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**THE SELENIUM FUEL EXPERIMENT – PROGRESS REPORT
AFTER 2 CYCLES**

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ABSTRACT

Since 2008, SCK•CEN has supported the SELENIUM U(Mo) dispersion fuel development project in an attempt to find a way to reduce the interaction between U(Mo) fuel kernels and the Al matrix to a significantly low level to allow high burnups to be reached at high power levels. SELENIUM aims at evaluating the solution of coating the U(Mo) kernels to reduce or inhibit the interdiffusion of Al and U, which is the source of the interaction phase formation. Two coating types were included in the current experiment : Si and ZrN. A PVD coater for coating particles was designed, built and licenced for U(Mo) powder. Several batches of atomised low-enriched U(Mo) powder were coated and used for fuel plate fabrication. Two fuel plates containing 8g_U/cc U(Mo) coated with respectively 600 nm Si and 1000 nm ZrN in a pure Al matrix, were introduced in the BR2 reactor in cycle 02/2012 in the E-FUTURE basket at the start of March 2012. The fuel plates have been irradiated for two cycles and the third and final cycle is ongoing at the time of this conference.

This paper provides a status report of the SELENIUM project and an outlook to future possibilities offered by the surface engineering of U(Mo).

1. Introduction

Recent attempts to qualify the LEU(Mo) dispersion fuel with Si addition to the Al matrix up to high power and burnup have not yet been successful due to unacceptable fuel plate swelling at elevated burnup (>60% ²³⁵U). The LEONIDAS E-FUTURE I experiment was able to complete its 3 cycles but all 4 fuel plates showed pillowing in the high power zones [1, 2]. The subsequent LEONIDAS E-FUTURE-II experiment, in which higher Si concentrations and a finer dispersion of the Si in the matrix were used [3, 4], had to be stopped prematurely due to excessive fuel plate swelling.

Nevertheless, the atomised U(Mo) fuel kernels themselves have consistently shown very stable and predictable behaviour under irradiation [5]. In particular, the fission gas behaviour shows a formation of the nanobubble lattice up to a certain burnup [6], followed by a recrystallization of the kernels [7]. This leads to a breakdown of this lattice with formation of small, spherical fission gas bubbles, first on the Mo-depleted cell boundaries and at higher burnup throughout the whole kernel.

The root cause of the failures, at least in the case of the E-FUTURE-I experiment and its predecessors, was clearly related directly to the formation of the U(Mo)-Al(Si) interaction layer [8, 9, 10, 11]. Excessive formation of these layers around the kernels severely weakens the local mechanical integrity, leading to formation of large pores on the interaction layer-matrix interface. At these interfaces, a front of fission products swept up by the growing interaction layer is located, which causes a reduced cohesion at these points. Where the matrix and the interaction layer detach, a void grows, which takes a characteristic crescent shape. When the local stresses, related to the gradual swelling of the fuel as burnup is accumulated, exceed the yield strength of these interfaces, cracks start to develop and heat transfer is impaired, eventually leading to pillowing of the plate. For the E-FUTURE II experiment, we can so far only speculate about the cause, but it is suspected that a different failure mechanism, possibly related to the use of 'alloy' Al-Si matrix power in the manufacturing, is at least contributing in view of the low burnup at which problems were encountered. All mitigation strategies for this now sufficiently understood mechanism therefore will need to address the formation of the interaction layer.

The introduction of Si in the matrix was shown to lead to improvements in the interaction phase development [11, 9]. However, the role of Si was shown to be most effective when there was direct contact between a Si particle and the fuel kernel surface, effectively eliminating formation of any interaction layer in some cases [5, 12]. The question therefore becomes if it is the chemical effect of the Si, stabilising the interaction layer properties, or the physical effect of the formation of an U-Si interaction layer (during manufacturing or the early phases of irradiation or both) which is the main cause for the improved behaviour noticed.

