STUDY OF THE LONG-TERM STABILITY OF MULTI-LAYER MHD COATINGS FOR FUSION REACTOR APPLICATIONS – B. A. Pint, K. L. More, J. L. Moser (Oak Ridge National Laboratory), A. Jankowski (Lawrence Livermore National Laboratory), and A. Suzuki (University of Tokyo, Japan)

OBJECTIVE

The objective of this task is to assess the long-term, high-temperature compatibility of high electrical resistance, multi-layer coatings with lithium at high temperatures. Electrically insulating coatings on the first wall of magnetic confinement reactors are essential to reduce the magnetohydrodynamic (MHD) force that would otherwise inhibit the flow of the lithium coolant. An assessment of the crack tolerance for these coatings determined that a multi-layer coating with metal and ceramic layers was needed to prevent Li from wetting cracks or defects in a single-layer ceramic coating. Experimental compatibility tests are being conducted on bulk materials and single and multi-layer coatings.

SUMMARY

Characterization of electron beam physical vapor deposition (EB-PVD) Y_2O_3 coatings after exposure to Li showed significant changes in the microstructure. Single and bi-layer PVD coatings of Er_2O_3 and Er_2O_3/vanadium have been fabricated and initial characterization has started. A new test rig was constructed for measuring coating resistivity during contact with Li at temperatures up to 500°C. Initial performance of the Er_2O_3 coatings in an in-situ test showed loss of insulating behavior after the Li became liquid (180°C) and significant degradation after exposure to Li at 500°C.

PROGRESS AND STATUS

Introduction

The current focus of the U.S. MHD coating program is the fabrication and testing of multi-layer coatings with a combination of ceramic, high-resistance layers and vanadium layers to prevent interaction between Li and the ceramic layer. A recent evaluation of the effects of cracks and defects on the performance of single-layer MHD coatings concluded that only a very small fraction of through-thickness cracks could be tolerated, assuming that Li will wet the cracks and short the coating.[1] Besides wetting, Li ions also could dope the ceramic layer, thereby increasing its conductivity. Thus, a more robust flaw-tolerant coating system would have a dense metallic layer in contact with the flowing Li. Vanadium would be the prime metallic coating candidate among refractory metals with good Li compatibility at 700°C. This strategy switches the main lithium compatibility requirement from the ceramic layer to the metallic layer and thereby increases the number of candidate materials. However, the ceramic layer must have some degree of compatibility in case the metallic layer has a defect or fails in service.

The results presented in this report include the final characterization work for the EB-PVD Y_2O_3 coatings before and after capsule exposures to Li at 800°C. The compatibility results for these coatings have been presented previously.[1-3] Initial results for a new batch of single layer Er_2O_3 coatings and two layer Er_2O_3/V coatings fabricated in late 2004 also are included.

Experimental Procedure

Current work focused on V-4Cr-4Ti 15mm diameter substrates with Y_2O_3 , Er_2O_3 or Er_2O_3/V coatings made by EB-PVD at Lawrence Livermore National Laboratory (LLNL). Before and after exposure to Li, Y_2O_3 coated specimens were sectioned by focused ion beam (FIB) thinning and examined by scanning electron microscopy (SEM) and analytical transmission electron microscopy (TEM). Additional information

