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Heavy ion irradiation of UMo/Al samples with protective Si and ZrN layers (SELENIUM)

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ABSTRACT

Surface engineering of UMo particles, i.e. the coating of UMo powder with diffusion limiting elements using DC magnetron sputtering, has been suggested as a remedy to excessive UMo/Al interdiffusion. Samples from full size plates produced with UMo powder coated with Si (300nm and 600nm) and ZrN have been examined before and after irradiation with Iodine at 80MeV.
In case of Si coated UMo particles, a dense Si rich layer developed around the UMo particles during plate fabrication. In contrast, the ZrN layer frequently revealed cracks.
During heavy ion irradiation, no UMo/Al interdiffusion occurred at spots that are protected by a sufficiently thick Si rich layer or a dense ZrN layer. In contrast, a conventional UMo/Al interdiffusion layer (IDL) occurred at spots where the UMo has not been protected by a Si rich layer layer or the ZrN layer was broken.

1. Introduction

It has been found that the addition of some wt% Si to the Al matrix enhances the in-pile performance of dispersion UMo/Al nuclear fuels by retarding the undesired UMo/Al interaction [1, 2, 3]. Since Si has a higher chemical affinity for U than Al [4] a silicon rich layer (SiRL) forms at the interface between the UMo and the Al already during plate production leaving a Si depleted zone around the UMo particles behind [5,6]. This SiRL retards the conventional UMo/Al interdiffusion during irradiation. However, a conventional UMo/Al interaction layer occurs as soon as the SiRL has been completely consumed [7]. Since not all the Si added to the Al matrix is used to form the protective SiRL it has been suggested to apply the silicon directly where it is needed: at the interface between the UMo and the Al, thereby maximizing the availability of Si in the interdiffusion process and minimizing the amount of Si inside the matrix to overcome reprocessing concerns [8, 9]. Another possibility to reduce the UMo/Al interaction is the application of a ZrN diffusion barrier [10].

To apply different types of coatings to UMo powder, a sputter coater has been developed by SCK•CEN in the framework of the SELENIUM project. Details on this project have been presented before in [8, 9]. It has been shown that it is possible to coat spherical UMo powder uniformly with Si or ZrN [9, 11]. For this study, UMo/Al dispersion samples prepared with the coated powder have been examined out-of-pile using heavy ion irradiation.

2. Experimental

Spherical U7wt%Mo powder provided by KAERI has been coated by SCK•CEN with ~300nm and ~600nm Si and ~1000nm ZrN using the STEPS&DRUMS sputter reactor that has been developed for this purpose. Details on the coating process and the as coated particles can be found elsewhere [8,9]. Using the coated powder, three test fuel plates have been produced by AREVA-CERCA using the conventional AREVA-CERCA rolling process. The plate temperature did not exceed 450°C during manufacturing. Pure Al has been used as matrix material. From the test fuel plates, small pieces (~1x1cm²) have been cut and the cladding has been removed on one side using abrasive paper and a cascade of diamond polishing paste (9µm - 1µm grain size) to get access to the meat layer.

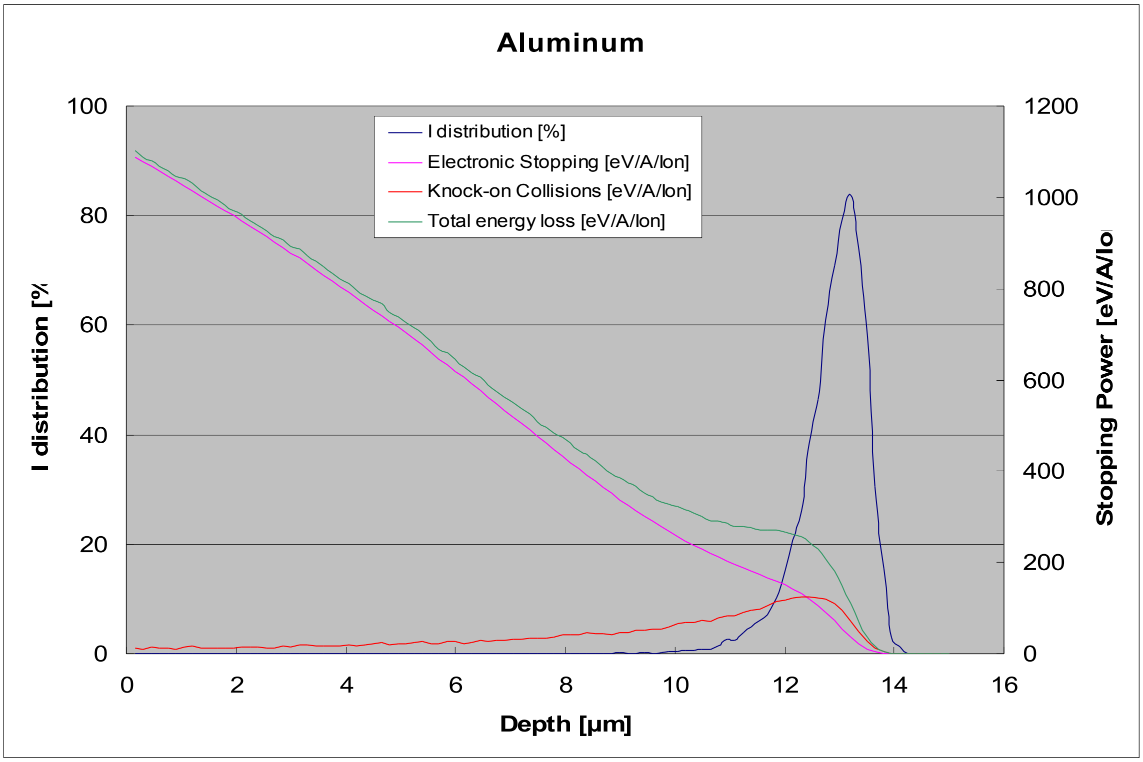
The samples have been irradiated with iodine at 80MeV perpendicular to the surface at the Maier-Leibnitz tandem accelerator in Garching, Germany, until an integral fluency of $1x10^{17}$ ions/cm² has been reached. Fig 1 shows the Ion distribution (left scale) and the energy deposition (right scale) inside Aluminum (a) and UMo (b) [12] . The total energy of the incoming ion is deposited within 14µm inside Al and 6µm within UMo. This means for a pure Al target in total $5.7x10^{21}$MeV/cm³ are deposited, for a pure UMo target $1.3x10^{22}$MeV/cm³ are deposited. Since we have a mixture of UMo and Al the true value can be found between those two extremes – assuming a mixture of 50vol% UMo and 50vol% Al at around $9.4x10^{21}$ MeV/cm³.

