: Open EFT-1 rig where the fuel plates were stuck in the 2 halves of the device.
3.1.1.2 LHMA hot cell: individual plate inspections.

After arrival of the fuel plates in the LHMA hot cell, the plates were photographed to record their general aspect. The results are shown in Figure 293.

The following observations can be made:

- Comparing the backside of plate 1201 and the front side of plate 0703, the location where the plates were in close proximity or even in contact is clearly visible. A spot with a different coloration as the rest of the plates is visible on both plates. Also on the reverse sides of the plates, at the same location, a different color is seen, indicating that the effect of the non-optimal cooling in this location has had an effect that penetrated the plates. Probably, local temperatures have reached elevated values, causing a more pronounced oxidation in these locations, on both sides of the plates.

- The plate profiles (edge-on) were also inspected to get an idea of the extent of the deformation. Particularly plate 0703 is severely affected. The shape of the plate is indicative of buckling under compressive forces in all directions. The lower part of the plate is curved opposite to the top part, giving the plate an S-shape. When one is concave, the other is convex and vice versa. This is true in both the longitudinal and in the transversal direction.

- On the backside of plate 0703, a second smaller spot is seen at a lower position on the plate. This spot could be indicative of the close proximity or contact point of the plate to the basket structure.
• For plates 1202 and 1211, observations of the facing sides (front of 1202 and back of 1211) slight discolorations are observed at 2 locations on the plates. The discolorations are less marked than on the plates 0703 and 1201 and are not in the same locations. Plates 1202 and 1211 are generally less deformed.

• The coloration of the plates by the oxidation pattern is clearly more visible on these plates thanks to their 2 cycle irradiation. The pattern is relatively regular on plate 1211, but plate 1202 shows some disturbances of the pattern.

• On the backside of plate 1202, which faced the divider plate, discolorations are visible in approximately the same locations as on the front side. These discolorations are clearer on this side of the plate, indicating that they may have originated on this side. On the front side of plate 1211, which faced the basket, only minor discolorations are visible.

• On plate 1202, a clear blister can be observed close to the highest power location. The blister, although present on both sides of the plate, indicative of a pillowing phenomenon, is markedly larger on the front, numbered side of the plate than on the backside. The blister is not associated to the observed discolorations.

![Figure 294 Overview of front sides of plates overlaid with burn-up profiles as calculated by MCNP.](image)

On Figure 294 the photographs of the front sides of the fuel plates were overlaid with the burn-up profiles as calculated by MCNP. Of course, this overlay is only very approximate, but it gives some idea of the association of the oxide profiles with the burn-up distribution. Clearly, for the discolored areas on the different plates, there is no direct association with
the burn-up distribution. The blister on plate 1202, however, is located in the high burn-up/high power zone.

### 3.1.2 Thickness measurements

For the measurements on the E-FUTURE-II fuel plates, a measurement grid of 5×1 mm² was adopted, with measurement points every 1 mm in the longitudinal plate direction. A line scan was performed every 5 mm in the transversal plate direction.

The coordinate system adopted for the plate measurements is shown in Figure 295.

![Figure 295: Coordinate system adopted for the BONAPARTE measurement results.](image)

Due to the deformation of the plates, the plate thickness measurements are heavily disturbed by the non-perpendicularity of the probes with respect to the (deformed) surface. This can be understood by examining the diagram in Figure 296: when a plate thickness is measured at an angle, it shows an apparent thickness $t_{\text{app}}$, which is not the real thickness $t_{\text{real}}$ of the plate.

![Figure 296: Diagram showing the apparent plate thickness $t_{\text{app}}$ resulting from a measurement of a real plate thickness $t_{\text{real}}$ at an angle.](image)
This effect is further complicated by 2 additional phenomena: the lateral deformations of the plates (in the width direction) cause the plate to be lifted up by the support wheels in some locations. This causes constant changes in the reference plane of the individual (upper and lower) probes. Although this has no effect on the thickness measurements, the individual probe signals, which will be used to derive the plate shapes, are affected. The diagram in Figure 297 clarifies this further.