The idea of an interdiffusion barrier to avoid formation of an interaction phase was developed further within the Surface Engineering Low ENriched Uranium Molybdenum (SELENIUM) fuel project initiated and supported by SCK•CEN in collaboration with the University of Ghent [13, 14]. In this project, U(Mo) kernels are coated by Physical Vapour Deposition (PVD), magnetron sputter deposition more precisely, in a rotary drum. Coatings of 600 nm Si and 1000 nm ZrN were selected.

2. Kernel and plate production

The coating of the SELENIUM kernels was treated in a previous paper [15]. Low enriched and depleted kernels were coated. The coated kernels were shipped to CERCA for fuel plate manufacturing. After production of test plates with depleted uranium kernels, the LEU plates were manufactured. The following plates were produced :

Plate	Coating	Measured mean coating T	Cladding	Remarks
U7MD1221	Si	815 nm	AG3-NE	Irradiation
U7MD1222	Si	550 nm	AG3-NE	Stored
U7MD1231	ZrN	1160 nm	AG3-NE	Irradiation
U7MD1232	ZrN	815 nm	AG3-NE	Blistered & cut

Fresh fuel characterisation on the depleted uranium based plates using optical microscopy, scanning microscopy, electron probe microanalysis, high energy X-ray diffraction and ion irradiation were performed on samples of the depleted test plates. Also samples were characterised after thermal anneals. Results of the ion irradiations have been reported by R. Jungwirth [16], while high energy X-ray Diffraction work was reported by H. Palancher [17]. Thermal anneals of the coated particles embedded in a compacted Al pellet were reported previously by A. Leenaers [18], but since then also thermal anneals of the SELENIUM test plates were performed and characterised.

The results of the thermal anneals of a model system of individual coated particles embedded in an Al pressed powder, show that the kernels do not react with the Al, even at very high temperatures and after long annealing times. No reaction was found between a 1000 nm ZrN coated U(Mo) particle and a pure Al matrix even after 4h at 550°C and very little interaction is observable for the 600 nm Si coated particles [15]. However, during the

manufacturing of a real fuel plate, the coated particles are subjected to the wear and abrasive forces applied during the hot rolling process. This causes the layers to show defects (particularly in the case of ZrN) and/or creates a different wetting between the matrix and the coated kernels. Therefore, the annealing results of the test plate samples differ from the model systems.

3. Annealing study of the SELENIUM fuel plates

The microstructure of the as received fuel plates reveal that the Si coating has been damaged, especially of those particles located at the meat / cladding interface (fig.1).

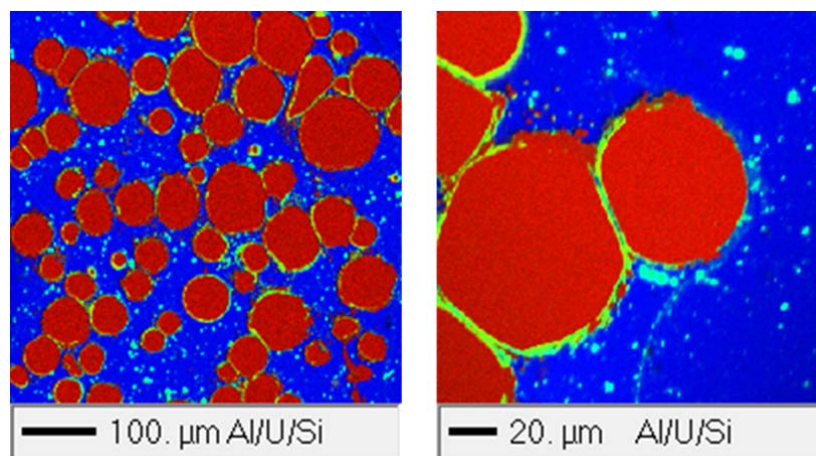


Figure 1 Combined X-ray map of the as received fuel plate containing Si coated U(Mo) dispersed in an Al (Si) matrix : Al (blue), Si (green) and U (red)

Even though there is direct contact between U(Mo) and Al, almost no interaction between the matrix and the fuel with damaged coating has occurred resulting from plate fabrication (hot rolling and blister testing). HE-XRD of the as received fuel plate, identified the formation of two crystalline phases : a distorted form of U_3Si_5 and $U(Al,Si)_3$ [17]. Submitting the as received fuel plate to an additional annealing 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 where most particles with damaged coatings are located (fig. 2).

