

COMPATIBILITY OF MULTI-LAYER, ELECTRICALLY INSULATING COATINGS FOR THE VANADIUM-LITHIUM BLANKET—B. A. Pint and J. L. Moser (Oak Ridge National Laboratory), A. Jankowski and J. Hayes (Lawrence Livermore National Laboratory)

OBJECTIVE

The objective of this work is to demonstrate that a multi-layer, electrically-insulating coating will be an acceptable solution to reduce the magneto hydrodynamic (MHD) force in the first wall of a lithium cooled blanket. Coatings of Er_2O_3 or Y_2O_3 with an overlying coating of vanadium have been fabricated by physical vapor deposition. Coatings have demonstrated acceptable as-received resistivity at 800°C and at 600°C in contact with Li. When the Y_2O_3 coating was completely covered with a 10 μm vanadium layer, it survived exposure to Li at 800°C without degradation. The interaction between V alloys and Li at 800°C is now the critical compatibility issue and a loop test is being planned. New ceramic materials based on the Y-Ti-O system also are being explored.

SUMMARY

Multi-layer coatings are being investigated to reduce the MHD pressure drop in a lithium-cooled blanket. As the fabrication process is improved, the performance of the coatings is improving with adequate as-deposited and in-situ resistance, and good compatibility being demonstrated in a recent capsule test. The compatibility of a thin (10-100 μm) vanadium overlayer is now critical to coating durability. Initial experiments showed no dissolution of V-4Cr-4Ti after 1,000h at 800°C although the specimens were embrittled after exposure. A planned monometallic loop experiment will help verify the compatibility of V-4Cr-4Ti in Li at 700°C. New insulating ceramic materials are being investigated with $\text{Y}_2\text{Ti}_2\text{O}_7$ showing some promise for this application.

PROGRESS AND STATUS

Introduction

A self-cooled lithium blanket concept is an attractive concept for a fusion reactor because of lithium's tritium breeding capability and excellent heat transfer characteristics. Due to compatibility issues with conventional alloys[1-2] and SiC[3], vanadium alloys[4-6] are the most likely structural materials for this concept. One of the critical issues for this, and any liquid-metal concept, is the need to reduce the pressure drop associated with the magnetohydrodynamic (MHD) force due to the high magnetic field in the reactor.[7-8]

One solution to the MHD problem is to apply an electrically insulating coating to decouple the structure wall from the liquid metal.[9] The coating must be thin, durable and have a high electrical resistivity. It also must be almost crack-free to prevent shorting.[10,11] For many years, the idea of a "self-healing" CaO insulating coating was promoted and investigated.[12-15] However, thermodynamic and experimental results suggested poor long-term stability.[16] Therefore, the current focus of the U.S. program on reducing the MHD pressure drop is on durable multi-layer coatings or a flow-channel insert.[16,17] Both of these solutions has been previously proposed,[8,18,19] however, little experimental verification has been conducted. Therefore, multi-layer coatings have been fabricated for screening and qualification testing. With a multi-layer coating, the compatibility between the V or V alloy overcoat and Li becomes more critical and this issue is being investigated, including plans for a loop experiment. Finally, new ceramic Y-Ti-O candidate coating materials are being explored.

Experimental Procedure

Multi-layer coatings were fabricated on 15mm diameter V-4Cr-4Ti substrates using electron-beam physical vapor deposition (EB-PVD) at Lawrence Livermore National Laboratory (LLNL). Coatings were either Er_2O_3 or Y_2O_3 with vanadium overlayers. The resistivity of as-received coatings was measured in vacuum at temperatures up to 800°C, and specimens were sectioned by focused ion beam (FIB) thinning and examined by scanning electron microscopy (SEM). Bowl shaped V-4Cr-4Ti specimens (5cm diameter, ~1mm thickness) provided by NIFS in Japan were coated by the same process for measuring the in-situ resistivity in contact with Li (~0.5g placed in the bowl) at temperatures up to 600°C.[20] 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 600°C in an Ar-filled 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 compatibility of V-4Cr-4Ti specimens with and without coatings was investigated by conducting capsule experiments using a Mo inner capsule and a type 304 stainless steel outer capsule. High-purity, unalloyed Li (5g) was added to each capsule. The capsules were exposed isothermally at 800°C in resistively heated box furnaces. To explore new materials, mixtures of Y_2O_3 and TiO_2 powder were mixed in a ball mill, cold compacted and sintered in air at temperatures up to 1600°C. The phase composition was checked using x-ray diffraction (XRD).

