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The effect of silicon on the interaction between metallic uranium and aluminum: A 50 year long diffusion experiment

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ABSTRACT

The core of the BR1 research reactor at SCK•CEN, Mol (Belgium) has a graphite matrix loaded with fuel rods consisting of a natural uranium slug in aluminum cladding. The BR1 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 fuel rods have been examined. Fabrication reports indicate that a so-called AlSi bonding layer and an $U(Al,Si)_3$ anti-diffusion layer on the natural uranium fuel slug were applied to limit the interaction between the uranium fuel and aluminum cladding. The microstructure of the fuel, bonding and anti-diffusion layer and cladding were analysed using optical microscopy, scanning electron microscopy and electron microprobe analysis. It was found that the AlSi bonding layer does provide a tight bond between fuel and cladding but that it is a thin USi layer that acts as effective anti-diffusion layer and not the intended $U(Al,Si)_3$ layer.

1. Introduction

The BR1 research reactor has been in operation since 1956. It 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 reactor has been operational for 3 days per week at a power of 700 kW for a maximum of 8 h 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 burnup is calculated to be only 0.07% FIMA.

The fuel rods consist of a natural uranium (enrichment 0.7% $^{235}U/U_{tot}$) cylindrical bar in aluminum cladding. At the manufacturing stage of the fuel rods, it was decided [1] to apply a so-called AlSi bonding layer and an $U(Al,Si)_3$ anti-diffusion layer on the natural uranium fuel slug. The bonding layer ensures good heat transfer and the anti-diffusion barrier limits the interaction between the uranium and the aluminum cladding. This type of interaction is likely to occur even at temperatures as low as 200 °C and is also clearly observed in modern plate-type fuel [2].

2. Fuel fabrication history

The ORNL graphite reactor X-10 [3], which is of similar design as the BR1, was powered by natural uranium fuel rods clad with aluminum and sealed with a cap (Fig. 1(a)).

The first U slugs for the ORNL 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 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 fuel-cladding interface.

Adequate bonding and reduction of the U–Al interaction were achieved by applying an aluminum–silicon layer to the fuel slug.

As shown in Fig. 2(a) and (b), dipping the heated uranium slug in a molten aluminum–silicon alloy of eutectic composition produced an adherent layer of $U(Al,Si)_3$ on the surface (henceforth referred to as anti-diffusion layer). The use of a molten aluminum–silicon alloy during the subsequent canning of the slug (Fig. 2(c)) 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 (this layer is henceforth referred to as the bonding layer). Details of this process, called flux-alpha canning process, can be found in [4] but the most important steps in the procedure are described below.

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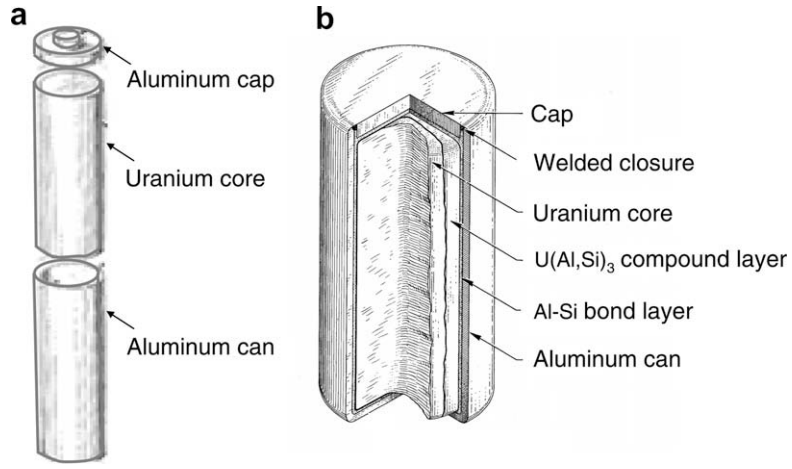

Fig. 1. (a) Exploded view of the different components used to manufacture ORNL natural uranium fuel rods; (b) schematic section of the canned fuel rod (from [3]).

