

RERTR 2015 – 36<sup>TH</sup> INTERNATIONAL MEETING ON  
REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS

OCTOBER 11-14, 2015  
THE PLAZA HOTEL  
SEOUL, SOUTH KOREA

**Post Irradiation TEM Investigation of ZrN Coated U(Mo)  
Particles Prepared with FIB**

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**ABSTRACT**

In the framework of the Selenium project, two dispersion fuel plates were fabricated with Si and ZrN coated fuel particles and irradiated in the BR2 reactor of SCK•CEN to high burn-up. The first analysis of the irradiated plate proved the reduced swelling of the fuel plate and interaction layer growth up to 70% <sup>235</sup>U (~ 5.3×10<sup>21</sup> fissions/cm<sup>3</sup>) burn-up. The question was raised how the structure of the interaction layer had been affected by the irradiation and how the structure of the fuel particles had evolved. Hereto, samples from the ZrN coated U(Mo) particles were prepared for transmission electron microscopy (TEM) using focused ion beam milling (FIB) at INL. The FIB technique allowed to precisely select the area of the interaction layer and/or fuel to produce a sample that is TEM transparent over an area of 20 by 20 μm. In this contribution, the first TEM results will be presented from the ~66% <sup>235</sup>U (~ 5×10<sup>21</sup> fissions/cm<sup>3</sup>) burn-up sample.

## 1. Introduction

The SELENIUM (Surface Engineering of Low ENriched Uranium-Molybdenum) fuel development project of SCK•CEN [1] was initiated to investigate coatings as a way to inhibit fuel/matrix interaction layer formation (IL). The project consists of the production, irradiation and post-irradiation examination of 2 flat, full size plates containing coated U(Mo) atomized powders dispersed in a pure Al matrix. Next to silicon, ZrN was selected as coating material as it is metallurgically inert towards the U(Mo) and the Al matrix. In that way, direct contact between uranium and aluminum is prevented and the formation of the interaction layer is inhibited. The choice of ZrN was also based on the experience of the Russian MIR irradiated mini rods containing ZrN coated U(Mo) [2]. After a two cycle irradiation in the BR2 reactor, the SELENIUM plates were unloaded from the reactor and allowed to cool down. In 2013, the fuel plates were transported to the Laboratory for High and Medium Activity (LHMA) and submitted to an extensive post irradiation campaign [3,4].

The PIE clearly showed the positive effect of the coatings. For the ZrN coated fuel, a virtual absence of reaction between the U(Mo) and the Al is observed, up to a fission densities of about  $4.5 \times 10^{21}$  fissions/cm<sup>3</sup>, after which an interaction layer formation starts. It was stated that the cracks observed in the unirradiated ZrN coating [5] most probably form the entrance path for Al to the fuel kernel, resulting in the formation of an IL. However, as the formation of the IL is only seen at high fission densities, a healing of the ZrN layer must have occurred. This restorative effect is probably due to mobility of Zr and N atoms generated by the fission fragments, which on the other hand also causes intermixing of the ZrN coating with the Al matrix.

Non-destructive testing [4] of the SELENIUM plates revealed a very linear evolution of the fuel swelling with the fission density with a slope change around  $3 \times 10^{21}$  fissions/cm<sup>3</sup> which was linked to the onset of fuel restructuring. Evidence of recrystallization occurring in the fuel was found during destructive analysis, in the formation of large intragranular bubbles (release of Xe filled nanobubbles) and in the precipitation of solid fission products. It was concluded that the U(Mo) swelling is strongly influenced by the recrystallization effect.

To investigate the evolution of the ZrN coating with irradiation, samples over a range of different fission densities will be prepared by FIB and studied with transmission electron microscopy (TEM). This paper reports the first results obtained on samples of ZrN coated U(Mo) fuel irradiated up to a burnup of 66% <sup>235</sup>U ( $5 \times 10^{21}$  fissions/cm<sup>3</sup>).

## 2. Experimental

The fuel plates in the SELENIUM experiment consist of an 8g<sub>U</sub>/cc dispersion of coated, atomized LEU (19.7% <sup>235</sup>U) based U-7w%Mo alloy particles in a pure Al matrix. The atomized U(Mo) powder was fabricated by KAERI and the coatings were applied at SCK•CEN in the STEPS&DRUMS coater. Fuel plates were fabricated by AREVA-CERCA using the standard 'picture frame' plate production process. The plates selected for irradiation were identified as U7MD1221 (600 nm Si coating) and U7MD1231 (1 μm ZrN coating).