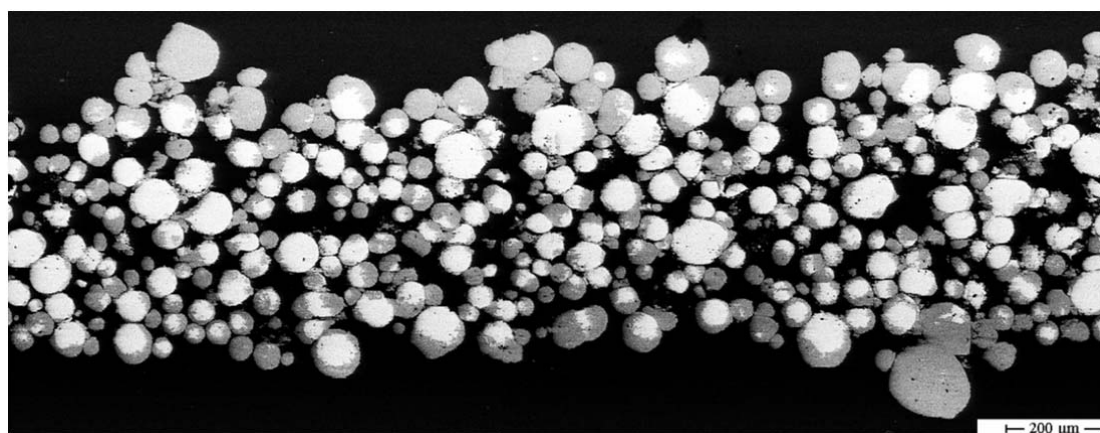


Figure 2 BSE image of the fuel plate containing Si coated U(Mo) particles submitted to a heat treatment of 550 °C for 4h

Quantitative X-ray analysis (Electronprobe microanalysis) of the interaction layer shows that the ratio Al+Si/U+Mo is ~ 3 , indicating the growth of the $U(Al,Si)_3$ layer already identified with HE-XRD in the as received plate.

The microstructure of the as received fuel plate containing ZrN coated U(Mo) also show that the coating has been damaged during plate production. As can be seen in figure 3, cracks have formed perpendicular to the U(Mo) surface. The thermal expansion coefficient for U10Mo is 11.5×10^{-6} m/m K while that for ZrN is 7.24×10^{-6} m/m K. When the coated particles are cooled down after the heat treatment during plate production (hot rolling - blister test), the thermal expansion mismatch between coating and substrate results in thermal residual stress. Tensile stresses in the films could cause through thickness microcracking [19]. The cracks may also result from mechanical forces on the fragile, ceramic ZrN. Metallic coatings are expected to be more resistant due to their ductile nature.

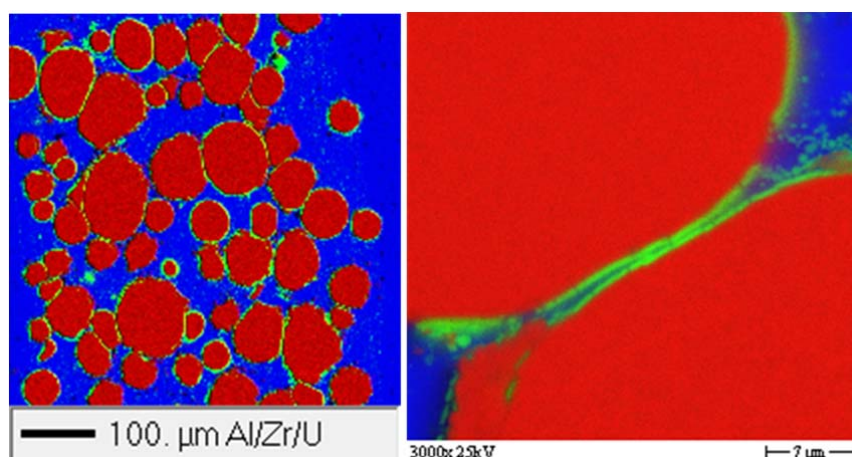


Figure 3 Combined X-ray map of the as received fuel plate containing ZrN coated U(Mo) dispersed in an Al matrix : Al (blue), Zr (green) and U (red).