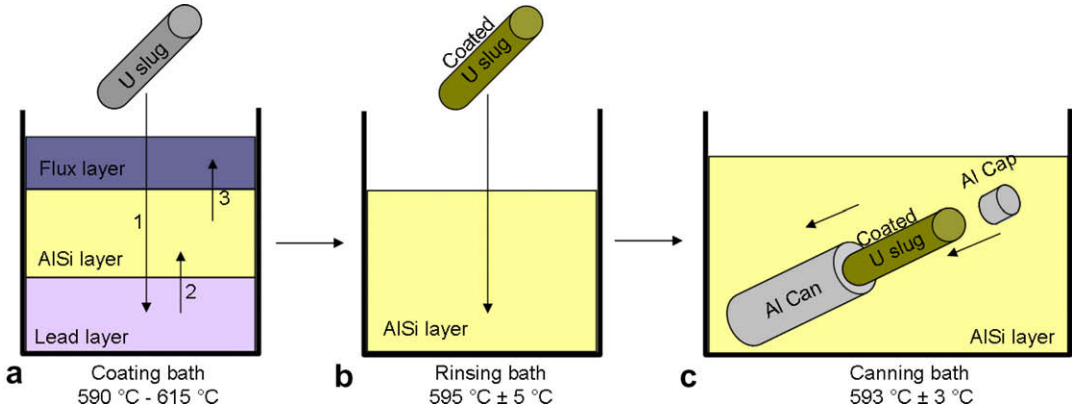

Fig. 2. Schematic overview of the flux-alpha canning process. The uranium slugs are first coated (a), then rinsed (b) and finally inserted into an Al can (c).

The Al cans were deep-drawn from commercially-pure Aluminum 2S (currently called alloy 1100) sheet stock, while the caps were machined from wrought stock free from porosity. The uranium slugs were machined from rods, degassed and heat treated to provide a randomly-oriented grain structure.

In the canning operation three molten metal baths were used (Fig. 2), 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 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.

In the second bath, consisting of Al–Si alloy (11.2–11.5 wt% Si) at a temperature of 595 ± 5 °C, the coated slugs were rinsed so the final Al–Si canning bath would not become contaminated. In the third bath, the bonding layer between the fuel rod and the aluminum can and cap was applied. The Al can was submerged and filled with Al–Si, after which the U slug was submerged and inserted into the can. Finally, the cap was submerged in the canning bath and inserted into the top of the can and pressed against the uranium slug. 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. The various features of a U slug, canned using this technique, are illustrated in Fig. 1(b).

3. Microstructure

The microstructure of an irradiated BR1 fuel rod used for over 50 years has been analysed. 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.

The top part of a fuel rod, containing the Al cap, part of the fuel slug and the Al cladding can, was cut off. A segment of the sample was embedded in an epoxy resin in such a way that a complete section of the rod (fuel, cap and cladding) could be observed. The mount was polished with SiC paper of successively finer grain size, finishing on cloth with 3 μm and 1 μm diamond paste.

The samples were analyzed using a shielded JEOL 6310 scanning electron microscope (SEM) combined with an energy dispersive X-ray system (EDX).

Electronprobe microanalysis (EPMA) was performed with a shielded CAMEBAX-R Microbeam, upgraded with digital image and X-ray acquisition hardware and software. X-ray mappings gave the lateral distribution of several elements and the elemental composition was quantified using wavelength dispersive X-ray analysis (WDX). Prior to each measurement, a calibration was performed using the appropriate standards.

The main features investigated, on both samples, are the bonding layer and the anti-diffusion layer.

3.1. Bonding layer (BL)

The backscattered-electron image of the top of the fresh fuel rod (Fig. 3(a) and (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 composition (Fig. 3(c)).

It should be noted that the observed white needle-shaped inclusions (Fig. 3(a) and (b)) are probably peeled-off flakes of the U–Al–Si anti-diffusion layer. This layer is reported to be very brittle [3]. The flakes probably peeled off during the canning process.

3.2. Anti-diffusion layer (ADL)

The detailed EDX maps of the fresh fuel (Fig. 4) 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 Si Kα map in Fig. 4, it is clearly seen that the anti-diffusion layer actually consists of two layers (the coating layer or CL and the interaction layer or IL). Such a duplex anti-diffusion layer is also observed in the irradiated fuel (Fig. 5).

Comparing the thickness of the anti-diffusion layer formed in the fresh fuel (Fig. 4) and in the irradiated fuel (Fig. 5) shows that the CL has tripled in size during irradiation, while the IL is unchanged.