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 24<sup>th</sup>, 2012 and discharged after the last cycle on October 23<sup>rd</sup>, 2012. The maximum power at Beginning Of Life (BOL) was close to 470W/cm<sup>2</sup> for both plates. 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/cm<sup>2</sup> at EOL, attaining

a plate average burn-up of ~48%  $^{235}\text{U}$  and a local maximum burn-up just below 70%  $^{235}\text{U}$ . The fabrication characteristics and irradiation conditions are summarized in Table 1.

Plate Id.	U7MD1221	U7MD1231
	Fabrication data	
<b>Cladding</b>	AG3NE	AG3NE
<b>Matrix</b>	Al	Al
<b>Coating</b>	600 nm Si	1000 nm ZrN
<b>Loading (gU/cm<sup>3</sup>)</b>	8	8
<b>Enrichment (% <math>^{235}\text{U}</math>)</b>	19.75	19.75
<b>wt% Mo</b>	7	7
	Irradiation data	
<b>EFPD</b>	69	69
<b>Mean BU (% <math>^{235}\text{U}</math>)</b> <b>(fissions/cm<sup>3</sup> U(Mo))</b>	47.9 ( $3.5 \times 10^{21}$ )	47.5 ( $3.5 \times 10^{21}$ )
<b>Max BU (% <math>^{235}\text{U}</math>)</b> <b>(fissions/cm<sup>3</sup> U(Mo))</b>	69.2 ( $5.3 \times 10^{21}$ )	69.6 ( $5.3 \times 10^{21}$ )
<b>Peak Heat Flux (W.cm<sup>-2</sup>)</b>	466	466

Table 1 Fabrication and irradiation history of the SELENIUM fuel plates.

Several samples were prepared from the two fuel plates at locations of different local burn-ups. Currently, one sample has been analyzed in the focused ion beam (FIB) and transmission electron microscope (TEM). It was cut from the U7MD1231 fuel plate, the ZrN coated U(Mo) fuel plate, at a location with a calculated burn-up of 66% ( $5 \times 10^{21}$  fissions/cm<sup>3</sup>). A slice was cut off in hot-cell with a rotating diamond blade saw and mechanically polished on both sides to reduce the thickness to about 100  $\mu\text{m}$ , in which the slice was oriented such that the plan-view side contains cladding-meat-cladding. One side was polished up to 220 grit, while the other side was polished up to 4000 grit to reduce the surface damage layer. A small segment was broken off and was shipped to the Idaho National Laboratory for the creation of TEM samples using a FEI Quanta 3D FIB. Two TEM lamellas were produced from the 66% burnup sample. Both lamellas were produced from areas where two U(Mo) particles were in close proximity to each other. The TEM lamellas were 20  $\mu\text{m}$  x 20  $\mu\text{m}$  by roughly 75 nm thick. TEM lamellas were produced using the standard liftout method. Polishing energies were lowered during the thinning process to reduce FIB damage in the TEM lamella. The final milling energy used was 2kV.

Before shipping the TEM lamella back to SCK•CEN, the samples were analyzed using a JEOL 2010 LaB<sub>6</sub> microscope equipped with energy dispersive spectroscopy (EDS) at the Idaho National Laboratory. At SCK•CEN a JEOL 3010 LaB<sub>6</sub> microscope was used to characterize the microstructure. Bright field and dark field images were obtained from the microstructure and selective area diffraction was performed to determine the crystal structure of the samples. EDS line scans and point analysis were performed to obtain qualitative chemical compositions of various regions in the microstructure.

### 3. Results

Of the two TEM lamellas finalized in the FIB, one was located at the interface between the U(Mo) kernel and the Al matrix and one at a location where two U(Mo) kernels meet. Figure 1 shows two secondary electron (SE) images recorded while the TEM lamella are being thinned in the FIB. Apart from the U(Mo) kernel, the Al matrix and the ZrN coating, two interaction layers

were formed during irradiation. One layer results from the interaction between the U(Mo) fuel and the Al matrix and is indicated in Figure 1. This layer is referred as IL UMo-Al. Another layer was formed at the interface of the ZrN coating and Al matrix and is referred to as the Al-ZrN interaction layer (IL Al-ZrN).