The current fuel element of the FRM II has a maximum burn-up of $1.98x10^{21}$ fissions/cm³ (52.6% U235 burn-up), i.e. $3.96x10^{21}$ fission products/cm³ are produced [13]. The total energy deposited by the fission products is 166MeV [14], i.e. a maximum of $3.29x10^{23}$MeV/cm³ are deposited during burn-up inside the meat.

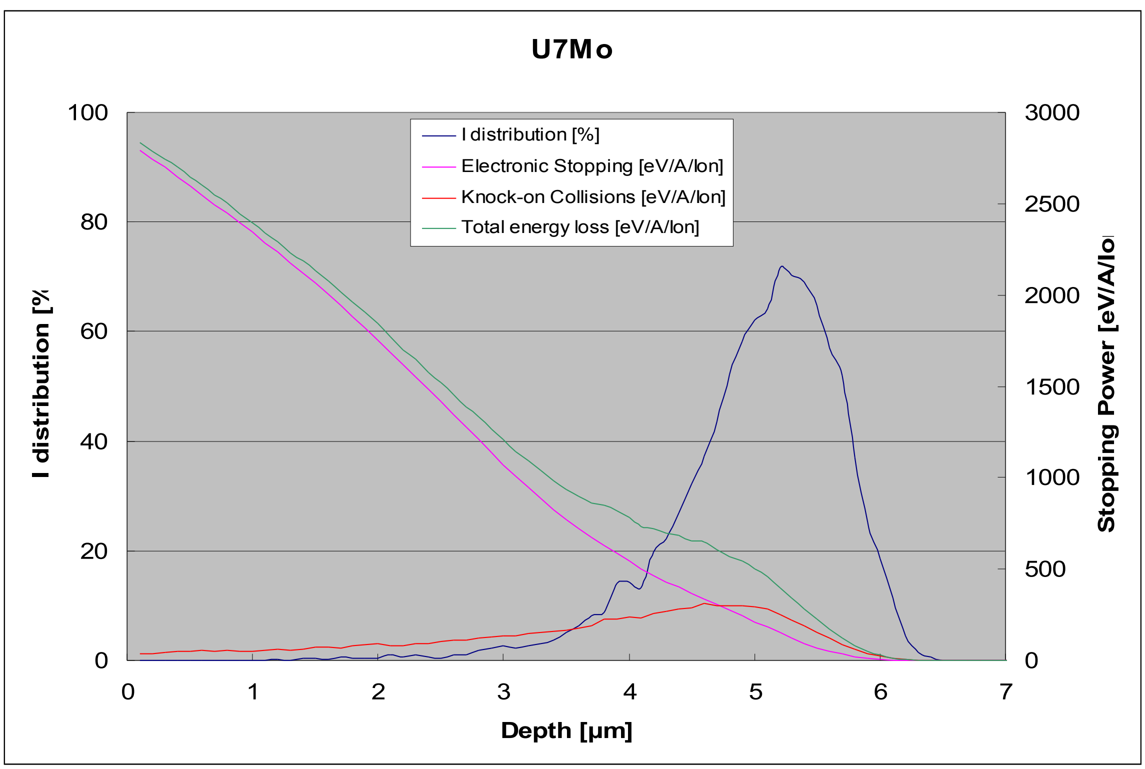
Comparing this value with the ones obtained from the energy deposition of the incoming ions, a ion fluency of $1x10^{17}$ ion/cm² corresponds to at least 2.8% of the peak burn-up of the FRM II fuel element which may be regarded as representative for a high performance research reactor.