As can be seen from fig.3, no interaction between Al and U(Mo) has occurred during plate production. However submitting the ZrN/U(Mo) fuel plate to an additional annealing at 550 °C for respectively 2 and 4 hours, will result 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 (fig.4).

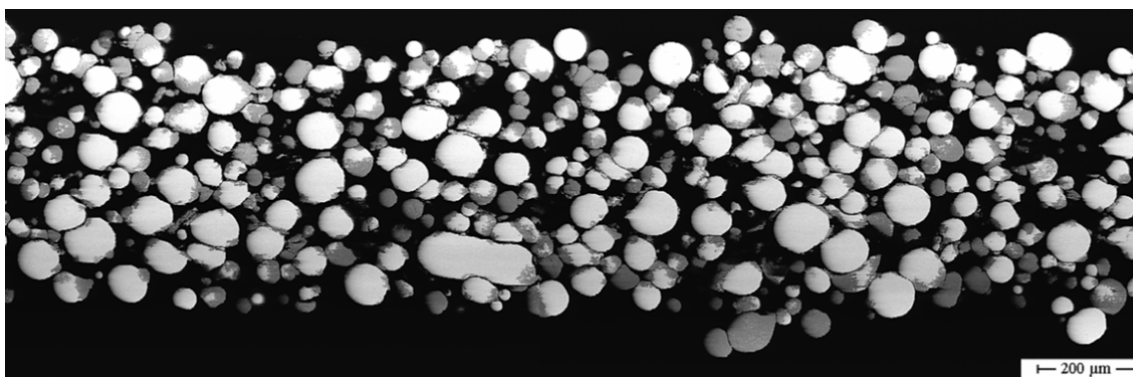


Figure 4 BSE image of the fuel plate containing ZrN coated U(Mo) particles submitted to a heat treatment of 550 °C for 4h

4. Anticipated in-pile influence of coatings

The annealing studies show that interaction between the coated fuel and matrix will only occur at elevated temperatures even if the layer is damaged. Since fuel temperatures remain relatively low in research reactor irradiation conditions, thermally driven diffusion is not expected to play an important role and the main origin for the U(Mo)-Al(Si) intermixing is the fission fragment induced displacement cascades, in essence a ballistic process enhanced by fission spikes and introduction of lattice defects. Roughly a few thousand fission fragments pass through each μm^2 of kernel surface each second at moderate to high power, leading to a total fluence of the order of 10^{10} ions/ μm^2 of kernel surface at maximum burnup. The knock-on atoms (mostly U, Mo, Al and Si) will be displaced and intermix. This intermixing will take place over only a few 100 nm, but as the burnup increases, atoms will be displaced multiple times and eventually interaction layers of some 10 μm are produced, filling the complete matrix volume between the kernels and leading to the development of the pillowing. Physico-chemical effects also come into play, keeping the composition of the interaction phase close to the $(\text{U},\text{Mo})(\text{Al},\text{Si})_3$ stoichiometry, even though the interaction phase remains amorphous.

Post irradiation examination of a low enriched U(Mo)/AlSi dispersion fuel plate (from the EFUTURE I experiment [5]) irradiated up to an average burnup of 65 % ^{235}U reveals that the Si rich preformed layer covering a stray depleted U(Mo) particle remained intact. The absence of large quantities of Al in this layer (fig.5), clearly shows that fission fragment induced interdiffusion and not thermal driven diffusion causes the formation of interaction layers.