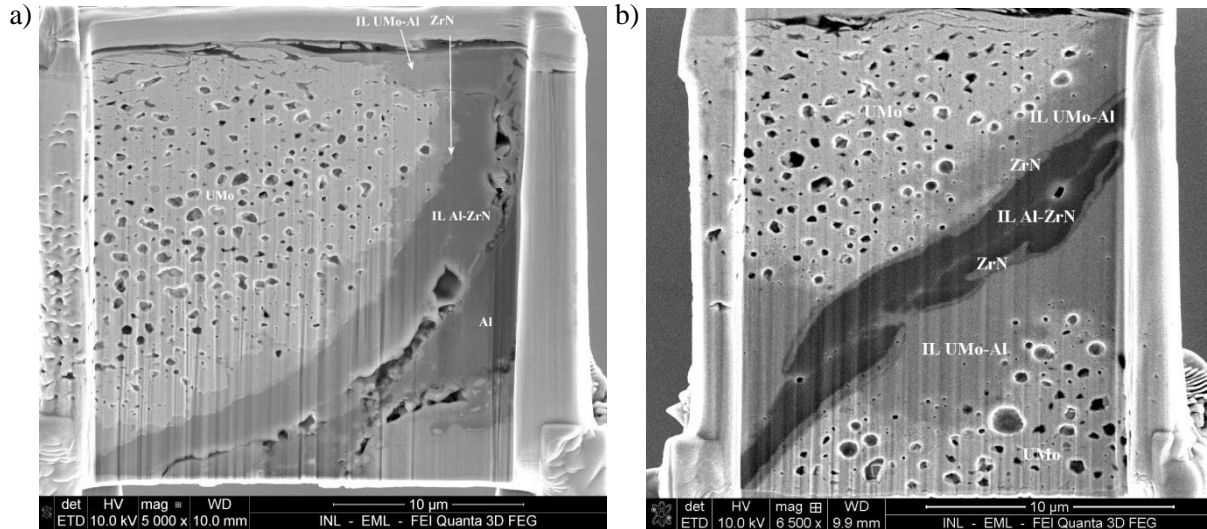


Figure 1. a) and b) SE images of the two TEM lamella showing the various phases observed in the microstructure.

The compositions of the different phases were measured on a qualitative level with energy dispersive X-ray spectroscopy (EDS) in the TEM. Figure 2 shows the results of a linescan starting in the U(Mo), passing through the IL UMo-Al interaction layer, the ZrN coating, and into the IL Al-ZrN layer. The EDS results of the IL UMo-Al region show that the U and Mo content is reduced and replaced by Al. The Zr content measured in the IL UMo-Al region is low and, if present, it is most likely a fission product. It indicates that the Zr does not diffuse into the U(Mo) and IL UMo-Al regions. The location of the ZrN layer is marked by a strong increase of the Zr signal. The measurements may suggest that the layer is contaminated with U(Mo) and Al, but because of the large spot-size of 20-30 nm in the TEM, the signal was probably generated in the neighboring interaction layers. The IL Al-ZrN region is marked by a high concentration of Al and Zr. Results show an increased Zr content in the Al matrix indicating diffusion of Zr from the coating into the Al matrix. It is unclear from this analysis where the N from the ZrN layer has diffused due to the inability to measure N efficiently in EDS analysis.

