6.1 ADDITIONAL CHARACTERIZATION OF V-4Cr-4Ti AND MHD COATINGS EXPOSED TO FLOWING Li – B. A. Pint and K. A. Unocic (Oak Ridge National Laboratory)

OBJECTIVE

A flowing Li thermal convection loop was operated with V-4Cr-4Ti specimens and multi-layer electrically-insulating coatings needed to reduce the magneto hydrodynamic (MHD) force in the first wall of a lithium cooled blanket. Characterization is being completed to conclude this experiment.

SUMMARY

Additional results are presented on the characterization of a dual layer (Y_2O_3/V) MHD coating exposed to flowing Li at ~688°C. This coating was exposed at the highest temperature and had the largest volume of a "new" phase formed at the V-4Cr-4Ti substrate-Y_2O_3 interface. Extensive analytical transmission electron microscopy has not definitively identified the phase, partly because it is unstable under the electron beam. However, it is assumed to be $LiYO_2$ that formed due to Li ingress along the substrate-V overlay coating interface.

PROGRESS AND STATUS

Introduction

A monometallic Li loop experiment with a peak temperature of 700°C was run for 2,350 h in 2007.[1] Subsequent reports have characterized the tensile behavior of the V-4Cr-4Ti specimens exposed in the loop and characterized the microstructure and electrical resistance of the dual layer (Y_2O_3/V) MHD coatings deposited by physical vapor deposition (PVD) that were exposed in the same loop.[2-7] The coating resistivity was degraded for specimens exposure in the loop above ~500°C. One remaining issue was the identification of a new phase at the V-4Cr-4Ti substrate-Y_2O_3 interface.[5,6] The amount of this phase appeared to be dependent on the exposure temperature in the loop but no new phase was formed when one of the coatings was annealed for 2,350 h at 700°C. Therefore, it was suspected that this phase contained Li, such as $LiYO_2$, observed in previous compatibility studies.[8-10] The characterization of the MHD coating exposed at ~688°C in the loop is presented to conclude this work.

Experimental Procedure

Details of the thermal convection loop exposure have been presented previously.[1] The specimens consisted of 25mm tensile specimens, tab specimens and specimens with a dual layer MHD coating linked in a chain held together with V-4Cr-4Ti wire. The exposure temperature for each specimen was estimated by using a linear extrapolation of the temperatures measured at the top and bottom of the each leg. For the MHD coated specimens, characterization included scanning electron microscopy (SEM), electron probe microanalysis (EPMA), x-ray photoelectron spectroscopy (XPS), and scanning transmission microscopy (STEM), including energy x-ray dispersive spectroscopy (EDS), selected area diffraction (SAD) and electron energy loss spectroscopy (EELS) with TEM specimens prepared by focused ion beam (FIB) milling.

Results and Discussion

Figure 1a shows the TEM cross-section of the 688°C coating as-prepared and Figure 1b shows the same region after EDS and SAD analysis. The "new" phase appeared to degrade after exposure to the electron beam, which is consistent with a Li-containing oxide with mobile Li atoms. The EDS line profile marked in Figure 1a is shown in Figure 2. It is not possible to detect Li by EDS. The substrate-oxide interface