The irradiation temperature was around 200°C (sample holder temperature ~5mm beside the irradiated area). It has been shown before that such irradiation conditions cause comparable effects to in-pile irradiation [15, 16].

After irradiation the samples were sectioned through the irradiated area. One of the pieces has been embedded into an epoxy resin and the cross section has been polished using abrasive Si-free disks and a cascade of diamond polishing paste (9 µm-1 µm). Afterwards, some atomic layers of gold have been deposited on the samples to increase the SEM/EDX contrast. SEM/EDX analyses have been carried out using a ZEISS EVO MA 25 microscope equipped with a ultra-dry silicon drift EDX detector by Thermo Fisher. Standard less EDX analysis has been used.



(a)

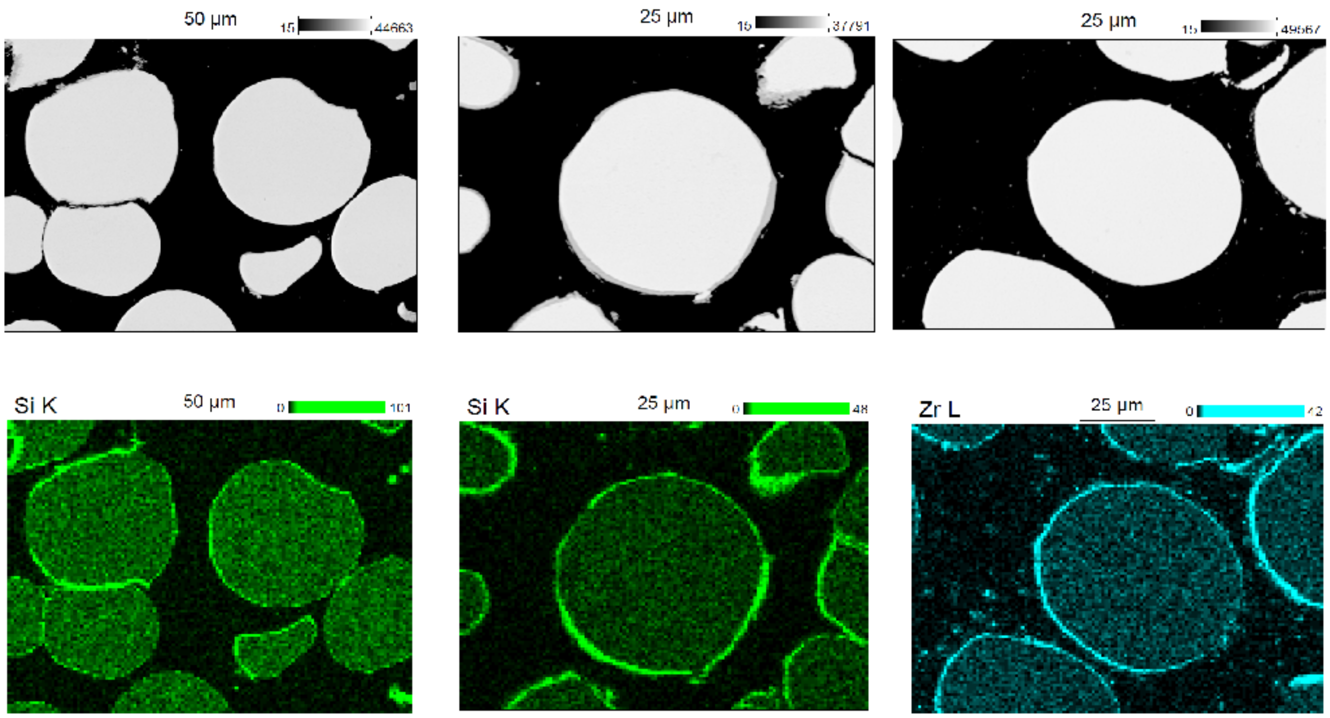


(b)

Fig 1: Ion range distribution (left scale) and energy deposition (right scale) inside (a) Al and (b) U7Mo [Fehler: Referenz nicht gefunden].

3. Results

Fig 2 shows BSE images and corresponding EDX maps of the three samples before irradiation: In the case of 300 nm Si (a) and 600 nm Si (b) deposited on the UMo a SiRL is visible around the UMo particles. The Al matrix contains only small amounts of Si precipitates. In case of 1000 nm ZrN (c) the particles are surrounded by a Zr rich layer. A huge amount of ZrN precipitates is visible inside the matrix.
The Si and ZrN precipitates were already present as dust in the coated powder since during the coating process in the STEPS&DRUMS device not only the UMo powder but also the walls of the device are coated, which may spall off during the coating process. The UMo powders are sieved after coating, but small pieces of the spalled-of layers may end up in the powders.