Results and Discussion

X-ray diffraction of the as-deposited EB-PVD coatings on V-4Cr-4Ti substrates showed that the coatings were poly-crystalline Er_2O_3 when deposited with a substrate temperature of >950K. However, at lower substrate deposition temperatures, additional phases were detected, possibly ErO_6 . The first batch of coatings had a 2 μm vanadium overlayer which only covered the center of the Er_2O_3 coating. Due to the roughness of the underlying oxide, the vanadium layer was convoluted and not likely fully dense [17]. Figure 1 shows the resistivity of an 8 μm EB-PVD Er_2O_3 coating as a function of temperature. The

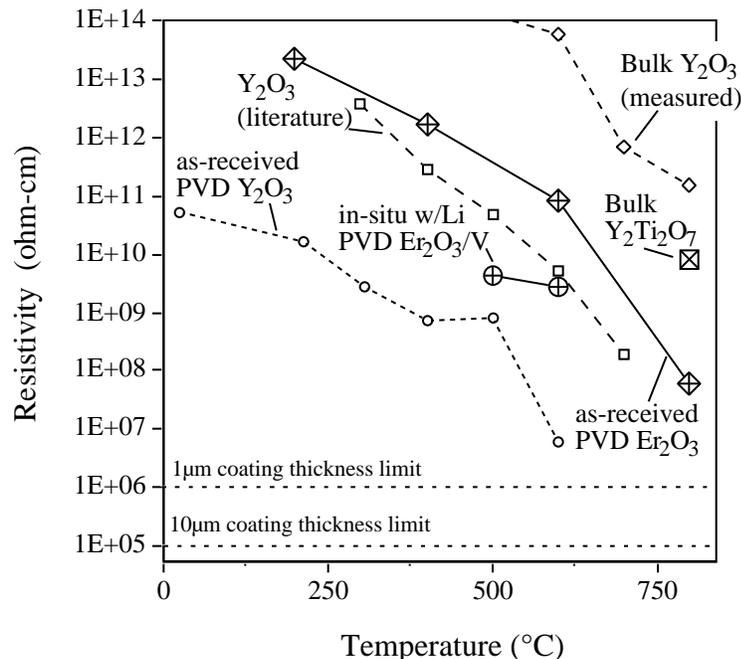


Fig. 1. Resistivity as a function of temperature for as-received EB-PVD Er_2O_3 and Y_2O_3 coatings compared to literature and measured values for bulk Y_2O_3 and bulk $\text{Y}_2\text{Ti}_2\text{O}_7$.

resistivity was higher than the first batch of 12 μm thick EB-PVD Y_2O_3 coatings¹⁶ and well above the minimum requirements.^{9,12} One specimen from this batch was exposed to Li in a capsule test for 1000h at 800°C. The coating was highly degraded. Thus, neither a single layer of Y_2O_3 or Er_2O_3 is likely to meet the durability goals.

In order to better test the multi-layer concept, a second batch of coatings was produced with a 10-14 μm vanadium overlayer which completely covered the $\sim 10\mu\text{m}$ thick Y_2O_3 or Er_2O_3 oxide layer. The surface morphology of the vanadium outer layer is shown in Fig. 2. Because the vanadium overlayer was in contact with the V-4Cr-4Ti substrate, it was not possible to measure the resistivity of the as-deposited coatings in this batch but it is expected that the as-deposited resistivity would be similar to prior batches. One coated coupon from this batch was exposed to Li in a capsule test for 100h at 800°C and survived with a minor mass gain (0.16mg/cm²) which is consistent with other exposures (see next section). In order to measure the post-test coating resistivity, the outer V layer needs to be partially machined away in order to isolate it from the V-4Cr-4Ti substrate. This procedure is currently being developed.