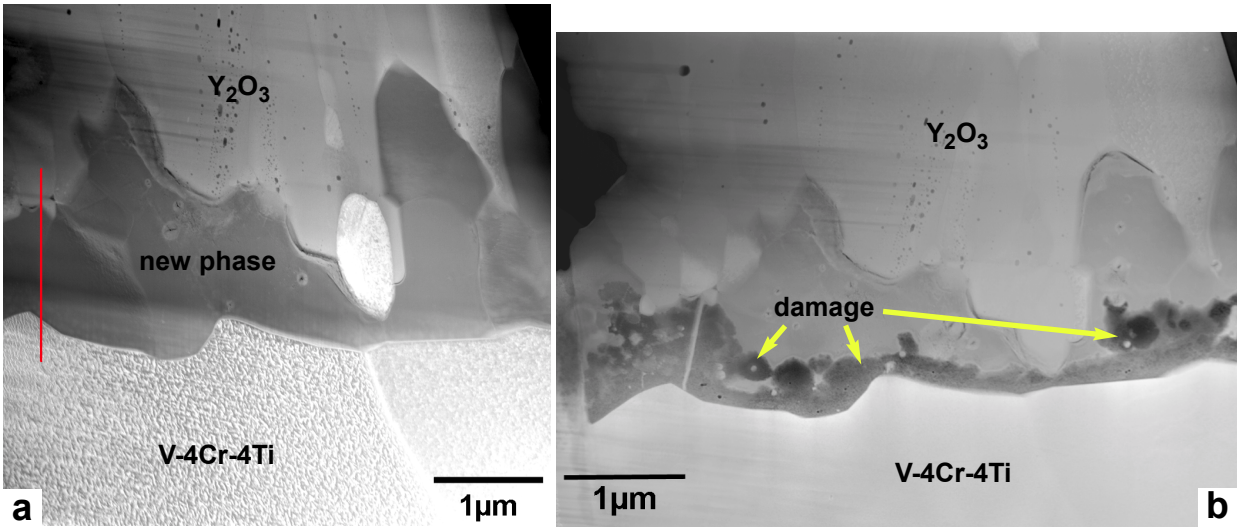

Figure 1. STEM annular dark field images of the dual layer MHD coating after Li loop exposure at 688°C; (a) original image showing new dark gray phase and location of line profile, (b) same region after analysis appears to have been damaged by the electron beam.

appears to be very sharp in the Cr, Ti and Y profiles but some V does appear to be present in the oxide phase near the metal interface. The high O signal in the V-4Cr-4Ti substrate may be attributed to the higher specimen thickness in the metal. There does not appear to be any change in the Y and O concentration profiles at the interface between the Y_2O_3 phase and the new phase. The d-spacing of the SAD patterns did not match any known phases. It was difficult to align the specimen for SAD because the specimen was being damaged by the electron beam.

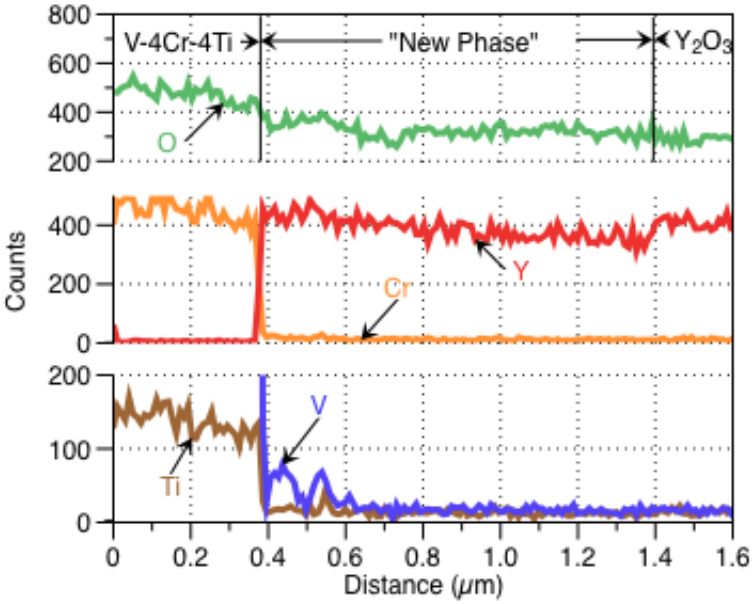

Figure 2. EDS line profile from the line marked in Figure 1a.