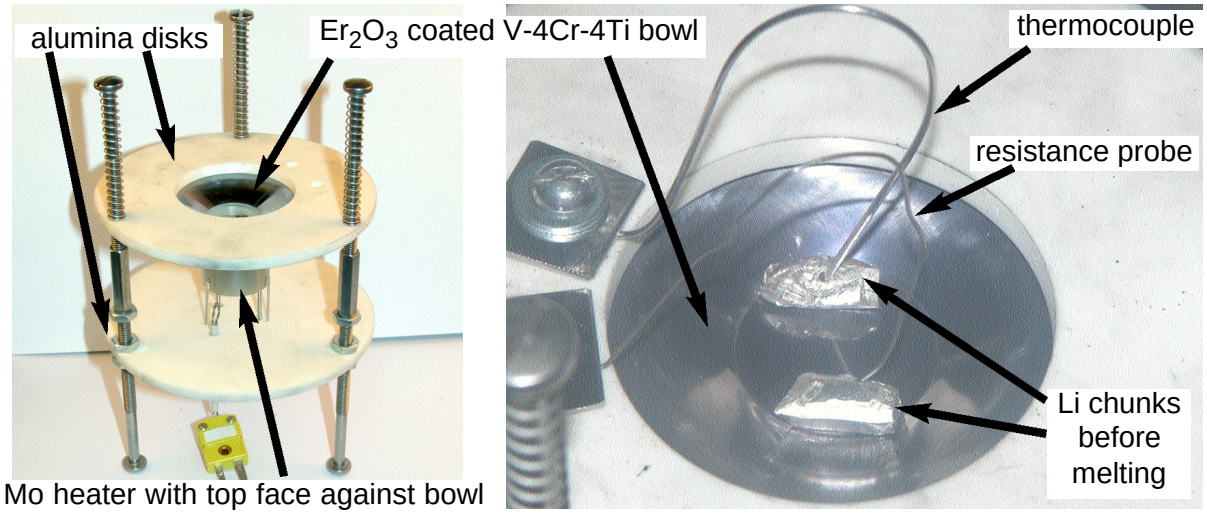

Fig. 1. Photographs of the in-situ rig in an ORNL glove box used to measure resistance of the coatings in contact with liquid Li at temperatures up to 500°C.

about the as-deposited Y_2O_3 coatings are included elsewhere.[1-3] Coatings of Er_2O_3 and Er_2O_3/V were received in late 2004 and characterization is currently underway. An initial test was performed to evaluate a new in-situ test rig shown in Fig. 1. The unit was designed to measure resistance of a coating on a bowl shaped specimen filled with 0.5g of Li at temperatures up to 500°C in a glove box (to minimize Li reaction with O and N). Springs hold the bowl in contact with an alumina disk and a Mo heater. The unit was tested with an uncoated bowl and it was found that Li vaporization was excessive above 500°C, and after 48h at 500°C the Li began to react significantly with impurities (1-2ppm O_2, N_2, H_2O, etc.) in the Ar glove box atmosphere.

Results and Discussion

TEM Characterization. In order to better understand the previously reported[1,4] interaction between Y_2O_3 and Li, characterization work has continued to include polished cross-sections of the 12.5µm thick EB-PVD Y_2O_3 coatings and TEM cross-sections near the substrate-coating interface. The as-deposited EB-PVD coating is shown in Fig. 2. The microstructure is typical of the EB-PVD process. The TEM image in Fig. 2b shows a clean interface between the coating and V-4Cr-4Ti substrate and a coating with a columnar morphology and limited porosity along some grain boundaries.

A very different microstructure was observed after exposure to Li at 800°C. Figure 3 shows polished cross-sections of coatings exposed for 100h and 1000h. After 100h, the original coating microstructure was not retained and gaps between the coating and substrate are apparent, Fig. 3a. After 1000h, the coating crumbled during specimen preparation, Fig. 3b. However, remnants of the Au electrode that was applied after exposure to measure the resistivity were observed. Cross-sections for TEM were made of these specimens near the coating-substrate interface. Unlike the as-deposited columnar micro-structure (Fig. 2b), the grains near the interface were much larger and equiaxed after 100h at 800°C in Li with a few large intergranular pores, Fig. 4a. (Before exposure, only fine intergranular pores were observed, Fig. 2b.) Near the coating-substrate interface, a fine-grained layer was observed with a porous layer above and below it. Energy dispersive x-ray analysis (EDX) showed that the Y/O ratio was slightly higher in this layer. It is not certain if this is because of Li incorporation in the outer layer (which is undetectable by EDX) or O depletion due to interdiffusion with the vanadium alloy substrate. (Vanadium has a high O solubility and will dissolve surface oxides during annealing.[5,6]) Both the inner and outer layers had a cubic structure