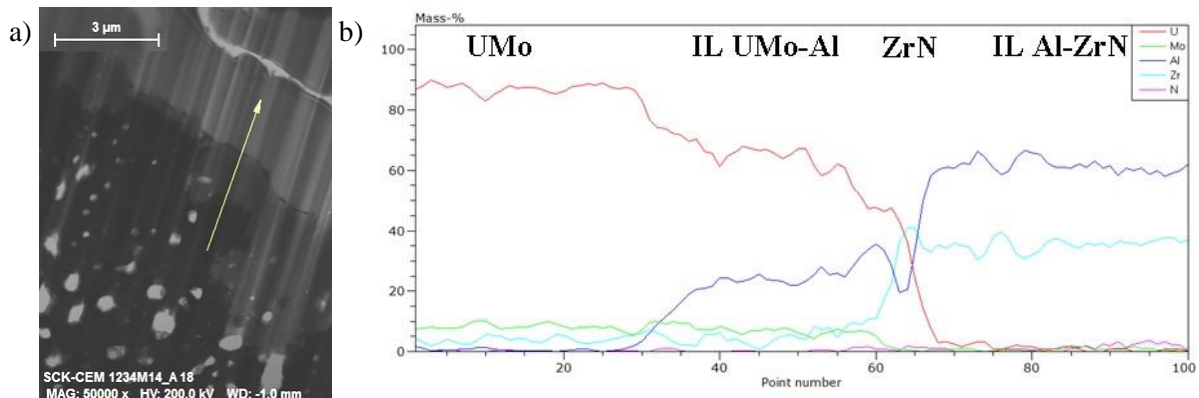


Figure 2. EDS linescan giving the qualitative composition of the different regions. The arrow in a) indicates the position and direction of the line scan. The graph in b) gives the composition in mass %. The U(Mo) kernel, the U(Mo)-Al interaction layer, the ZrN coating and the Al-ZrN interaction layer are indicated.

The microstructures of the different phases were characterized using the TEM. Figure 3 shows the typical microstructure of the U(Mo) fuel kernels. In the overview image (Figure 3a), it was observed that large fission gas bubbles were formed, creating a porous structure. The bubbles are faceted, which agrees with the crystalline structure of the U(Mo) fuel, as confirmed by the diffraction pattern shown in Figure 3b. Within the bubbles, solid fission product precipitates were found. Qualitative EDS analysis revealed that the fission product precipitates contain a series of elements such as Ba, Ce, Nd, Sr and Y. At higher magnification (Figure 3b), the defect structure in the U(Mo) grains is revealed. The grains are recrystallized, during which the size of the grains is reduced from a few micrometer to sub-micron sized grains. The diffuse diffraction intensity in the diffraction pattern in the inset of Figure 3b, indicates the oxidation of the U(Mo), but this only occurred due to exposure to air after the FIB sample preparation. At most locations in the fuel, the superlattice of fission gas bubbles, which is present in lower burn-up samples [6], was removed. However, at some locations, mainly at the newly formed grain boundaries, small areas were found where the bubble superlattice remained. The residual bubble lattice is distorted and on the verge of collapsing. Similar results have been reported on other high-burnup U(Mo) dispersion fuels [7,8].

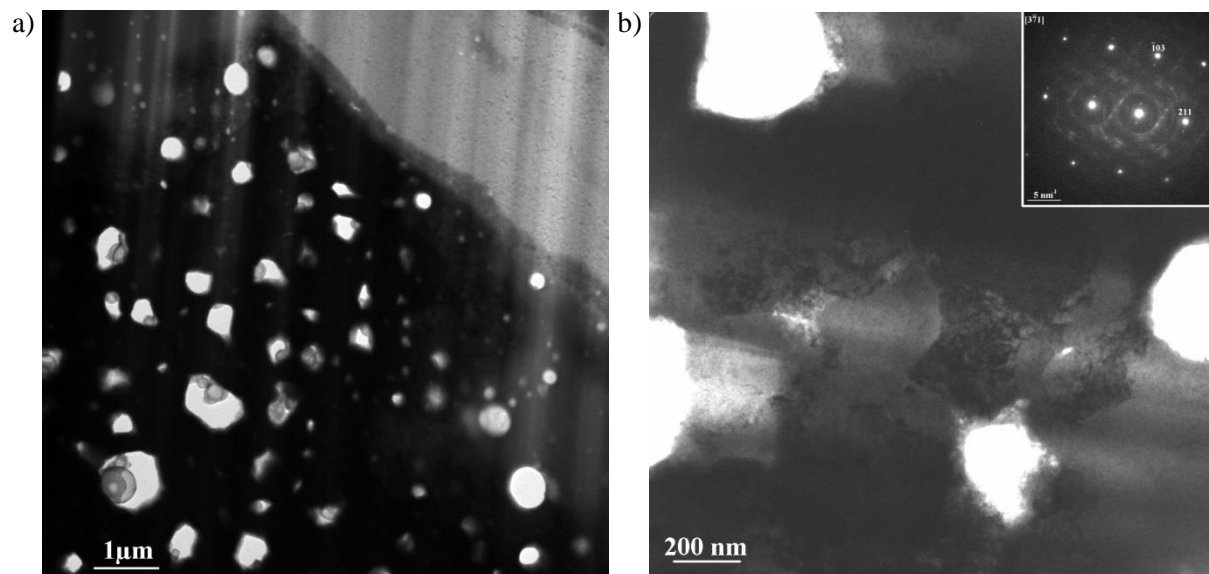


Figure 3. a) Overview bright field image of the U(Mo) fuel. b) Detailed bright field image, revealing a sub-micron grain structure. The inset shows the diffraction pattern confirming the crystalline nature of the U(Mo).