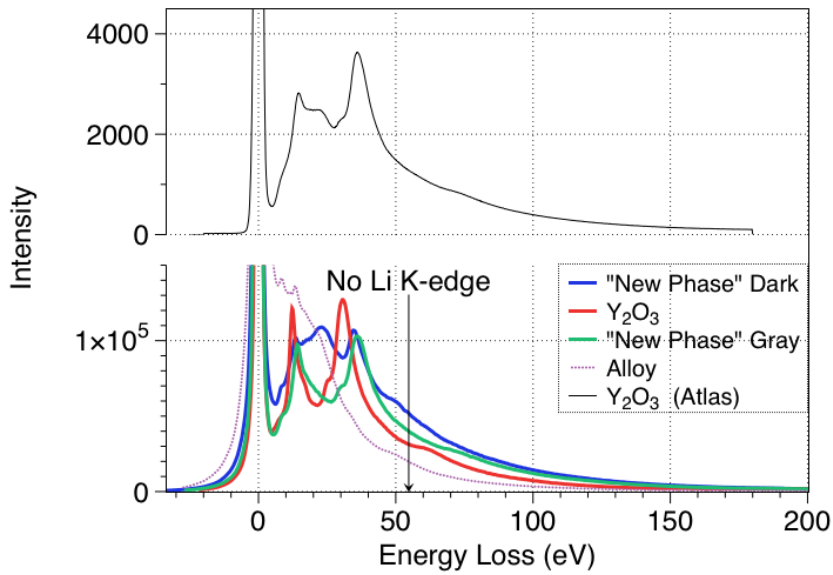

Figure 3. EELS profiles for the various phases in Figure 1b. A slight bump at 55eV in the dark phase may be due to Li.

In order to identify Li in the new phase, XPS and EELS were subsequently used. However, in both cases, Li was not detected. Figures 3 and 4 show EELS profiles from the different areas in Figure 1b where both "light" and "dark" new phases can be seen after the EDS and SAD analysis. No significant Li peak was detected at 55 eV using EELS, Figure 3. One concern is that to detect Li a very thin specimen is needed to minimize the signal (noise) between the 0 eV peak and 100 eV. Even with the current specimen

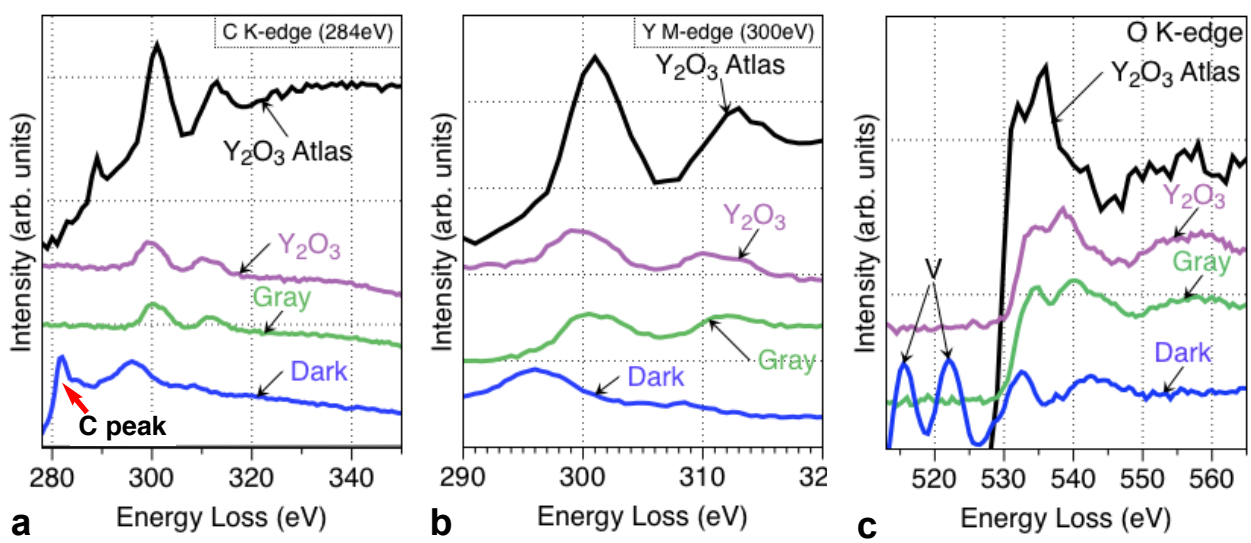

Figure 4. EELS profiles for three energy loss ranges for the Y_2O_3 and new "gray" and "dark" phases in Figure 1b (a) C at 284eV, (b) Y(M edge) at 300eV and (c) O(K edge) at 532eV. The atlas values for Y_2O_3 are shown for comparison.