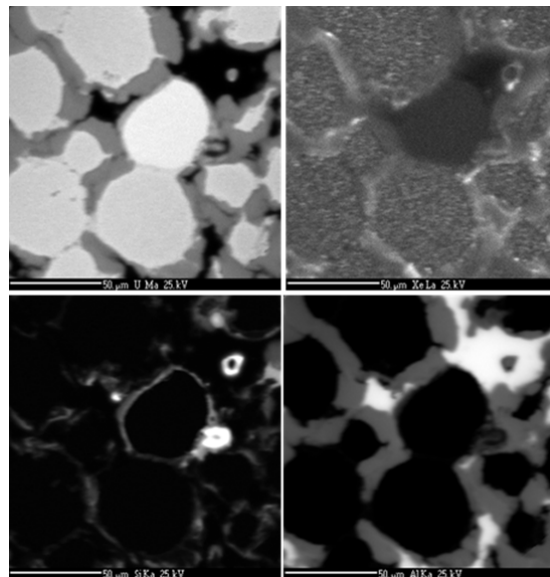


Figure 5 U,Xe, Si and Al X-ray map of a stray depleted U(Mo) particles in fuel plate U7MC6301 of the EFUTURE I experiment.

Any coating on the fuel kernels can thus be considered a barrier for intermixing of Al and U. SRIM/TRIM [20] calculations show that, the formation speed of such an intermixing layer will strongly depend on whether the 'protective' layer around the fuel kernel already contains aluminium or not. This is believed to be exactly the difference between thermally formed as-fabricated Si rich layers in a U(Mo) dispersion in an Al-Si matrix and the layers found on the coated U(Mo) kernels after fabrication. Simulations were performed 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). The simulation was set up to stop most fission fragments in the simulated interface (5 μm U(Mo)

– coating – 2 μm Al). 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 $>1\text{MeV}$ and are displaced over larger distances.

Figure 6 shows the distribution of final recoil positions in a simulation of ion bombardment of respectively a 0.6 μm pure Si and a 0.6 μm U(Mo)(Al,Si)₃ coating between U(Mo) and Al after 20000 ions. The interfaces are located at dotted lines in the graph

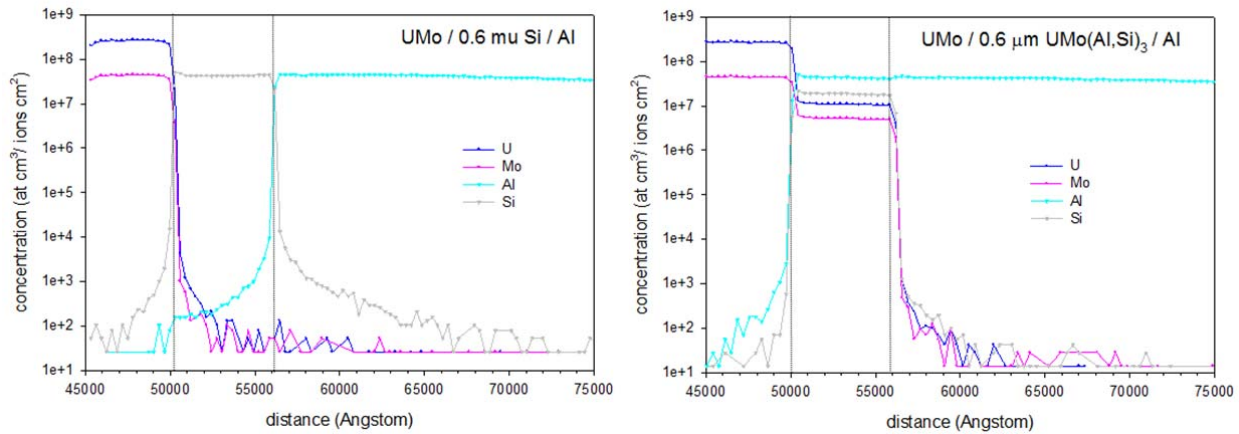


Figure 6 The distribution of final recoil positions obtained by TRIM calculation of Si based coatings.

By applying a coating of a substance that is chemically/metallurgically inert to the U(Mo) and the Al matrix, direct interaction between uranium and aluminum can be avoided (fig. 7) until fission fragment induced intermixing (multiple displacement of the same atoms) or the associated thermal spikes and defects formed reduce the protective nature coating and puts U in contact with Al. This process however is believed to occur only at very high ion fluences (i.e. burnup). The ballistic aspects of the intermixing process will be influenced by any type of coating, with an advantage for heavier coatings. This is illustrated by the calculation result in fig. 7 using a Mo coating. However, the ion driven interdiffusion has more aspects than only the ballistic effect. Some of these effects may influence the interaction layer formation even more than the ballistics. In any case, the ion driven interdiffusion process is influenced markedly by the presence of a barrier layer.