In between the U(Mo) kernel and the ZrN coating layer, an interaction layer, the IL UMo-Al region, is formed in some areas. The ZrN coating prevents the formation of the IL UMo-Al in various locations in the fuel. The EDS analysis showed that this IL UMo-Al layer mainly contains U, Mo and Al. No Zr is measured or only a small quantity which should be related to the fission product Zr. It is formed by the diffusion of Al beyond the ZrN coating. Figure 4a shows an example of the IL UMo-Al interaction layer near the ZrN coating. A breach is formed in the ZrN coating and the diffusion of the Al and the interaction with the U(Mo) starts at that location. At places where the ZrN coating is intact and which are not too close to a breach in the coating, no interaction layer is formed. The diffraction pattern given in the inset of Figure 4a shows that the interaction layer is amorphous in structure [6].

Fission gas bubbles were observed in the IL UMo-Al interaction layer. Because of the amorphous nature of IL UMo-Al layer, the bubbles are rounded instead of faceted. The size of the bubbles varies from 10 to a few hundred nanometers. In particular it was observed, like in Figure 4b, that the smaller bubbles are aligned near the ZrN coating. It suggests that the bubbles are moving towards to Al matrix, but that they are blocked by the crystalline ZrN coating and/or the crystalline IL-Al-ZrN layer. It was noticed that the bubbles do not coalesce into larger bubbles, but a collection small individual bubbles is observed. The

larger, roughly 100 nm sized, bubbles were found closer to the crystalline U(Mo) fuel. Not only near the ZrN coating, a collection of bubbles was observed, but also at certain areas within the interaction layer a similar collection was found. Further analysis is required to determine why bubbles collect at these locations or what is preventing the bubbles from coalescing.

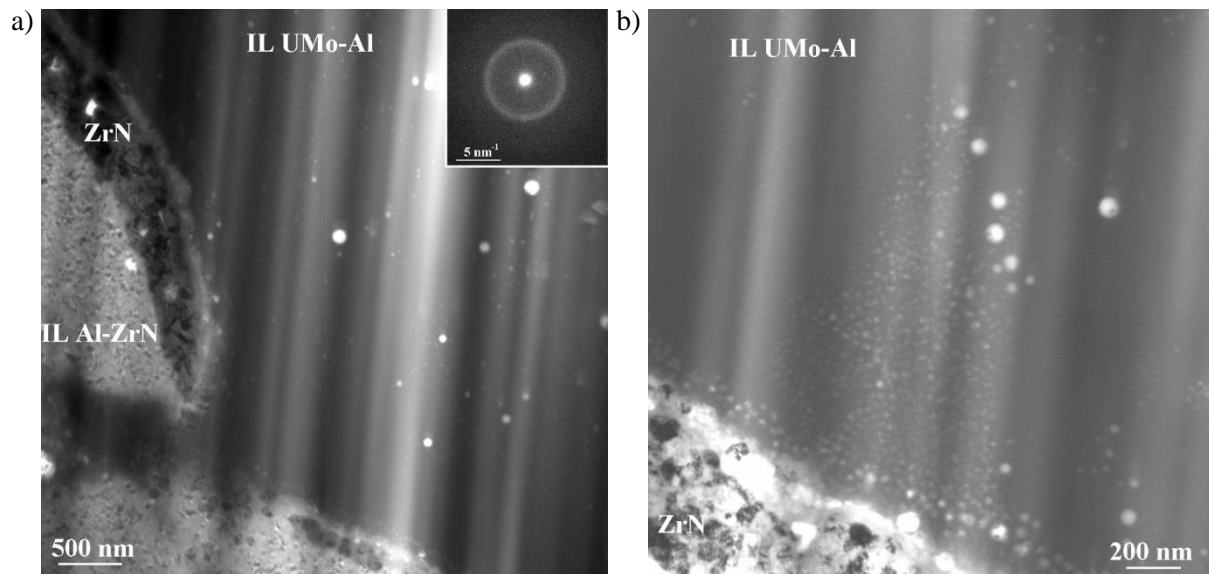


Figure 4. a) IL UMo-Al interaction layer b) Agglomeration of fission gas bubbles in the interaction layer near the ZrN coating.