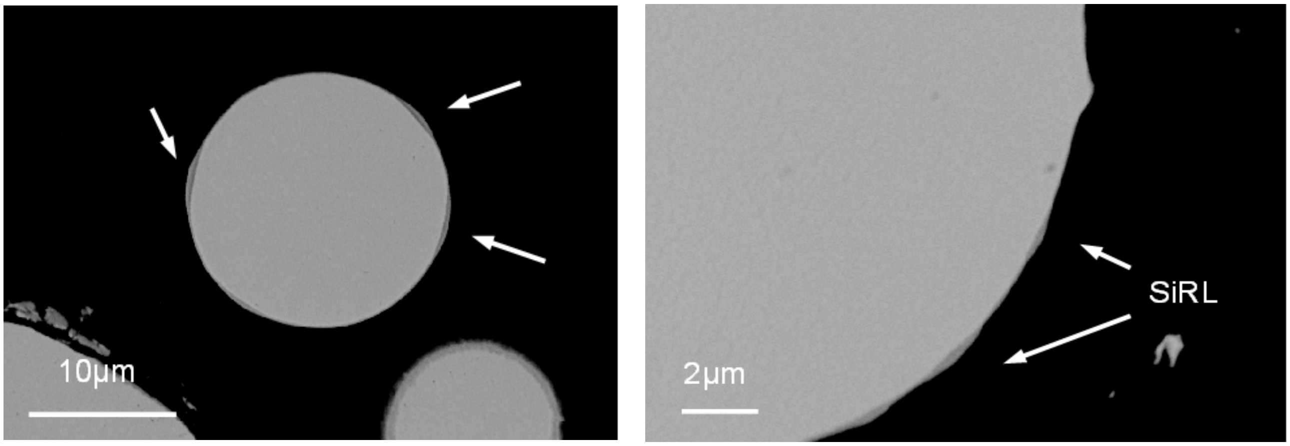


(a) 300 nm Si *(b)600 nm Si* *(c) 1000 nm ZrN*

Fig 2: BSE images and corresponding EDX maps of UMo particles dispersed inside an Al matrix before irradiation.

3.1. 300 nm Si coated UMo dispersed in Al

Fig 3 shows BSE images of the sample coated with 300nm Si before irradiation. The thin, but dense Si-layer that has been sputtered on the UMo particles (compare Fig. 3 in reference [9]) has been transformed into a SiRL which contain also some U and Al (determined by EDX analysis) beside Si. Furthermore, the Si agglomerated frequently at some spots (compare Fig 3b, white arrows). The UMo particles are therefore often not entirely protected by a SiRL. The thickness of the SiRL is in general <1µm. The Si content inside the layer is between 20at% and 30at% (EDX analysis), however with important local variations.



(a) (b)

Fig 3: Low resolution (a) and high resolution (b) BSE image of a UMo particle coated with 300 nm Si after plate production and before irradiation. White arrows indicate the position of the SiRL.