The increase in the coating-layer thickness is also clearly observed in the optical micrographs taken of the fresh and irradiated fuel (Fig. 6).

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.

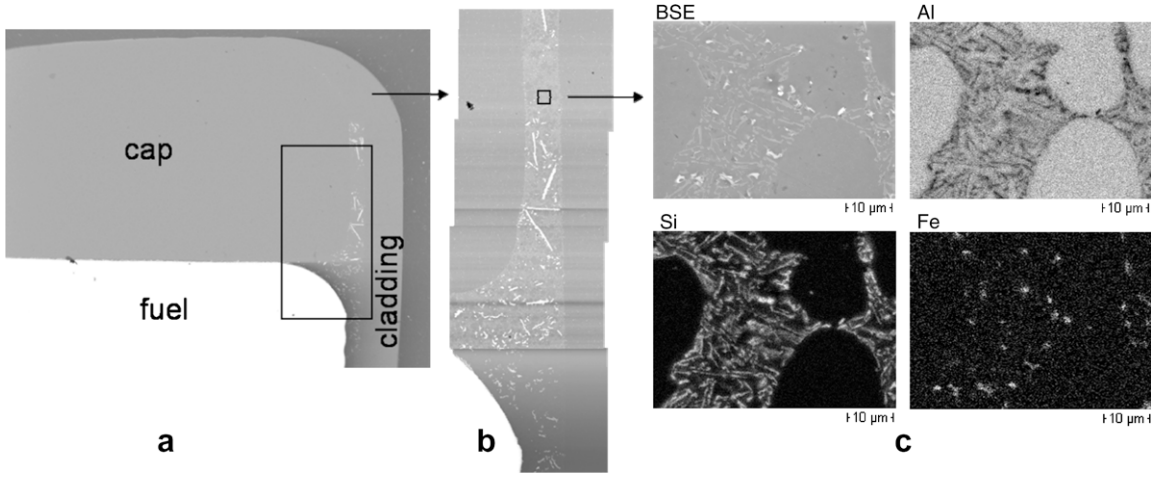

Fig. 3. Backscattered electron images of (a) the complete section of top of the fuel rod revealing, (b) the Al–Si bonding layer and (c) composition of the alloy from the X-ray maps.

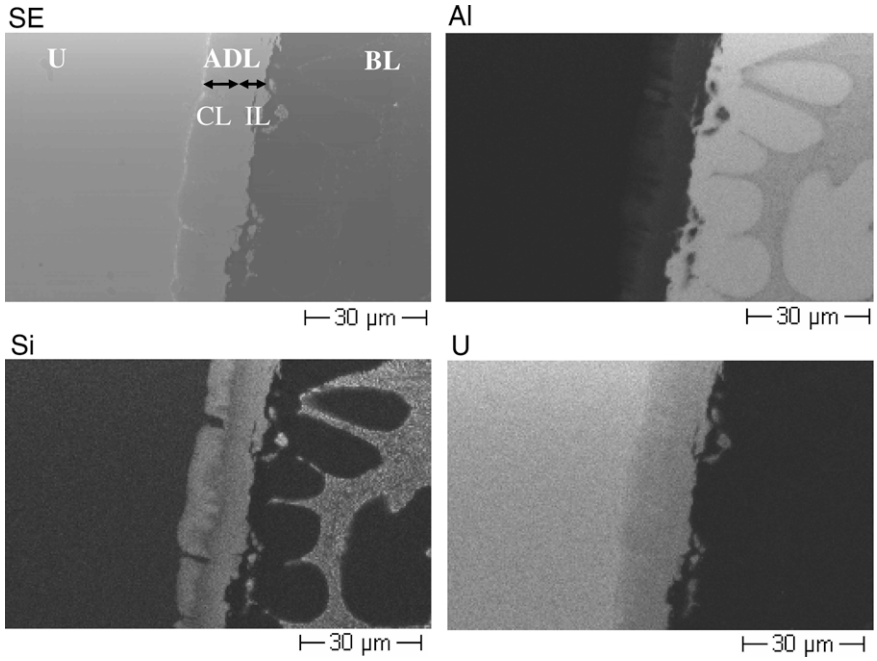

Fig. 4. SE image and Al Kα, Si Kα, and U Mα X-ray map of an area covering the uranium (U), the anti-diffusion layer (ADL) and the bonding layer (BL) of the fresh fuel rod.