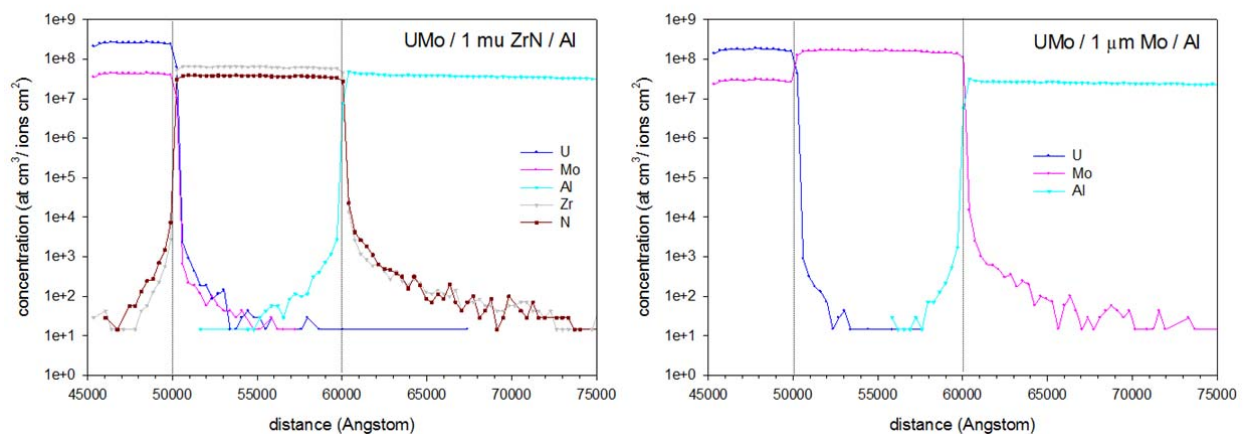


Figure 7 The distribution of final recoil positions obtained by TRIM calculation of ZrN and Mo coatings.

5. Irradiation and intercycle observations

SELENIUM plates U7MD1221 (600 nm Si) and U7MD1231 (1000 nm ZrN) were introduced in the BR2 reactor in cycle 02/2012, starting on April 24th, 2012 and ending on May 15th. The initial maximum local power on the plates was around 470 W/cm², gradually reducing due to the burning of the fissile material and the absence of burnable poisons. The second irradiation cycle started on August 7th, ending on September 3rd. The third cycle has started on October 2nd and is foreseen to end on October 23rd. The final burnup is foreseen to be around 50% ²³⁵U plate average, with local maxima exceeding 70% ²³⁵U.

In between cycles, the plates are wet sipped in their basket to detect fission product release by the plates and visually inspected under water to ascertain their condition and identify any signs of pillowing. All wet sipping were negative, showing no leaks, and visual inspections of the fuel plates between cycles have shown the plates to be sound. After the first irradiation cycle, the main coloration was only a slight darkening of the plate surfaces, consistent with the relatively low burnup. After the second cycle, a more pronounced color pattern can be distinguished with a much darker color in the high burnup regions. The plate U7MD1231 (ZrN coating) also showed some bright spots in the dark region, related to oxide spallation. This indicates that the oxide thickness in those regions has reached around 30-35 µm, not uncharacteristic for this burnup at high power. No indications for excessive swelling of the plates in the high burnup regions were noticeable in the underwater inspections.

