STUDY OF THE LONG-TERM STABILITY OF MHD COATINGS FOR FUSION REACTOR APPLICATIONS -- B. A. Pint and L. D. Chitwood (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to assess the long-term, high-temperature compatibility of high electrical resistance 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. Initial experimental work was conducted on bulk ceramics to determine basic lithium compatibility and maximum-use temperatures of candidate ceramics such as AlN and Y_2O_3. As the next step, coatings of Y_2O_3 are now being evaluated.

SUMMARY

Coatings of Y_2O_3 (12.5µm thick) were formed on V-4Cr-4Ti substrates using electron-beam assisted, physical vapor deposition (EB-PVD). The resistivity of the as-received, 12.5µm thick coatings was lower than literature values for bulk Y_2O_3, possibly due to cracks or pores in the coating. Coated substrates were exposed to Li in vanadium alloy capsules at 700° and 800°C for up to 1000h. One specimen was exposed to Li for three sequential 100h thermal cycles at 800°C and was cooled to room temperature between cycles. All of the exposed specimens were largely intact after exposure although x-ray diffraction indicated some reaction with the Li. The resistivity of several exposed coatings was measured to 500°C. The specimen exposed for 3, 100h cycles at 800°C showed no drop in resistivity after exposure while the specimen exposed for 1000h at 800°C showed a lower resistivity.

PROGRESS AND STATUS

Introduction

Previous work[1,2] where the Li compatibility of bulk ceramics was examined in capsule tests suggested that Y_2O_3 was an attractive MHD coating candidate. Polycrystalline Y_2O_3 specimens showed little mass change after 1000h exposures in Li at 700° and 800°C. Also, its resistivity at 700°C was sufficient for the MHD coating application.[3] Therefore, Y_2O_3 coatings were fabricated to examine their performance before and after exposure to Li.

Experimental Procedure

Current work focused on Y_2O_3 coatings made by EB-PVD at Lawrence Livermore National Laboratory by A. Jankowski and J. Hayes. Ten 12.5mm diameter x 1mm thick V-4Cr-4Ti substrates polished to a 1µm finish were coated with Y_2O_3 in two batches by rastering an electron beam over a pressed powder Y_2O_3 target. Using laser profilometry, the thickness of the as-received coatings was determined to be 12.5µm. The experimental procedure for lithium exposures has been outlined elsewhere.[4,5] Coated specimens were exposed for 100h and 1000h at 700° and 800°C. To check the adhesion of the coating in thermal cycling, one specimen was heated to 800°C for 100h and cooled to room temperature three times before the capsule was

opened and the specimen removed. Specimen dimensions and mass were measured before and after exposure (0.01mg/cm^2 accuracy). After exposure to Li, the first specimen was distilled in vacuum at 500-550°C to remove residual Li from the specimen. (The same procedure was used to clean the bulk specimens.) However, the V-4Cr-4Ti substrate oxidized due to a leak in the vacuum system. To avoid this problem, subsequent specimens were cleaned by submerging them in methanol for 24h at room temperature. Before and after exposure, the coated specimens were characterized using field emission gun, scanning electron microscopy (SEM), auger electron spectroscopy (AES) and x-ray diffraction (XRD) with 300kV Cu Kα radiation. The resistance was measured by sputtering a gold electrode (5.1mm diameter) and surrounding guard ring to limit current leakage on the surface of the coating. The specimen was then heated to 500°C in a vacuum system with a pressure of ≈10^{-6} Torr to limit oxidation of the V-4Cr-4Ti substrate. Voltages of 5-30V were applied with a Hewlett-Packard voltage source and current was measured as a function of temperature using a Keithley picoammeter.

Results and Discussion

As-received coating specimens were characterized using SEM and XRD. Figure 1 shows the as-received surface morphology which is typical of the EB-PVD process and indicates the coating grain size is <0.5µm. Figure 2a shows the coating's diffraction spectra from the coating which was a near perfect match with the Y_2O_3 standard (JCPDS card #41-1105). The resistivity of one coated specimen as a function of temperature is shown in Figure 3. It was significantly less than that reported for bulk Y_2O_3.[3] Two additional Y_2O_3 specimens were coated with an electrode to check the resistivity of the as-received coating. In both cases, a short circuit was measured suggesting that Au had infiltrated the coating and that cracks or pores in the as-received EB-PVD coating may have reduced its measured resistivity.