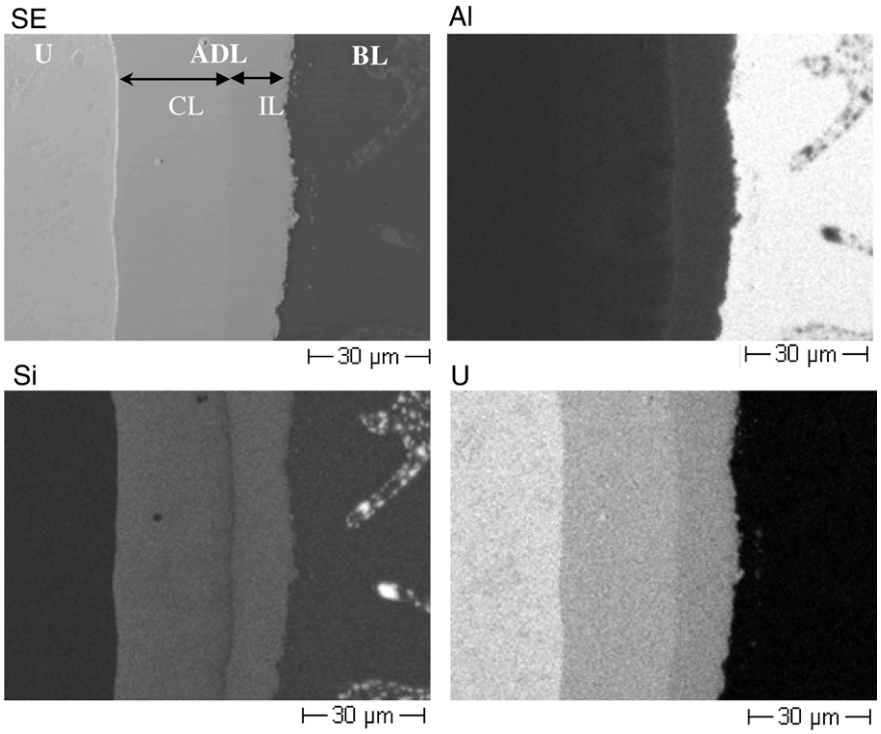

Fig. 5. SE image and Al Kα, Si Kα, and U Mα X-ray map of an area covering the uranium (U), the double anti-diffusion layer (ADL) and the bonding layer (BL) of the irradiated fuel rod.

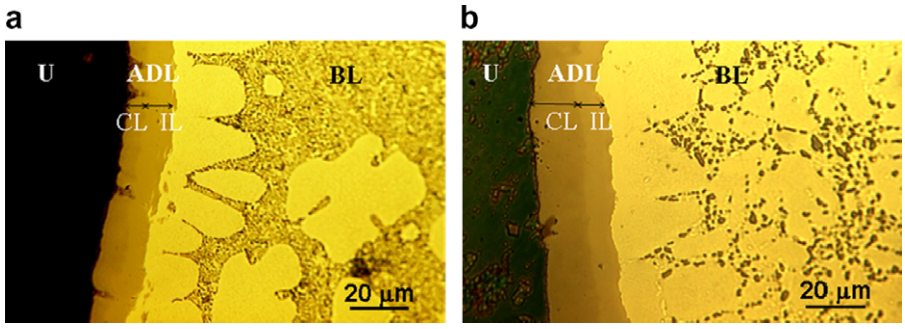

Fig. 6. Optical micrograph of the fuel (U), the double anti-diffusion layer (ADL) and the AlSi bonding layer (BL) in the fresh fuel (a) and irradiated rod (b).

4. Quantitative analysis

4.1. Fresh fuel rod

A linescan starting in the fuel slug, covering the complete anti-diffusion layer and ending in the bonding layer has been defined. The quantitative data in Fig. 7 clearly show that the ADL indeed consists of two distinct layers. The coating layer is approximately 5 μm thick and is composed of 84 wt% U, 10 wt% Si and 4 wt% Al (mean values). The interaction layer is approximately 7 μm thick and contains 76 wt% U, 11 wt% Si and 16 wt% Al (mean values).