Figure 5 shows the ZrN coating. As already mentioned, the ZrN coating did not remain fully intact at this high burn-up. In the overview image of Figure 5a, variations in the coating thickness can be observed, ranging from 0 to 400 nm. Where the ZrN coating is breached, it no longer protects the U(Mo) kernel from interaction with the Al matrix, thus forming the IL UMo-Al region.

Figure 5b shows a bright field image of the ZrN coating recorded at higher magnification. At this location, the coating is still intact, yet some amorphous IL UMo-Al interaction layer is formed on the side of the U(Mo) kernel due to a neighbouring breach in the coating. It can be observed that the coating has a polycrystalline structure with a particle size of the order of 100 nm. The diffraction pattern in the inset confirms the polycrystalline nature of the ZrN coating. The irradiation up to a high burn-up of 66% appears to not affect the crystallinity of the ZrN coating.

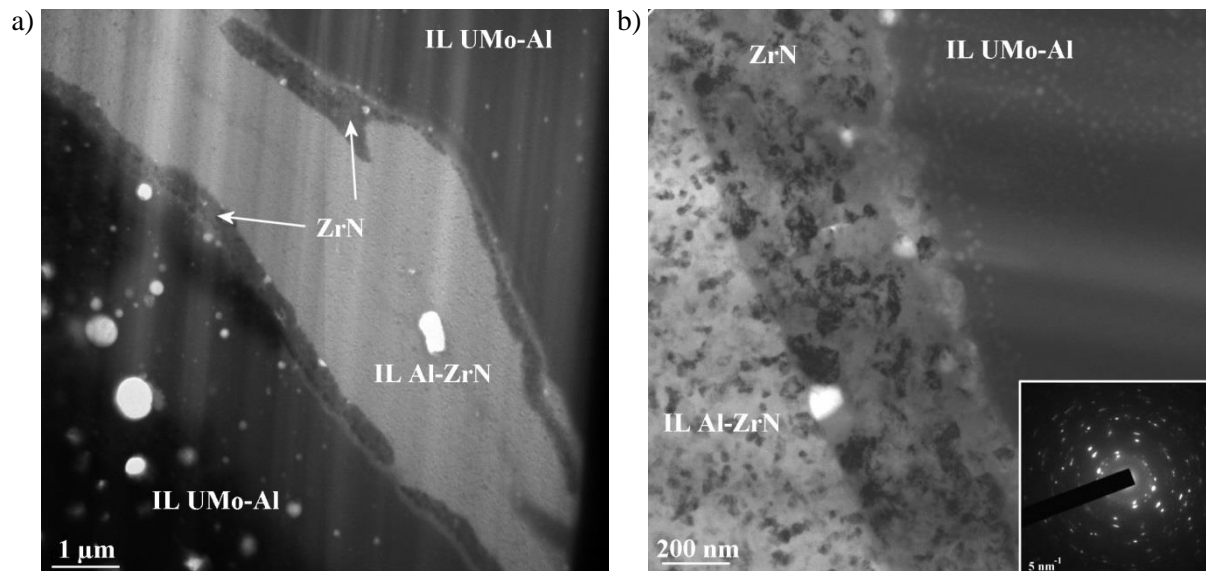


Figure 5. a) Bright field overview image of the ZrN coating. b) Bright field image and diffraction pattern revealing the polycrystalline nature of the ZrN coating.

On the other side of the ZrN coating, a different interaction layer is formed, which is called IL Al-ZrN. EDS analysis revealed that Al and Zr are the main elements present. The EDS technique is not sensitive for N and therefore it is not excluded that nitrogen is present as well. In view of the presence of Zr, it is even very likely that N is present as well. Figure 6a shows a bright field image of the IL Al-ZrN interaction layer. It can be observed that, contrary to the Al in the matrix, the IL Al-ZrN layer consists of a small polycrystalline microstructure. Figure 6b shows the diffraction pattern of the IL Al-ZrN region. The ring pattern is typical for a polycrystalline structure. The ring spacings agree with a simple cubic lattice with a lattice parameter of about 0.4 nm, which is close to the lattice parameter of Al. At other locations in the IL Al-ZrN region, the crystal structure is slightly different. There, the diffraction still shows a ring pattern, but only the rings typical for a face centered cubic structure are present. The lattice parameter is still about 0.4 nm, which means that the particles in the IL Al-ZrN layer have the Al structure.