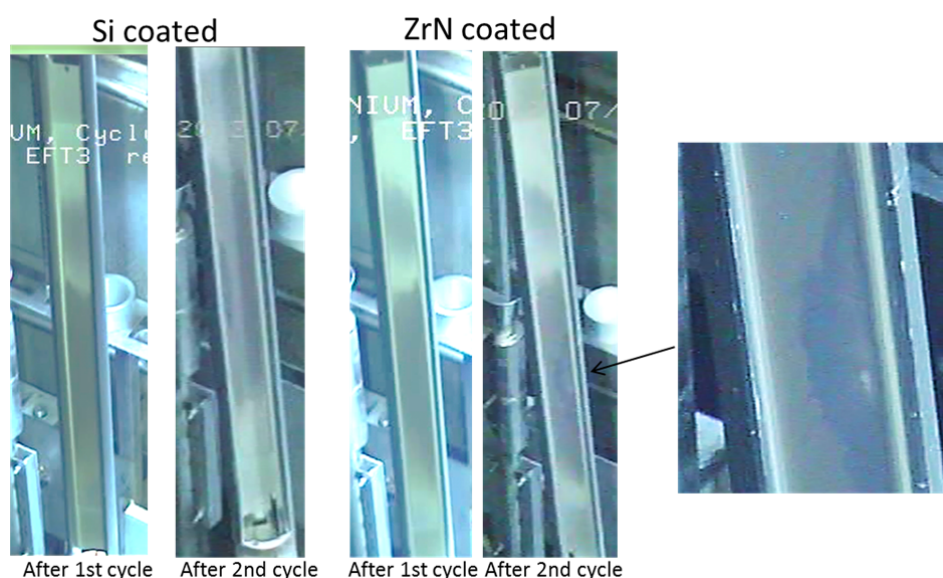


Figure 8 Underwater inspection of the SELENIUM plates after the first and second cycle.

6. Outlook

With the U(Mo) dispersion fuel system under some pressure due to the latest experiences, alternatives to the addition of Si to the fuel matrix are being formulated to overcome the difficulties. It appears that the addition of Si in itself may be insufficient to meet the requirements of relatively high power at high burnup. It is clear that the existing solution needed to be tested to its maximum extent before alternatives become a viable option. The information gathered in the U(Mo) irradiations so far are highly useful for the qualification of the eventual solution, but any alternative will now require some testing before its qualification program can be started. If the SELENIUM irradiation results show the benefits of using coatings, it can be a viable option.

To develop the option of coating into a fuel system, a new set of decisions will have to be taken, for which some screening will need to be done. The optimum coating material and thickness will have to be selected, based on our knowledge base of U(Mo)-Al(Si) behaviour,

the results of the SELENIUM experiment and probably an intelligent screening irradiation experiment. Once the coating selection is narrowed down, the irradiation campaigns generally required for qualification of a new fuel type [21] can be performed. These include an irradiation campaign similar to the E-FUTURE campaigns, followed by a high power test in true fuel element geometry (mixed element test).

For the manufacturing of coated U(Mo) kernels, an upscaling of the STEPS&DRUMS laboratory coating equipment will also be required. Since PVD magnetron sputter deposition is a process used in a number of industrial applications (window coatings, semi-conductor industry, etc.), a very important knowledge base can be found outside of the nuclear sector. It is certain that industrial think-tanks can be used to scale up the existing setup, using know-how they have acquired in other fields. For example, rotating cathode sputter deposition machines, used in glass window coating, look like promising platforms. Combined with the rotating drum technology used in the STEPS&DRUMS prototype, such setups should be able to readily produce sufficient quantities of coated particles to supply the fuel plate industry.

It is likely that the development of these alternatives will be possible in a shorter timeframe than was required to study the Si addition to the matrix, partly accelerated by the SELENIUM irradiation. The gathered know-how in the past years will certainly serve as a stepping stone for qualification of a reliable high-density low-enriched dispersion fuel for high power – high burnup applications.