After the double anti-diffusion layer, a nearly pure aluminum zone precedes the AlSi alloy.

4.2. Irradiated fuel rod

A similar quantitative linescan has been made on the irradiated rod. The results (Fig. 8) confirm that the width of the anti-diffusion layer has substantially increased in comparison to that in the fresh fuel.

The coating layer is approximately 21 μm thick and contains 80 wt% U, 16 wt% Si and 3 wt% Al (mean values), while the interaction layer is approximately 6 μm thick and composed of 70 wt% U, 18 wt% Si and 10 wt% Al (mean values). The anti-diffusion layer is followed by a pure Al zone and the AlSi alloy, respectively.

5. Discussion

The irradiation of a natural uranium fuel rod with an aluminum cladding for more than 50 years up to a burnup of 0.07% FIMA appears to have had no detrimental effect on the fuel or the cladding. The only difference found, is the growth of the anti-diffusion layer on the fuel slug, which was applied during fabrication.

It was expected that after the initial deposition the ADL would be a single layer. However observation of both the fresh and irradiated fuel revealed a double structure with different compositions (the CL and the IL).

The formation of a double anti-diffusion layer was also observed in an out-of-pile diffusion experiment. In an U–AlSi diffusion couple annealed at 400 °C, the diffusion zone appeared

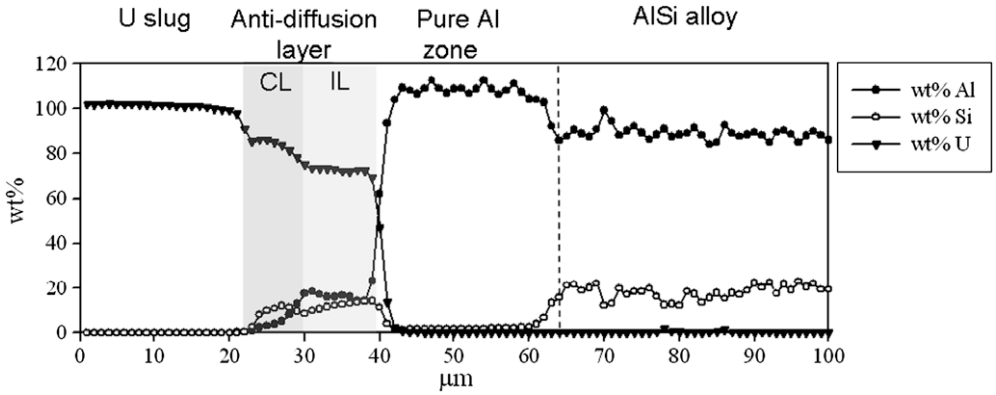

Fig. 7. Quantitative linescan over the U slug, anti-diffusion layer and bonding layer in the fresh fuel rod.

metallographically as two layers: UAl_3 (near the U interface) and USi_3 (near the AlSi interface) [5]. Based on those results, the CL was presumed to be $U(Al,Si)_3$ [3] or UAl_3 [5], while the IL was expected to be USi_3 [5]. However, these compositions do not agree with the quantification obtained by EPMA in this study.

From Fig. 7, it is seen that the CL on the fresh U slug consists mainly of silicon and uranium, the composition being close to USi (Fig. 9(a)). That the fuel slug preferentially reacts with silicon from the eutectic melt is supported by the fact that the energy of formation of all uranium silicides is larger than that of uranium aluminide [6].

The microstructure analyses further show that at the interface between the anti-diffusion layer and the bonding layer, zones of Si-free Al have formed [7]. These are probably created during the immersion in the first bath, where the preferential reaction of the U slug with the Si in the melt has locally depleted the melt and caused pure Al particles to solidify on its surface.

The formation of the interaction layer in the ADL occurs during the canning process. At this point, the surface of the coated U slug is again heated to almost 600 °C, allowing the pure Al zones to interact with the silicide CL on the slug and form the IL. At this temperature, the pure Al zones will not melt. From the measured composition, this IL can be identified as $U(Al,Si)_3$, with a Al/Si ratio of 1.3. The reaction is indicated on the ternary diagram of Fig. 10 and lies on the dotted line connecting USi and Al.