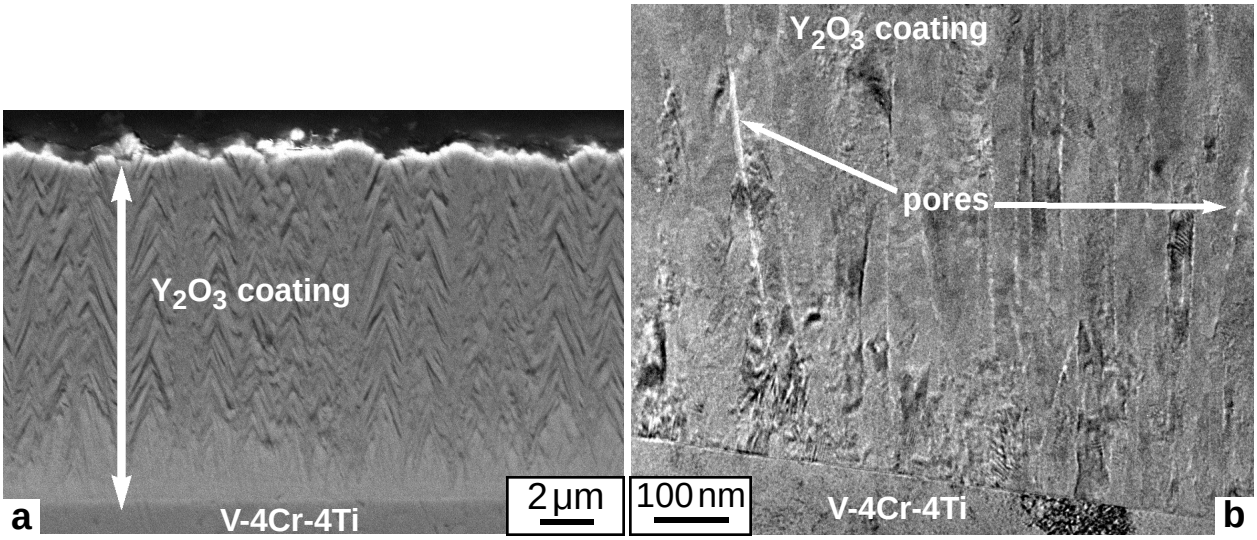

Fig. 2. Cross-sections of the as-received Y_2O_3 coatings. (a) secondary electron image of a polished section and (b) bright-field TEM image of FIB-thinned section near the coating-substrate interface. Arrows mark pores along some grain boundaries.

with a measured d-spacing of 3.12Å, identical to the as-deposited coating.

After 1000h at 800°C in Li, the general equiaxed microstructure was similar but the distinct inner layer was no longer observed, Fig. 4b. In this case, a thin interfacial layer was observed to be rich in vanadium (peak concentration of 6 at.%) and contain small Ti-rich oxide particles. Further characterization of the FIB cross-sections by Auger electron spectroscopy (AES) will be performed to detect Li within the coating.

Er_2O_3 Coatings. Twelve coatings on V-4Cr-4Ti coupons were fabricated in 4 batches in an initial attempt to assess the performance of EB-PVD Er_2O_3 coatings. The coupons were polished to a 600 grit surface before deposition. Two of the batches had a ≈8µm Er_2O_3 layer and two had a ≈20µm layer. The coatings were deposited at elevated substrate temperatures in anticipation of subsequent high-temperature exposures in Li. Substrate temperatures were incrementally varied from 550° to 720°C. One coating from each batch was then coated with 2µm of V in the center of the coupon to prevent the metallic coating from contacting the substrate. X-ray diffraction (XRD) of coated specimens showed that the coatings were poly-crystalline Er_2O_3. For example, Fig. 5 shows an XRD scan of a 21µm thick Er_2O_3 coating deposited at