Three coatings have been exposed at 800°C for times of 100h, 3x100h and 1000h. The coating exposed for 1000h at 800°C showed a mass gain of 1.5mg but since an uncoated V-4Cr-4Ti

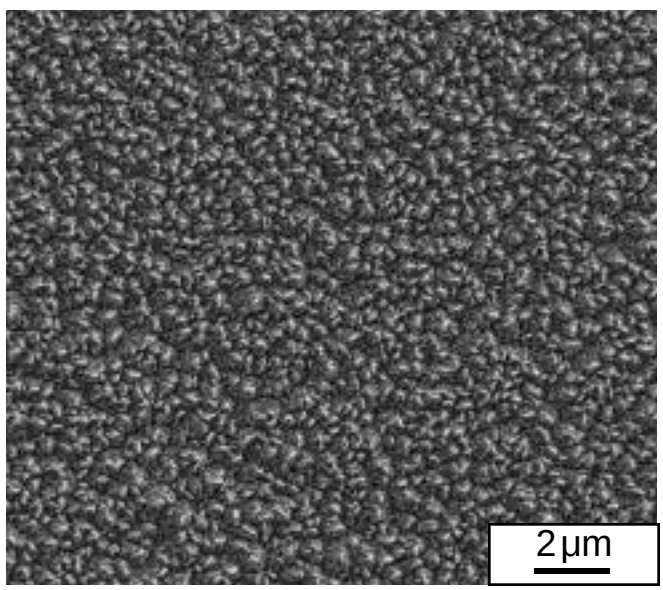

Figure 1. SEM secondary electron plan-view image of the as-received EB-PVD Y_2O_3 coating.

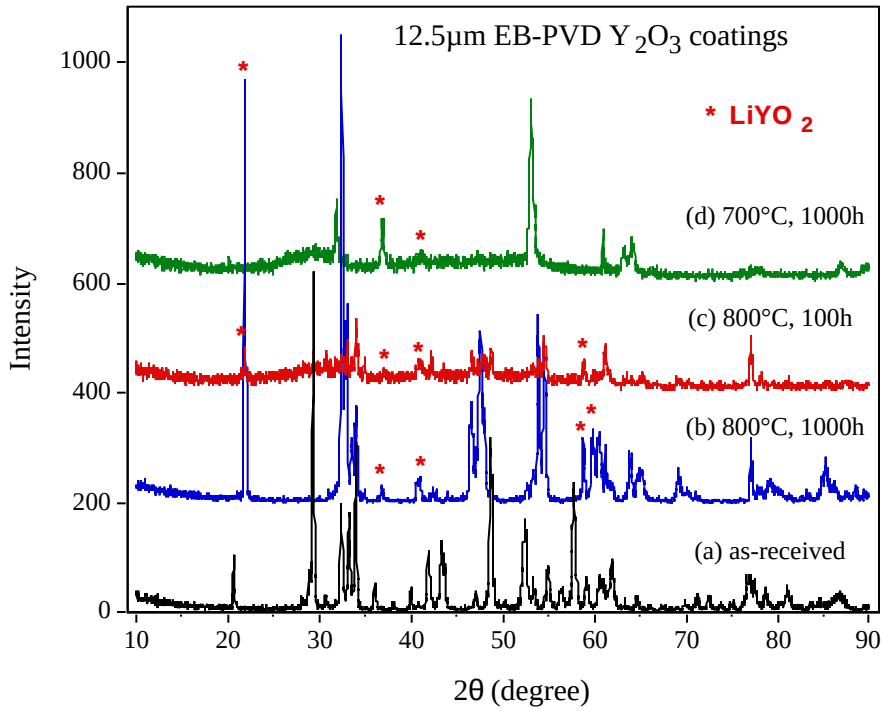

Figure 2. X-ray diffraction data from Y_2O_3 coatings (a) as-received and after exposure to Li for (b) 1000h at 800°C, (c) 100h at 800°C and (d) 1000h at 700°C. Asterisks mark $LiYO_2$ peaks.

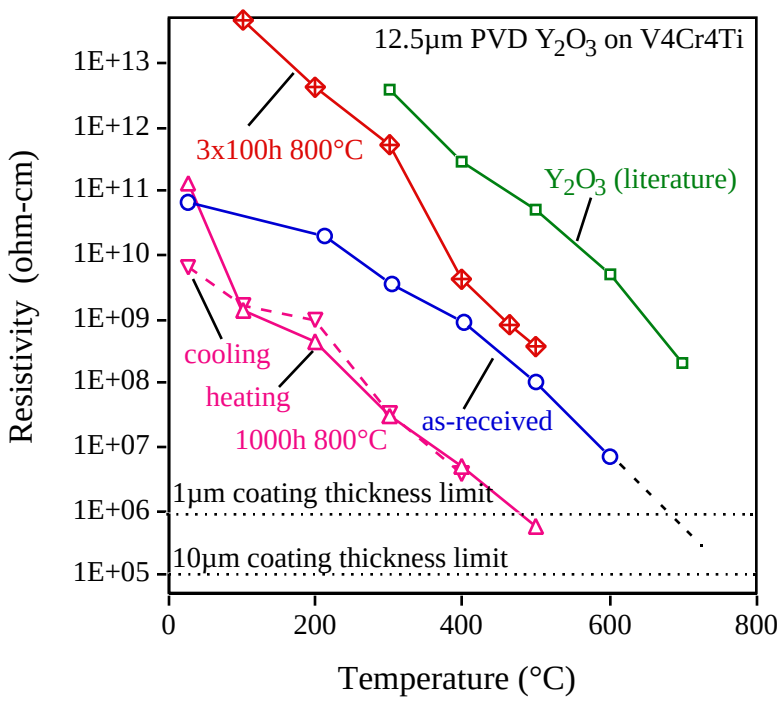

Figure 3. Resistivity as a function of temperature for EB-PVD Y_2O_3 coatings before and after exposure to Li at 800°C.

specimen has not been examined it was difficult to assess whether the mass gain was in the Y_2O_3 coating or the substrate. These specimens will be cross-sectioned at a later stage to better understand any changes in the coating microstructure.