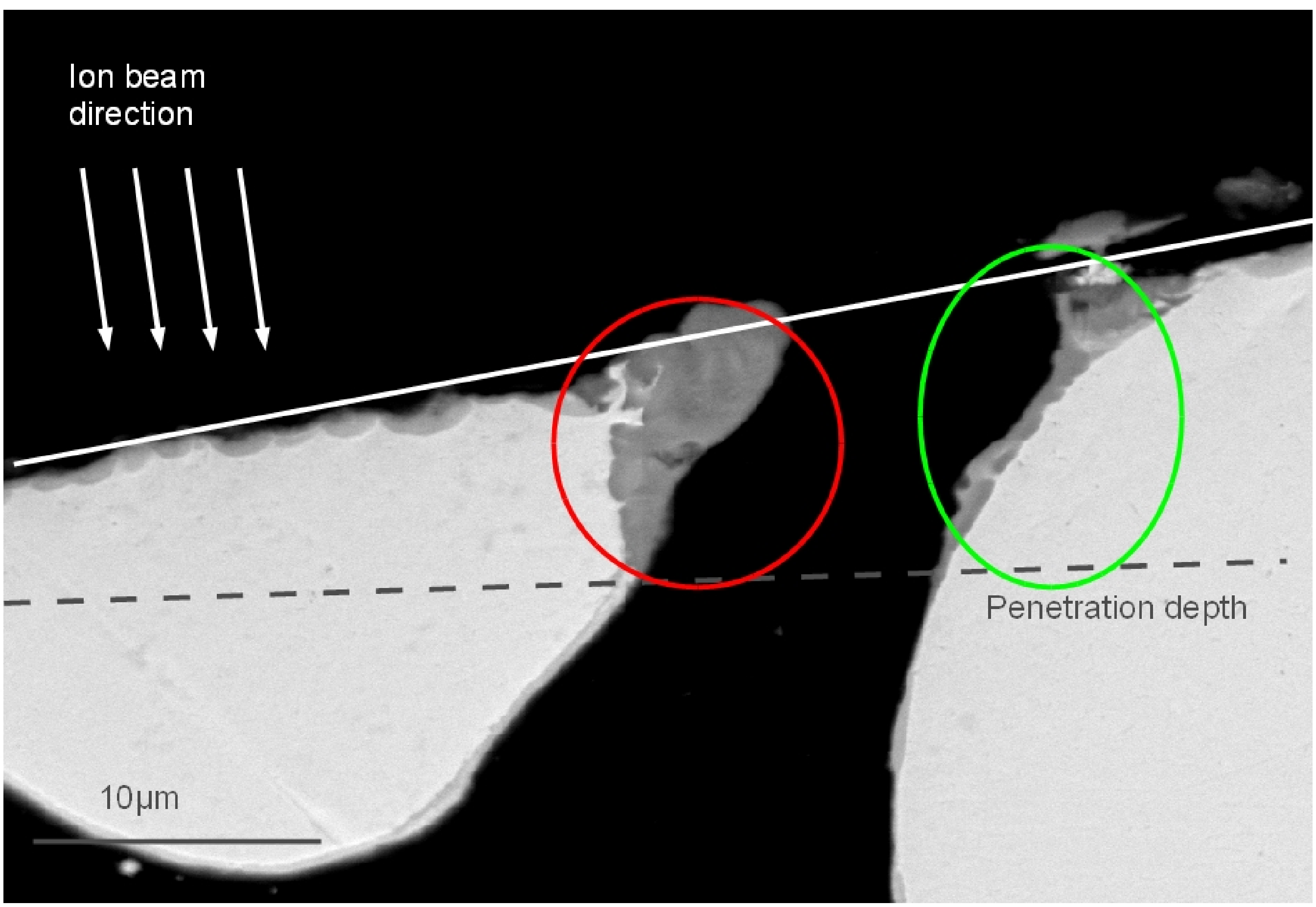


Fig 4: Cross section through the irradiated surface of the sample with 300 nm Si coating. In case of a sufficiently thick coating (green) no UMo/Al interaction occurs. Otherwise (red), a conventional IDL forms during irradiation.

Fig 4 shows a cross section through the sample after irradiation with heavy ions. In case the UMo particle was not protected by a SiRL or the SiRL was too thin a conventional UMo/Al diffusion occurred (red circle in Fig 4). In this case, no Si has been detected inside the IDL by EDX analysis.

In case the SiRL was sufficiently thick, the formation of a UMo/Al interdiffusion layer has been completely suppressed (green circle in Fig 4). Instead and in accordance with what has been observed before [7] the SiRL has been attacked by Al diffusion as can be seen from the change in gray contrast. Thereby, the Si content inside the SiRL has been decreased from 20at% to <10at%. The EDX measurement has been performed in the irradiated and non-irradiated area, respectively.

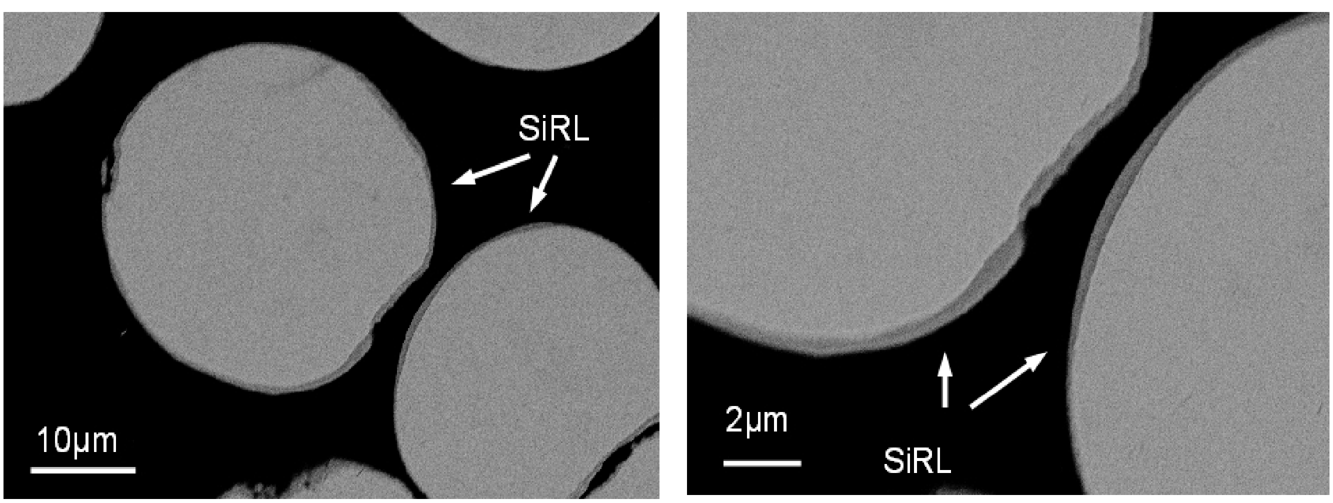
It must be pointed out that at most spots the SiRL was not sufficiently thick to prevent the formation of an IDL during sample irradiation.

3.2. 600 nm Si coated UMo dispersed in Al

Fig 5 shows a BSE image of the sample with 600 nm Si sputtered on the UMo powder before irradiation. Also here, the sputtered Si layer [9] has been transformed to a SiRL that contains U and Al beside Si. In contrast to what has been observed in the 300 nm Si case, the SiRL is present around every UMo particle at any position, i.e. almost all UMo particles are covered with a dense SiRL. The thickness is in general >1µm and reaches up to 2µm at some positions. The Si content inside the layer is ~40at% (EDX analysis).