Figure 297: Diagram showing the change in the reference plane as the deformed plate is lifted by the support wheels on the bench. This diagram is drawn viewing the plate in the longitudinal direction.

A final effect that influences the thickness measurements is the size of the probes. The probes are fitted with a small wheel to prevent scratching the plate surfaces. The width of these wheels also affects the measured plate thickness $t_{\text{meas}}$, further increasing the measurement result with respect to $t_{\text{app}}$. The diagram in Figure 298 also clarifies this effect.

Figure 298: Diagram showing the plate thickness measured $t_{\text{meas}}$ as a result of the use of probes that have a real dimension. In the case of the BONAPARTE measurements, the probes are outfitted with small wheel.
Because of these effects that hamper the thickness measurements, the plate thicknesses need to be determined in a different way. The approach that is adopted first considers the individual surfaces of the plates (front and back surface). These surfaces are defined by a set of coordinates, namely the (X,Y,Z) triplets of the individual probe measurements of the BONAPARTE bench. For each measurement point, the X and Y coordinates are known from the position of the probes and the Z position is the individual probe position. The X and Y coordinates are approximate, since the wheels of the probe also create deviations in the positioning, as can be understood from the diagram in Figure 298. Deviations in the X,Y position are believed to be relatively small and the effect of these deviations on the conclusions should be negligible. For each position, a pair of Z coordinates is known, namely the positions of the 2 surfaces of the plate. These 2 matrices of coordinates allow us to visualize the surface shapes and the resulting plots are shown in Figure 299. It should be clearly mentioned that these surfaces are not fully representative either, due to the effect
shown in Figure 297, which continually changes the reference plane. Nevertheless, they provide an appropriate indication of the general shape of the plates.

The figures confirm the visual observation of the flaring of the plates in 2 opposite directions.

3.1.3 Plate shapes

Using the measured plate profiles (top and bottom surfaces), one can derive a comparison of the observed plate shapes with the measured shapes. One should keep in mind that, following the explanation of Figure 297, the measured shapes only approximate the actual plate shapes due to the changes in reference plane during the measurements. For plate 0703, the comparison below shows a good correspondence of the measured and observed shapes. The most prominent deformation observed visually correlates quite well with the measured deformations.

![Comparison between the measured and visual deformation of fuel plate U7MD0703.](image)

A similar conclusion can be drawn for plate 1201, which was stuck together with plate 0703.

![Comparison between the measured and visual deformation of fuel plate U7MD1201.](image)
For plates 1211 and 1202, the comparison of the shapes is not as clear, probably mainly because the deformations are less severe.

![Figure 302 Comparison between the measured and visual deformation of fuel plate U7MD1211 and U7MD1202.](image1)

The presence of the blister on plate 1202 is, however, clearly detected by the measurements. The blister is found at the maximum burn-up position, which has a local burn-up of around 50-55%.

![Figure 303 Formation of a blister on fuel plate U7MD1202.](image2)
4 Conclusions

The E-FUTURE-II experiment consisted of the irradiation of 4 UMo dispersion plates with an Al-Si matrix. 2 plates were severely deformed after 1 irradiation cycle and the 2 other plates after 2 cycles. The non-destructive analysis with the BONAPARTE measurement bench allows – to some extent – to derive the plate shapes, but the plate thicknesses are severely influenced by the non-perpendicularity of the plate surfaces with respect to the probes. The effect of the deformation outweighs the swelling profile, so it is not really possible to derive conclusions on the plate behavior. However, important plate swelling phenomena, such as the observation of a blister on plate 1202, are visible. Therefore, we can conclude that the basis for the plate deformations is most likely not related to any important swelling and has not caused such swelling to occur, perhaps with the exception of the blister on plate 1202.
References


Publication list

First author


Contributed papers