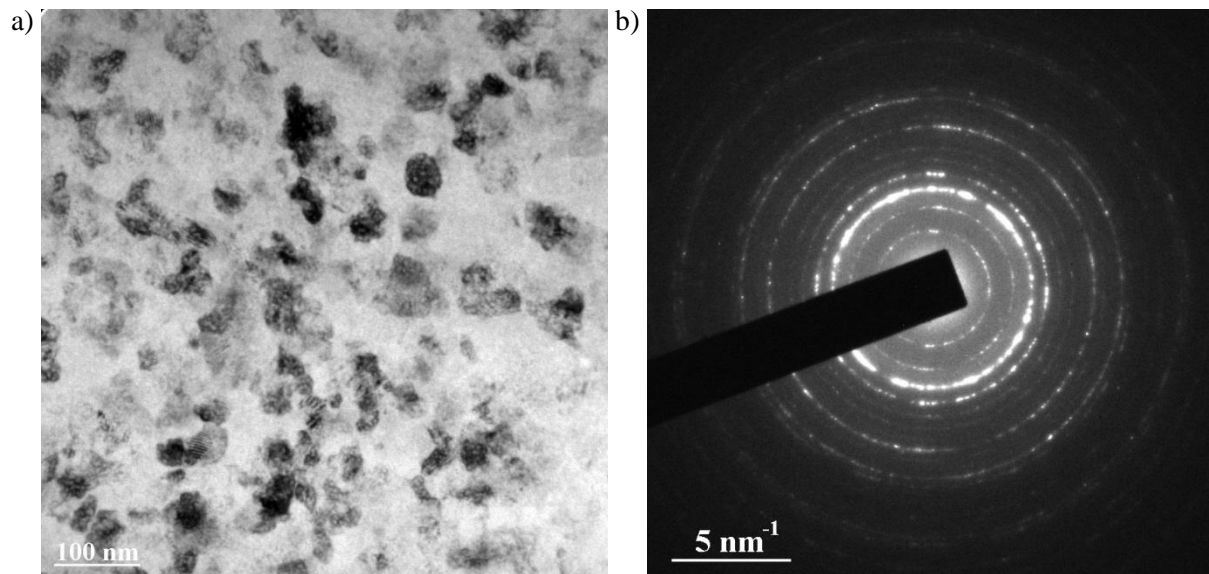


Figure 6. a) Bright field image of the IL Al-ZrN region, the interaction layer on the Al side of the ZrN coating. b) Diffraction pattern of the IL Al-ZrN region, revealing the polycrystalline nature.

#### 4. Discussion

The TEM investigation of the ZrN coated U(Mo) fuel irradiated to high burn-up (66%) revealed the effect of the coating on the microstructure of the irradiated fuel. In total, five distinct phases were found with different chemical composition and structure.

The first region is the U(Mo) fuel. The microstructure that was observed there is similar to other high burn-up fuels [7,8]. The U(Mo) is still crystalline, but the grains are recrystallized as a result of the stress imposed by the fission products and the grain size is reduced to about half a micron or less. The superlattice of fission gas bubbles, which is present at lower burn-up, is removed at most locations. Some areas of residual bubble superlattice bubbles remain near some of the grain boundaries of the fuel. The superlattice is still ordered, but the lattice is distorted indicating that the lattice is on the verge of collapsing. Most of the fission products have collected in the intergranular bubbles as precipitates. The large intergranular bubbles are faceted due to the crystalline nature of the U(Mo). Within the large bubbles, solid fission products are generally found as precipitates. The main elements present in the fission product precipitates are Ba, Sr, Y, Ce and Nd.