Fig 6 shows a cross section through the sample after irradiation. Since most positions were protected by a thick and dense SiRL, no UMo/Al diffusion occurred during the irradiation. However, the SiRL is affected by Al diffusion as can be seen by the gray contrast (green dotted line in Fig 6). The Si content inside the layer is thereby reduced from ~40at% before irradiation to ~20at% after irradiation.

Only one position has been found where a UMo particle was not sufficiently protected by a SiRL. A silicon free IDL grew at this position.



(a) (b)

Fig 5: Low resolution (a) and high resolution (b) BSE image of a UMo particle coated with 600 nm Si after plate production and before irradiation. A SiRL (white arrows) is clearly visible around the UMo particles.

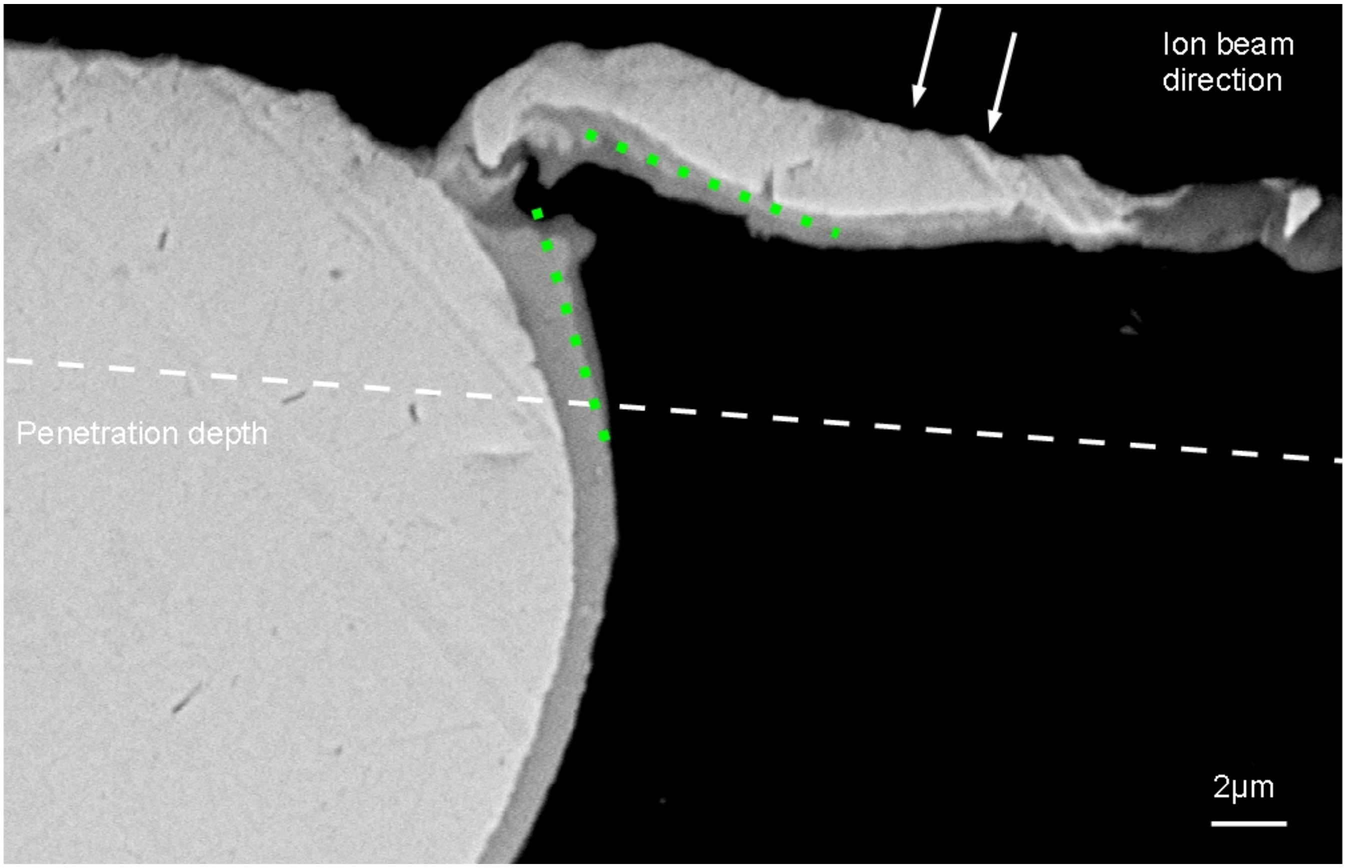


Fig 6: Cross section through the irradiated surface of the sample with 600 nm Si coating. The SiRL is in general sufficiently thick to prevent any UMo/Al interaction. However, the SiRL is attacked during irradiation by Al diffusion, which can be seen by differing gray values (green dotted line).