In both batches, bowl-shaped specimens were fabricated for in-situ testing. Previously it was reported that the coatings from the first batch, 8 μm Er_2O_3 alone and 11 μm Er_2O_3 + 2 μm V, were tested in-situ to 500°C but shorted when the Li became liquid at $\sim 180^\circ\text{C}$.¹⁷ After the Li was removed by cleaning with ethanol or by vacuum distillation, both coatings degraded and essentially were removed where the Li was in contact with the coating. The rapid degradation may have been due to the less-stable ErO_6 phase being present in the coatings. The second batch of materials included one bowl with 18 μm Er_2O_3 + 10 μm V and another with 16 μm Y_2O_3 and 14 μm V. The $\text{Y}_2\text{O}_3/\text{V}$ coated bowl was heated to 500°C without Li and the resistance was too high to be measured by the multimeter in the glove box. ($>10\text{M}$) When the Li was added, the specimen showed high resistivity up to 250°C but then shorted during heating to 500°C. As before, after vacuum distillation to remove the Li, the coating was degraded where the Li was in contact with the coating. The $\text{Er}_2\text{O}_3/\text{V}$ coated bowl showed a resistance of 8M at 500°C with no Li. When Li was added, a similar resistance was measured at 500°C and 600°C. The resistance values were converted to

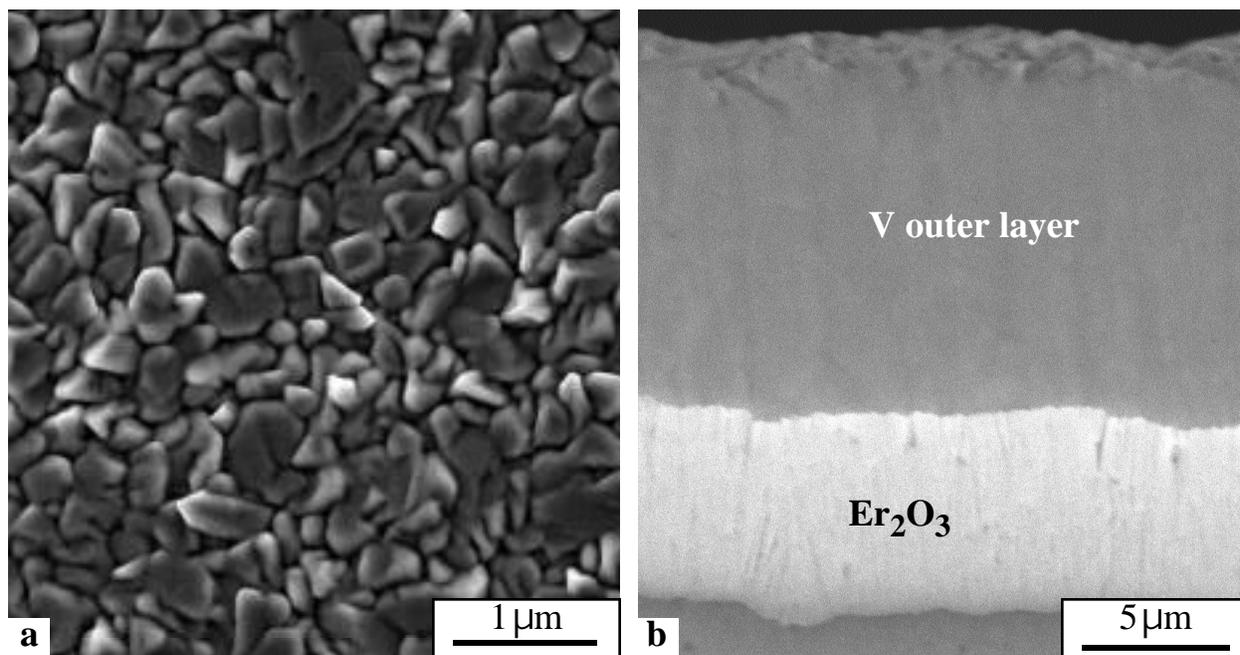


Fig. 2. SEM secondary electron images (a) plan-view of the as-received EB-PVD $\text{Y}_2\text{O}_3/\text{V}$ coating showing the outer V coating morphology and (b) FIB-section of the as-received EB-PVD $\text{Er}_2\text{O}_3/\text{V}$ coating.

resistivity and are shown in Fig. 1. The resistance dropped from 7.8 to 4.3MW when the bowl was held for 24h at 500°C but this was partially attributed to the Li evaporation and reaction in the glove box atmosphere. While these results were positive, the coating delaminated where it was in contact with Li after cleaning (Fig. 3).

Vanadium-lithium compatibility. Solutions to the MHD problem which use multi-layer coatings or a flow channel insert¹⁷ rely on excellent long-term compatibility between the vanadium overlayer and Li since this layer would be restricted to <100µm.²¹ A brief summary of the vanadium-lithium compatibility literature²² showed a wide range of results with no systematic study of the effects or relative importance of alloying elements and Li impurities. Ideally, a monometallic loop with relatively high purity Li and V specimens is needed and this experiment is currently being planned with V-4Cr-4Ti tubing ordered for loop construction.