The observations of the irradiated specimen show that 50 years at moderately low temperature (~140 °C) has caused the anti-diffusion layer to grow. Quantification of the two-part ADL (Figs. 8

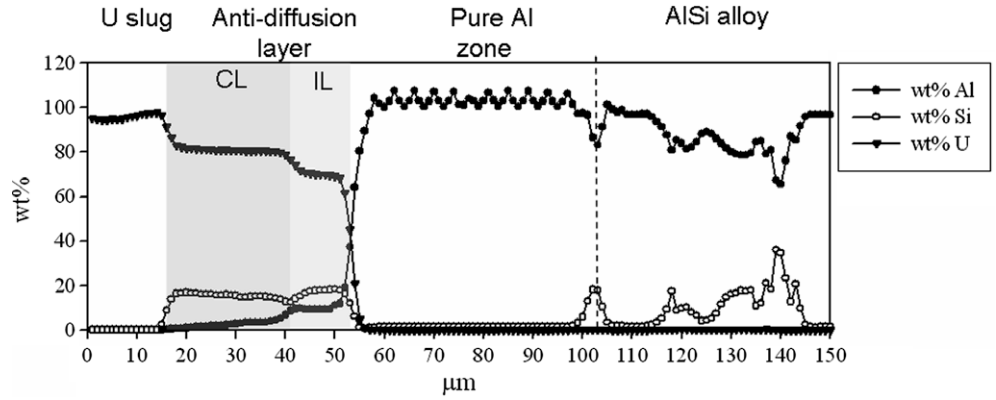

Fig. 8. Quantitative linescan over the U slug, anti-diffusion layer and bonding layer in the irradiated fuel rod.

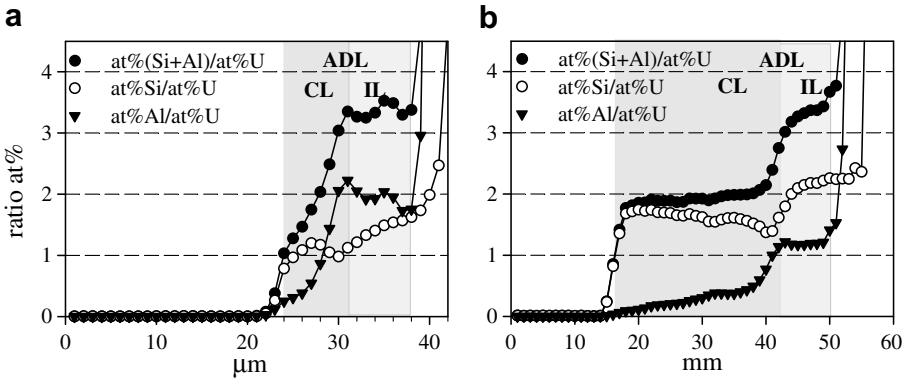

Fig. 9. The composition (at.%) of the double interaction layer observed in the fresh (a) and irradiated (b) fuel.

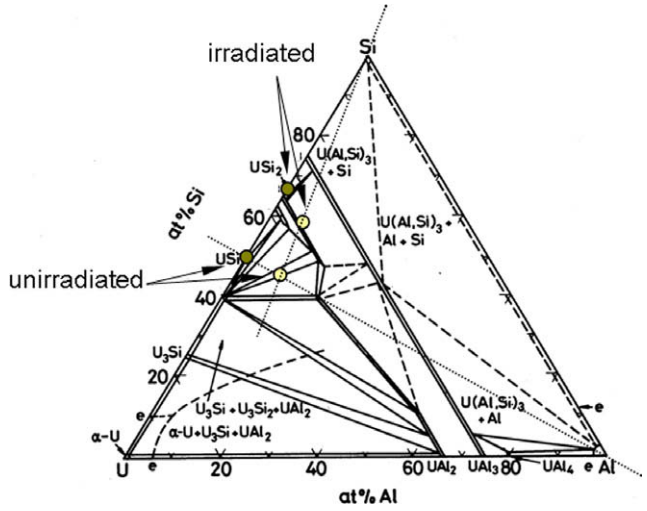

Fig. 10. Isothermal section at 400 °C of the ternary system U–Al–Si [14]. The composition of the coating layer CL (●) and the interaction layer IL (○) in the fresh and irradiated fuel rods are indicated by the dots.

and 9(b)) shows that the CL has increased in size (from ~5 μm to ~21 μm thick). This layer evolved from USi to USi_2. Again, only very small amounts of Al, increasing slightly towards the interaction layer, are found in the layer. The IL is still $U(Al,Si)_3$ but compared to the measurements on the fresh fuel rod, the Al/Si ratio has changed to 0.5. The thickness of this layer (~6 μm) is virtually unchanged during the 50 years of irradiation.