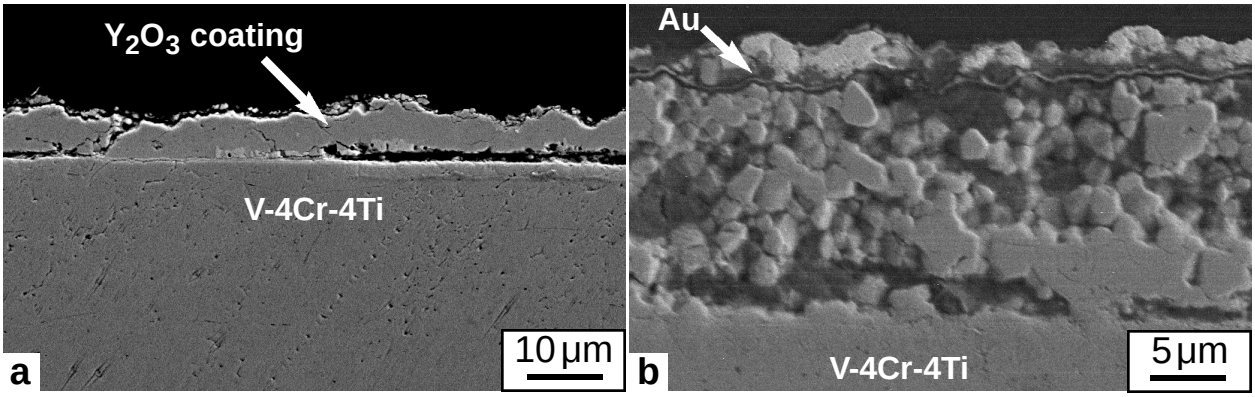

Fig. 3. Secondary electron images of polished cross-sections of the Y_2O_3 coatings after 800°C capsule exposures to Li for (a) 100h and (b) 1000h.

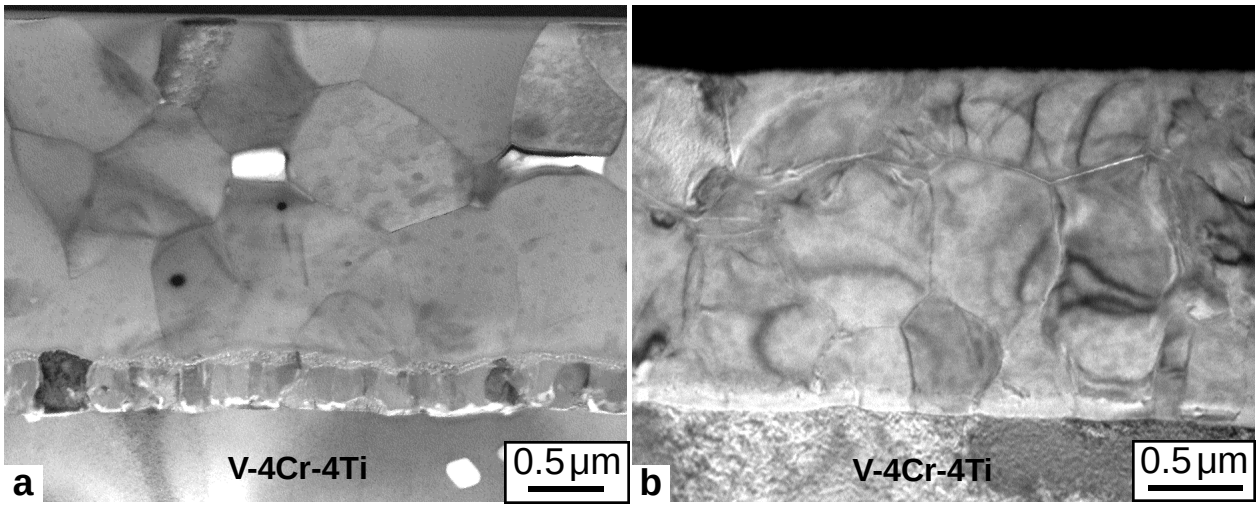

Fig. 4. TEM bright field images of cross-sections of the Y_2O_3 coatings near the coating-substrate interface after 800°C capsule exposures to Li for (a) 100h and (b) 1000h.