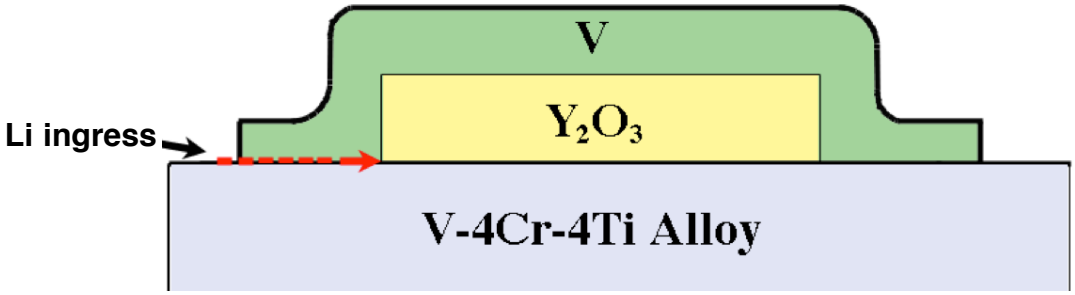

Figure 5. Schematic of the possible path for Li ingress from the loop environment to react with Y2O3 at the oxide-substrate interface.

thickness, the electron beam was making holes in the specimen, similar to the previous experience with $LiYO_2$ and $LiAlO_2$.[9,11] Figure 4 confirms that the outer layer is Y_2O_3 (compared to atlas values) and perhaps the lighter gray layer in Figure 1b has now transformed to primarily Y_2O_3, based on the similar EELS profiles in Figure 4. The dark gray oxide in Figure 1b appears to contain C (peak in Figure 4a) and V (peak in Figure 4c). The V was detected in the oxide by EDS and may have occurred by interdiffusion, but the C may be due to contamination in the microscope.

Finally, Figure 5 shows a schematic for how the Li may have penetrated the PVD coating during exposure in the loop and enabled the $LiYO_2$ phase to form. Native oxide on the V-4Cr-4Ti substrate could have been selectively attacked at this interface and provided a pathway for Li penetration. Nominally, such a pathway would not be available if the coating were applied to the entire flow channel.

References

[1] B. A. Pint, et al., J. Nucl. Mater. 386-388 (2009) 712.
[2] B. A. Pint, DOE/ER-0313/45 (2008) 11.
[3] B. A. Pint, DOE/ER-0313/46 (2009) 1.
[4] B. A. Pint and K. A. Unocic, DOE/ER-0313/51 (2011) 67.
[5] K. A. Unocic, M. Lance and B. A. Pint, submitted to J. Nucl. Mater.
[6] K. A. Unocic, D. N. Leonard, H. M. Meyer, M. J. Lance and B. A. Pint, in Proc.8th Int. Symp. High Temperature Corr. Protection of Materials, Les Embiez, France, May 2012, Paper#176.
[7] B. A. Pint and K. A. Unocic, DOE/ER-0313/52 (2012) 111.
[8] T. Terai, et al., J. Nucl. Mater. 233-237 (1996) 1421.
[9] B. A. Pint, K. L. More, H. M. Meyer and J. R. DiStefano, Fusion Sci. Technol. 47 (2005) 851.
[10] M. Nagura, A. Suzuki, K. Sasaki and T. Terai, Fusion Eng. Design 85 (2010) 1098.
[11] B. A. Pint and K. L. More, J. Nucl. Mater. 376 (2008) 108.