References

- [1] S. Van den Berghe, A. Leenaers and Y. Parthoens in: Proceedings of the International Meeting On Reduced Enrichment For Research And Test Reactors (RERTR), Santiago, Chili (2011).
- [2] S. Van den Berghe, Y. Parthoens, F. Charollais, Y. S. Kim, A. Leenaers, E. Koonen, V. Kuzminov, P. Lemoine, C. Jarousse, H. Guyon, D. Wachs, D. Keiser Jr, A. Robinson, J. Stevens and G. Hofman, *Journal Of Nuclear Materials* 430 (1-3) (2012) 246-258.
- [3] F. Charollais, P. Lemoine, Y. Calzavara, H. Guyon, E. Koonen, S. Van den Berghe, B. Stepnik, C. Jarousse and D. Geslin in: Proceedings of the 33rd International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Santiago, Chile (2011).
- [4] H. Palancher, X. Iltis, A. Bonnin, F. Charollais, P. Lemoine, S. Van den Berghe, A. Leenaers, E. Koonen, B. Stepnik, C. Jarousse, Y. Calzavara and H. Guyon in: Proceedings of the 16th International Topical Meeting on Research Reactor Fuel Management (RRFM), Prague, Czech Republic (2012).
- [5] A. Leenaers, J. Van Eyken, S. Van den Berghe, E. Koonen, F. Charollais, P. Lemoine, Y. Calzavara, H. Guyon, C. Jarousse, B. Stepnik, D. Wachs and A. Robinson in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Prague, Czech Republic (2012).
- [6] S. Van den Berghe, W. Van Renterghem and A. Leenaers, *J. Nucl. Mater.* 375 (2008) 340-346.
- [7] Y. S. Kim, G. Hofman and J. S. Cheon in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Prague, Czech Republic (2012).
- [8] A. Leenaers, S. Van den Berghe, E. Koonen, C. Jarousse, F. Huet, M. Trotabas, M. Boyard, S. Guillot, L. Sannen and M. Verwerft, *J. Nucl. Mater.* 335 (2004) 39-47.
- [9] A. Leenaers, S. Van den Berghe, W. Van Renterghem, F. Charollais, P. Lemoine, C. Jarousse, A. Röhrmoser and W. Petry, *J. Nucl. Mater.* 412 (2011) 41-52.
- [10] G. L. Hofman, Y. S. Kim, H. J. Ryu, J. Rest, D. M. Wachs and M. R. Finlay in: Proceedings of the 10th International Topical Meeting on Research Reactor Fuel Management (RRFM), Sofia, Bulgaria (2006).
- [11] Y. S. Kim, G. Hofman and A. B. Robinson in: Proceedings of the International Topical Meeting on Research Reactor Fuel Management (RRFM), Vienna, Austria (2009).

- [12] A. Leenaers, S. V. d. Berghe, S. Dubois, J. Noirot, M. Ripert and P. Lemoine in: Proceedings of the International Topical Meeting on Research Reactor Fuel Management (RRFM), Hamburg (Germany) (2008).
- [13] S. Van den Berghe, A. Leenaers, E. Koonen and L. Sannen, Adv. Sci. Techn. 73 (2010) 78-90.
- [14] S. Van den Berghe, A. Leenaers and C. Detavernier in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Marrakech, Marocco (2010).
- [15] S. Van den Berghe, A. Leenaers and C. Detavernier in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Rome, Italy (2011).
- [16] R. Jungwirth, T. Zweifel, H.-Y. Chiang, W. Petry, S. Van den Berghe and A. Leenaers in: Proceedings of the 33rd International Meeting of Reduced Enrichment for Research and Test Reactors (RERTR), Santiago, Chile (2011).
- [17] T. Zweifel, H. Palancher, A. Bonnin, F. Charollais, A. Leenaers, S. Van den Berghe, R. Jungwirth, W. Petry and P. Lemoine in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Prague, Czech Republic (2012).
- [18] A. Leenaers, S. Van den Berghe and C. Detavernier in: Proceedings of the International Conference on Research Reactor Fuel Management (RRFM), Rome, Italy (2011).
- [19] V. Teixeira, Vacuum 64 (2002) 393-399.
- [20] J. F. Ziegler (2000). SRIM-2000 computer code. The Stopping and Range of Ions in Solids. J. F. Ziegler, J. P. Biersack and U. Littmark, Pergamon Press (1985).
- [21] J. L. Snelgrove, "Good practices for qualification of high density low enriched uranium research reactor fuels.", International Atomic Energy Agency, IAEA nuclear energy series no. NF-T-5.2 (2009).