Previous testing of ceramic specimens in Li was conducted with V alloy capsules and no V was detected in the Li after exposures for up to 1,000h at 800°C.²³ The results of a recent capsule experiment using V-4Cr-4Ti tensile specimens (SS-3 type) and a relatively inert Mo capsule are summarized in Fig. 4. The mass gains can be explained due to the uptake of C and N in the system.¹⁷ However, the drop in room temperature ductility from ~30% total elongation to 0-5% was unexpected and could be related to the C and N uptake or H uptake during cleaning in methanol or to the formation of X-Li-N compounds.²⁴ The other important observation from this experiment was that neither V, Cr or Ti was detected in the Li after the test (Table 1). The high Mo content after the test was unexpected but very little Mo was detected on the specimens using Auger electron spectroscopy.¹⁷ Additional experiments are needed to better understand this system.

New ceramic materials. While Er₂O₃ and Y₂O₃ are the primary electrically insulating materials being investigated, it would be desirable to have a ceramic that was more compatible with Li in case of degradation of the V overlayer. All of the realistic binary compound oxides have been considered, thus ternary or higher compounds are now being examined. There has been significant recent interest in the formation of stable Y-Ti-O particles in dispersion-strengthened steels.²⁵ While there is little thermodynamic information available for these compounds,²⁶ the possibility of a ternary oxide inhibiting the formation of LiYO₂²⁷ is worth investigating.



Fig. 3. Photograph of the Er₂O₃/V coated specimen after exposure to Li. A pool of liquid Li was in the center of the bowl at up to 500°C.

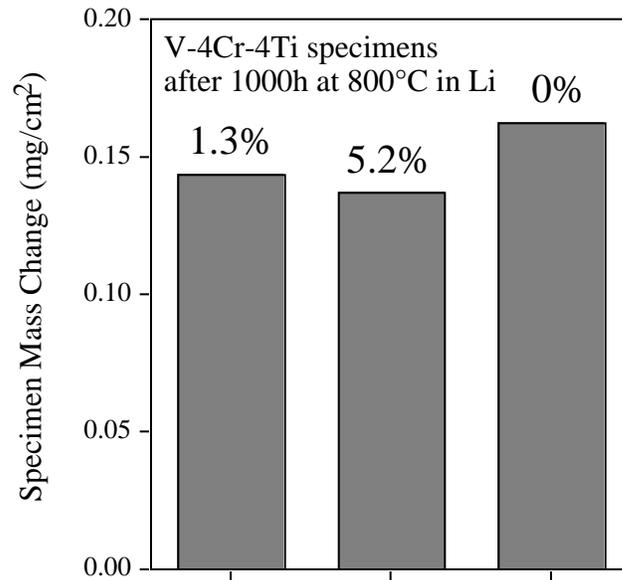


Fig. 4. Specimen mass gains for three V-4Cr-4Ti tensile specimens exposed to Li for 1000h at 800°C in a Mo capsule and the total elongation at room temperature after exposure.

Coupons (~1cm diameter, 3mm thick) of $Y_2Ti_2O_7$ were fabricated and found to be single phase by XRD. An initial resistance measurement showed a reasonably high value at 800°C (Fig. 1). Coupons with a 1:1 mixture of Y_2O_3 and TiO_2 did not form Y_2TiO_5 as expected, but instead XRD showed a mixture of Y_2O_3 and $Y_2Ti_2O_7$. The compatibility of bulk $Y_2Ti_2O_7$ in Li will be examined before coatings are fabricated.

Table 1. Chemical composition using inductively coupled plasma (metals), combustion (C), micro-Kjeldhal (N) and neutron activation (O) analyses of the starting Li and the Li after the 800°C 1000h capsule exposure (in ppmw)

Test	Al	Ba	C	Ca	Cr	Cu	Fe	Mg	Mo	N	Na	O	Si	Ti	V	Zn
Starting	<20	18	95*	20	<3	<5	<10	10	<8	65†	30	950*	<20	<3	<3	4
800°C	<30	17	<50	30	<3	6	10	<10	89	<100	30	1400	30	<3	<3	6

* average of 5 analyses

† vendor specification, <100 by analysis

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