720°C. The peaks are consistent with all of and only those reflections reported for polycrystalline Er_2O_3. The morphology of one of the two layer coatings with 8µm of Er_2O_3 and a center region coated with 2µm of V was examined by SEM. Figure 6a shows the Er_2O_3 morphology without the V layer. Figure 6b shows the same specimen in the region coated with V. The roughness of this underlying Er_2O_3 layer leads to a convoluted and likely porous V layer.

Two bowl-shaped specimens were EB-PVD deposited at coating temperatures of 545° and 555°C. These specimens were used to test the performance of the in-situ test rig. One bowl specimen had only a ≈8µm Er_2O_3 coating. At room temperature, chunks of Li weighing 0.5g were placed in the bowl, Fig. 1, and it showed high resistance, effectively an open circuit. The bowl was heated slowly to 500°C. At 180°C, when the Li became liquid, the coating shorted and the resistance was ≈8Ω up to 500°C. Before the Li solidified on cooling, the excess Li was poured out of the bowl and the bowl was cleaned by immersion in methanol for 5h. Figure 7 shows the bowl after cleaning. The coating was removed everywhere the liquid Li touched it. The residue looked like fine black flakes.

The second bowl specimen had ≈11µm Er_2O_3 and a 2µm V layer. It was heated in the test rig to 500°C in the glove box without Li and held for 2h to check the coating resistance. An open circuit (high

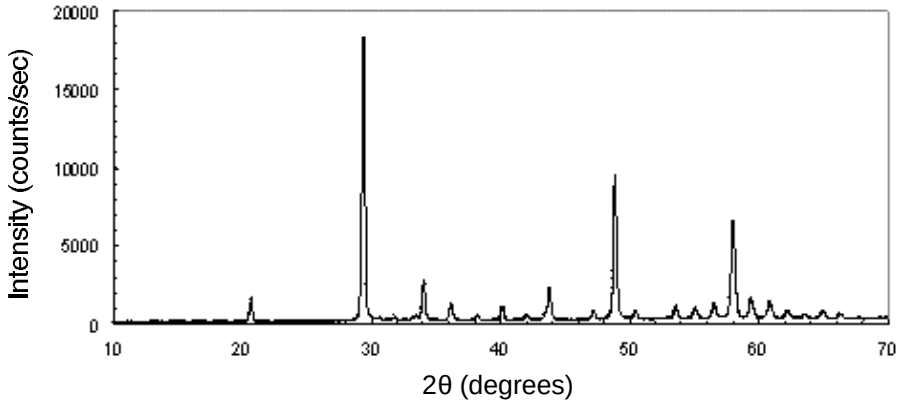

Fig. 5. XRD scan of a 21µm thick EB-PVD Er_2O_3 coating deposited at 720°C.