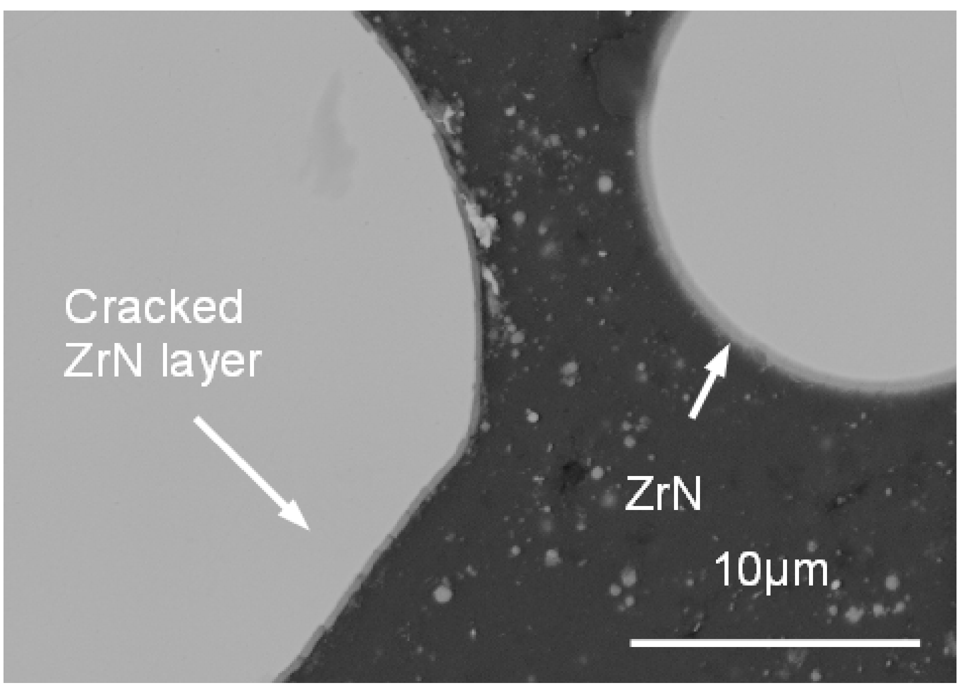


Fig 7: 1000 nm ZrN deposited on UMo particles. The ZrN layer frequently has got cracks. Considerable amounts of ZrN are dispersed inside the matrix. No reaction between the ZrN and the UMo or the Al has been observed after plate processing.

3.3. 1000 nm ZrN coated UMo dispersed in Al

Fig 7 shows un-irradiated UMo particles covered with 1000nm ZrN. The ZrN layer is present at almost every position around the UMo particles. The thickness is ~1 µm, in accordance with the production parameters. A significant amount of ZrN particles is present inside the matrix. No reaction between the ZrN and the UMo or the Al occurred during the plate production process. However, the ZrN layer frequently reveals small cracks with a diameter below ~100 nm that have not been found on the coated powder before plate processing [9]. The cracks are therefore a result of the plate production process and probably also to a certain extend due to the sample polishing procedure.

Fig 8a shows a cross section through the heavy ion irradiated sample. The UMo/Al interaction has been completely suppressed by a dense (i.e. non-cracked) ZrN layer. Furthermore, the ZrN layer is not affected by any Al or U diffusion. Fig 8b shows the case where the UMo particles have not been protected by a dense ZrN layer but where the layer was cracked. In case of cracks (red circles) a huge UMo/Al diffusion occurs that even dislocates the cracked parts of the ZrN layer. However, the ZrN layer is not affected by diffusion. In contrast, the UMo/A diffusion has been completely suppressed at positions where the ZrN layer was dense (green circles). Since the ZrN layer was cracked at most positions, Fig 8b is representative for the general behavior of the sample during ion irradiation.

4. Summary and conclusions

Samples from plates prepared with UMo powder coated with 300 nm Si, 600 nm Si and 1000 nm ZrN have been examined before and after irradiation with heavy ions.

In case of Si covered UMo, the Si layer has been transformed into a SiRL during plate processing. In case of 300 nmSi, the SiRL is rather thin (<1 µm) and not present at all positions. In case of 600 nm Si the resulting SiRL is thicker and present around the complete circumference of every UMo particle.

In case of ZrN, almost all UMo particles are covered by a ZrN layer. However, the layer usually reveals cracks that have been introduced during plate fabrication.

In case the UMo particle has been protected by a thick SiRL - what is usually the case with the 600 nm Si sample - or a dense ZrN layer, the UMo/Al diffusion has been completely suppressed. Otherwise, a huge IDL has grown during irradiation.

The samples with 600 nm Si and 1000 nm ZrN covered UMo particles showed the most promising irradiation behavior. However, the presence of cracks inside the ZrN layer is a clear drawback. It still has to be be clarified whether the cracks have been introduced during the plate fabrication or only during the sample polishing process.