These results indicate that irradiation has caused diffusion of Si into the ADL. The proposed mechanism for the Si diffusion, and according to the binary diagram [8], is that at low temperature the CL (initially USi), reacts with the silicon of the $U(Al,Si)_3$ IL and forms an USi_2 layer. This reaction is indicated on the ternary diagram of Fig. 10 and lies on the dotted line connecting $U(Al,Si)_3$ and Si. The Si reduction in the $U(Al,Si)_3$ layer is counterbalanced by a supply of silicon coming from the AlSi bonding layer. As the latter is a rich source of free silicon, the diffusion mechanism continues. As a result, the USi_2 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 $U(Al,Si)_3$ layer to remain virtually unchanged. The Al from the $U(Al,Si)_3$ IL only partly diffuses into the CL, as can be seen in the EPMA results. On average, the composition of the $U(Al,Si)_3$ IL remains the same but the ratio Al/Si changes in favor of Si.

The unintended growth of a thin USi layer on the uranium slug during fabrication, which during irradiation evolves to USi_2, 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 $(U,Mo)Al_x$ interaction layer develops between the fuel and the aluminum matrix or cladding (monolithic fuel). This layer continues to grow during irradiation and becomes amorphous during irradiation at moderate temperature [9,10]. The $(U,Mo)Al_x$ layer is not able to retain stable bubbles of fission gas which is released to the interface of the $(U,Mo)Al_x$ layer with the aluminum matrix or cladding. Depending on the irradiation condition (power and burn-up), these gas-filled pores continue to grow, link up and finally cause unacceptable swelling of the fuel plate [2].

Based on thermodynamic and metallographic analysis, it is suggested [11] that addition of silicon to the Al matrix would inhibit the growth of the $(U,Mo)Al_x$ interaction layer. The first irradiation tests indeed show that the average plate swelling decreases with increasing Si content in the matrix [11]. The underlying mechanism responsible for this effect is not yet fully understood. However, based on the results found in the current study, it appears that creation of a thin silicide layer on the fuel particles reduces the interaction. The intentional application of such a thin silicide coating during fabrication acted as an effective aluminum diffusion barrier in the BR1 fuel.

However, it should be noted that, considering the low burnup (0.07% FIMA) of the BR1 fuel rods, hardly any fission gas has been created. The behavior of fission gas in the silicides can not be deduced from these observations, but can be from the PIE on irradiated AlFeNi clad U_3Si_2 fuel plates [12]. It was observed here that most of the fuel particles were a mixture of U_3Si_2 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 U_3Si_2 zones, the bubble diameter could be as large as a few micrometers, but fewer bubbles were found. All the observed bubbles in USi and U_3Si_2 had a nearly perfect round shape and no evidence of bubble coalescence is seen, indicating very stable fission gas behaviour. Only for the silicides with higher uranium contents (U_3Si), unstable fission gas behaviour is observed under some irradiation conditions [13].

6. Conclusion

After being irradiated for more than 50 years in the BR1 reactor, the natural-uranium aluminum-clad fuel rods are found to be in very good condition.

It is observed that the AlSi bonding layer provides a tight bond between fuel and cladding. The applied anti-diffusion layer, however, is not homogenous $U(Al,Si)_3$, as was assumed at fabrication. Dipping the uranium slug in the molten eutectic AlSi coating bath created a thin USi layer and because of local Si depletion of the bath, left pure, solidified Al zones. During the canning process, the USi layer reacted with the latter and formed a second $U(Al,Si)_3$ layer.

Irradiation at moderate temperature causes the Si to diffuse through the $U(Al,Si)_3$ interaction 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 USi_2. The source of this additional Si is identified as the AlSi bonding layer.

It is 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.

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