The specimen was examined by AES and Li "nodules" were observed on the coating surface. These nodules were not present when the specimen was first introduced into the vacuum and therefore, must have grown during beam exposure. Their presence indicated that residual Li was present in the coating even after a second cleaning in methanol. Some regions contained only Y and O with no Li detected while other nodules contained Ti. The presence of Ti and Li may explain the specimen mass gain after exposure. The Ti could be from the substrate or the capsule walls. The as-received coating was checked by AES and no Ti was detected.

The specimen exposed for 1000h at 800°C also was examined by XRD and Figure 2b shows that many of the original Y_2O_3 peaks have disappeared and the coating has reacted with Li and possibly Ti to form additional phases. The large peak at 22° matches the pattern for $LiYO_2$ as do several other peaks, however, several of the other major peaks have not been conclusively identified. The observation of $LiYO_2$ is consistent with an earlier study of bulk Y_2O_3 in Li at 500°C.[6] The unidentified peaks could be from other Y-O or Y-Ti-O compounds. The specimen was then coated with a gold electrode to measure the resistivity. Compared to the as-received coating, the Li exposure for 1000h at 800°C appeared to show a significantly lower resistivity, Figure 3. On cooling to room temperature the measured current was significantly higher indicating a lower resistivity by more than an order of magnitude, Figure 3. However, examination of the specimen revealed that ≈30% of the electrode had disappeared. The degradation of the Au electrode has been attributed to a reaction with free Li in the coating, as observed by AES. Lithium readily dissolves Au. The resistance of this specimen will be remeasured with a layered Au-Ni electrode that may be more resistant to reaction with Li.

The specimen exposed for 100h also was examined by XRD, Figure 2c. Again, a mixture of Y_2O_3, $LiYO_2$ and unidentified peaks were observed but at somewhat different intensities than the 1000h exposure. Compared to the 1000h results, many of the $LiYO_2$ peaks were smaller after only a 100h exposure. This observation indicates there is a significant reaction with Li after only 100h and this reaction increases after longer exposures.

The resistivity of the specimen exposed for 3, 100h cycles at 800°C also was measured, Figure 3. In this case, the resistivity measured at low temperatures was higher than the as-received coating but the resistivity measured at higher temperatures was similar to the as-received coating at 400°-500°C. One difference with this measurement was that the voltage was maintained at 5V instead of varying it. By maintaining a constant, low voltage during heating, it was observed that there was less variation in the current measurements and more consistent results were obtained. This may be the reason that higher resistivity values were measured for this specimen. Additional resistance measurements need to be made in this manner with different voltages and dwell times in order to confirm these results.

Two specimens also were exposed at 700°C. The Y_2O_3 specimen exposed for 100h at 700°C showed no visual degradation, but the V-4Cr-4Ti substrate was oxidized during distillation and no further characterization was conducted. The XRD results for the specimen exposed for 1000h at 700°C are shown in Figure 2d. As with the specimens exposed at 800°C, the majority of Y_2O_3

peaks are missing and a few peaks match $LiYO_2$. However, the largest peak at ≈53° has not been identified. Unfortunately this specimen was damaged during handling in the diffractometer and no resistivity measurement was possible.

In terms of meeting the coating metrics of the U.S. Fusion Materials Program,[7] these results come close to showing that Y_2O_3 is a viable MHD coating candidate for Li loop testing. The Li capsule tests performed at 800°C are higher than the required 700°C exposure temperature. Yttria did not meet the requirement of limited (<10%) reaction with Li, but the remaining phases appear to have reasonable resistivity values. The resistivity measurements also need to be continued up to 700°C in order to satisfy the metrics. (The heating elements in the current system were not sufficient to heat the specimen and holder to 700°C. A smaller holder with higher temperature heating elements is being fabricated.) However, the effect of temperature appears to be consistent in each of the measurements suggesting that the current data can be extrapolated to 700°C, Figure 3. If this is done, the as-received coating would marginally meet the required resistivity as would the cycled specimen. However, the specimen exposed for 1000h at 800°C would not.

Based on these results, additional testing is being conducted on this set of coatings. Additional isothermal and cyclic tests are being conducted at 700°C. Because of the increased $LiYO_2$ peaks observed between 100 and 1000h at 800°C, a 2000h exposure at 800°C also is being conducted. The low resistivity of the as-received coating compared to literature values and the problems with measuring resistance on other as-received coatings suggests that the coating quality could be improved. This may result in improved resistivity performance. However, this coating did show good adhesion for a first attempt. Finally, the resistivity measurement was modified slightly for each specimen examined. This procedure needs to be standardized and verified to insure accuracy and reproducibility.

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