At some locations, an amorphous interaction layer is observed in between the U(Mo) and the ZrN coating. The layer is rich in Al, U and Mo, but limited Zr (from fission yield) and no N was

found. This layer is the normal interaction layer formed between Al and U(Mo) and is, therefore, named the IL UMo-Al layer in this paper. The thickness of IL UMo-Al layer varies significantly and at some locations, even no interaction layer is formed. There is a strong correlation between the thickness of the IL UMo-Al layer and the integrity of the ZrN coating. Where no interaction layer is formed, the ZrN coating is intact, while at places where the ZrN coating is breached, the layer is the thickest and even grows towards the Al matrix. Note that the ZrN layer can be fully intact but interaction layer may be present on the fuel side of the ZrN layer due to diffusion from a neighboring breach of the ZrN. Results suggest that the ZrN coating is a very effective barrier against Al diffusion. However, when a breach is created in the coating, the Al is able to interact with the U(Mo) fuel kernel. The formation of the IL UMo-Al progresses both in the radial direction, towards the centre of the fuel kernel, as in a lateral direction, forming an interaction layer below the adjacent intact ZrN coating. Fission gas bubbles were found throughout the IL UMo-Al region. Because the layer is amorphous, the bubbles are rounded and no longer faceted. Most of the bubbles were found to be empty, which indicates that they were filled with gaseous fission products. However, some bubbles with solid fission products were found as well.

The third region is the ZrN coating. The original width of the layer, as measured on the as-produced fuel particles, is about 1  $\mu\text{m}$ . In the high burn-up sample, it was found that the coating thickness was reduced everywhere and significant variations in thickness were found. Where the coating was least affected, the thickness reduced to about 400 nm, while at other locations, the coating was fully breached. The remaining ZrN coating is still crystalline and consists of 100 nanometer sized nanocrystals. In the as-produced coating, pores and cracks were observed in the cladding. During the irradiation and the reduction of coating thickness, most of the pores and cracks were removed as well, but some pores and cracks were still found in the remaining coating.

In between the ZrN coating and the Al matrix, a second interaction layer was found. The EDS analysis showed that it contains Al, Zr and N, but no U nor Mo. Therefore this second interaction layer is called IL Al-ZrN in this paper. The diffusion of Zr and N in the Al matrix during irradiation formed a new phase. There is not enough information at this moment to uniquely identify this phase and, in particular, data are lacking about the exact N content in this layer. The TEM images reveal that it consists of nanocrystals, which are even smaller than in the ZrN coating. The crystal structure depended on the location of the layer. Where the IL Al-ZrN layer was formed between the coating and the Al matrix, the diffraction pattern consisted with a face centered cubic lattice with lattice parameter of about 0.4 nm, which corresponds to the Al crystal lattice. At the location in between two fuel particles, where no Al matrix was left, additional rings appear in the diffraction pattern. Here the pattern is consistent with a simple cubic lattice with a lattice parameter of 0.4 nm. An additional ordering of the ZrN in the Al lattice could explain the difference, but more data on this interaction layer are required to fully identify this layer.

The final region in the microstructure is the Al matrix. As the amount of interaction layers is limited, not all the Al has interacted with either the U(Mo) fuel kernel or the ZrN coating and some matrix material is still intact. This phase was not studied in detail, but it was found that the original grain structure was not affected and only radiation induced defects were found there.

## 5. Conclusions

TEM samples have been successfully prepared from ZrN coated U(Mo) dispersion fuel irradiated in the BR2 reactor of SCK•CEN to a local burn-up of 66% ( $5 \times 10^{21}$  fissions/cm<sup>3</sup>). For the final preparation step, the samples were sent to INL, where FIB was applied to produce two TEM



lamellae near the edge of a fuel particle. Five phases of different composition and microstructure were found in the samples.

The first region is the U(Mo) fuel particle, which was found to be recrystallized in sub-micron sized grains. The fission bubble superlattice is removed apart from small areas near the grain boundaries and large faceted intergranular bubbles were formed. Most bubbles contained solid fission product precipitates. The second region is the amorphous U(Mo)-Al interaction layer. It was mainly formed by the diffusion of Al through breaches in the ZrN coating. The third region is the ZrN coating. The thickness of the coating was reduced during irradiation and locally, breaches were formed in the ZrN coating. The ZrN layer is polycrystalline with crystallites of the order of 100 nm. The fourth region is an interaction layer between the ZrN coating and the Al. This layer is polycrystalline with nanocrystals that are smaller than the crystals in the ZrN coating. The fifth region is the Al matrix, which only showed radiation induced defects.

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