Acknowledgments

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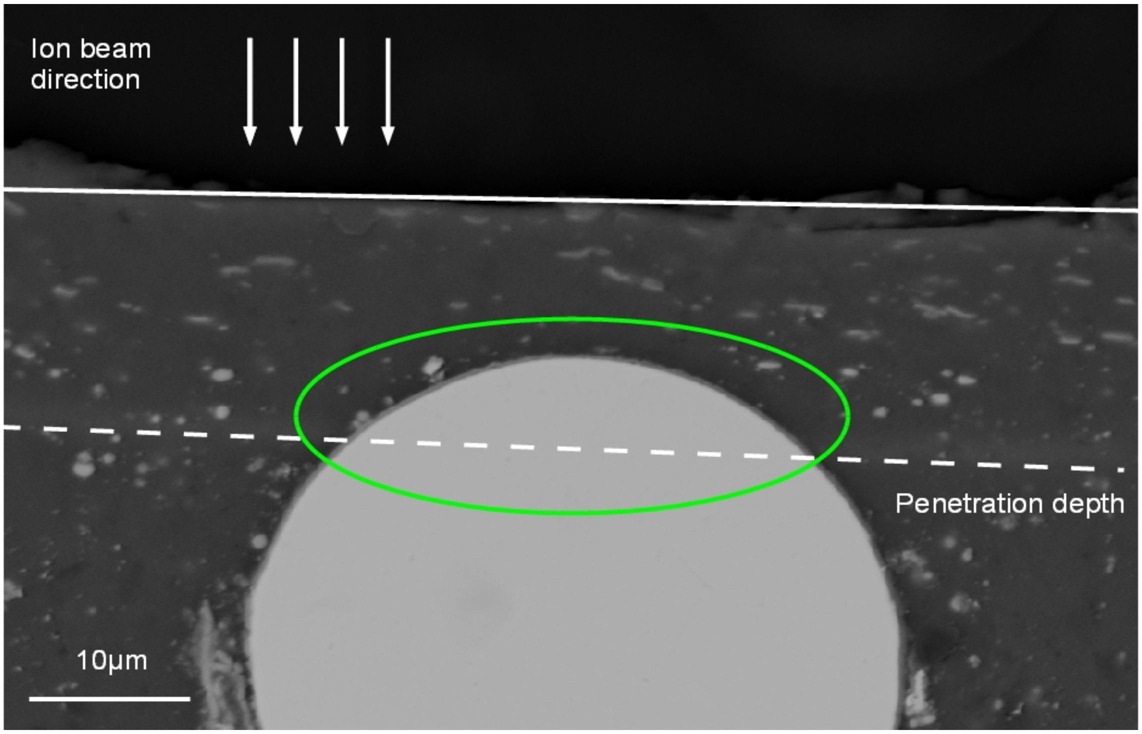
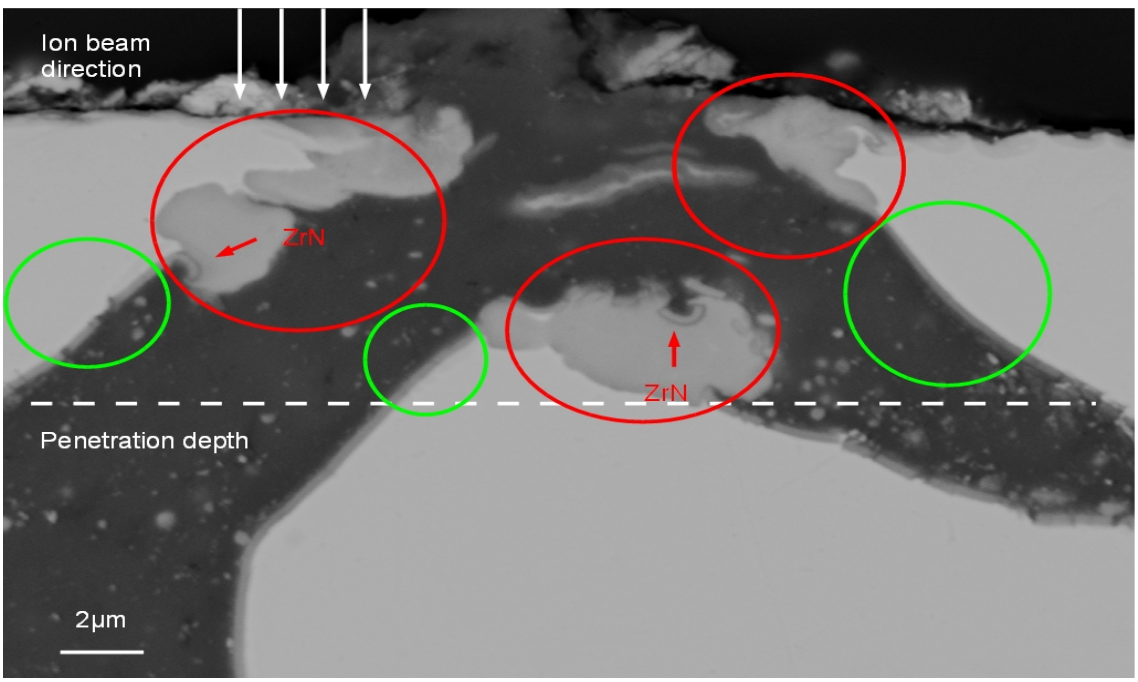


(a)



(b)

Fig 8: UMo particles covered with 1000nm ZrN after irradiation. In case of a dense ZrN layer (green circles) the UMo/Al diffusion has been completely suppressed. In case of a cracked ZrN layer a huge IDL has grown along the cracks.

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