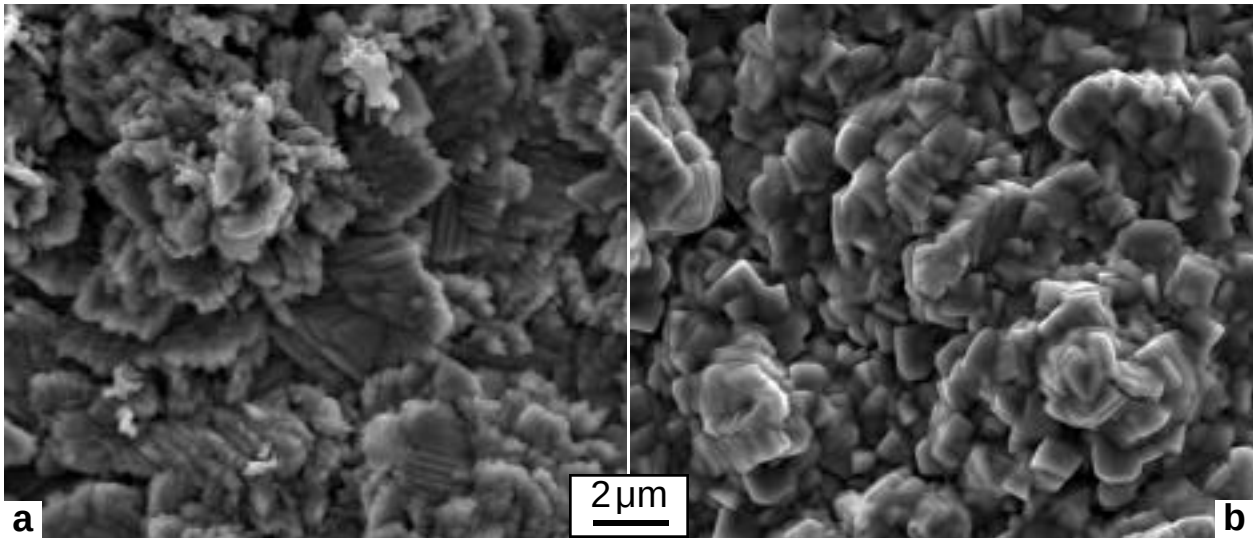

Fig. 6. SEM secondary electron plan-view image of the as-received EB-PVD Er_2O_3 bi-layer coating (a) outside region with only 8µm Er_2O_3 coating and (b) inner region with overlying 2µm vanadium layer.

resistance) was measured throughout heating and cooling to room temperature. However, when Li was added to this specimen, a similar result was observed with the coating shorting at 180°C. This specimen was cleaned by distillation. It had a similar appearance as the specimen shown in Fig. 7 with the coating removed as black flakes where it was in contact with Li. The residual coating and flakes will be characterized by Auger electron spectroscopy and XRD.

Several Li capsule tests with the Er_2O_3 and Er_2O_3/V coatings have been started at 800°C. Additional characterization of the as-deposited Er_2O_3 coatings also will be performed. Based on the morphology in Fig. 6b, a thicker V coating will be fabricated in the future to provide a dense, continuous Li barrier. Different insulating layer materials that have shown potential to meet the MHD coating performance metrics [7] (e.g., Y_2O_3) also may be evaluated in combination with a V overcoat.

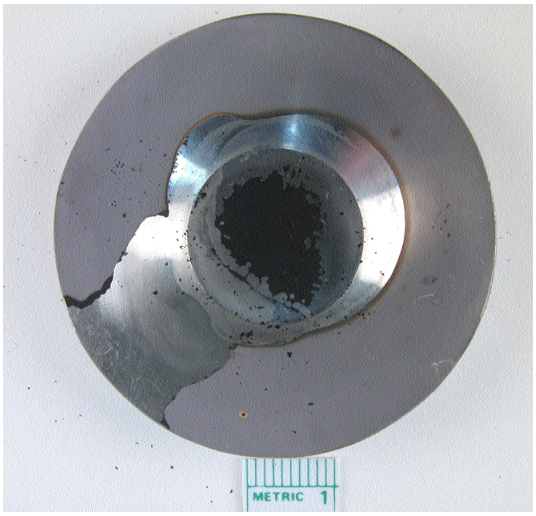

Fig. 7. Photograph of the Er_2O_3 coated specimen after exposure to Li. A pool of liquid Li was in the center of the bowl at up to 500°C. After cooling, excess Li was poured off before it solidified.

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