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Compatibility of multi-layer, electrically insulating coatings for vanadium–lithium blankets

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Abstract

The objective of this work is to demonstrate that a multi-layer, electrically insulating coating will acceptably reduce the magneto hydrodynamic (MHD) pressure losses in 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 in vacuum 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 for 100 h at 800 °C without degradation. The interaction between V alloys and Li at $\leqslant$800 °C is now the critical compatibility issue and a loop test is being constructed. New ceramic materials based on the Y–Ti–O system also are being explored.
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1. Introduction

A self-cooled lithium blanket 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 critical issue for 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 structural 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 US program 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 multilayer coating, the compatibility between the V or V alloy overcoat and Li becomes more critical and this

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issue is being investigated, including construction of a loop experiment. Finally, new ceramic Y–Ti–O candidate coating materials are being explored.

2. Experimental procedure

Multi-layer coatings were fabricated on 15 mm diameter, 1 mm thick V–4Cr–4Ti coupons 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 first 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 (5 cm diameter, ~1mm thickness) coated by the same process were provided by NIFS in Japan for measuring in-situ resistivity while in contact with Li. The unit was designed to measure resistance of a coating on a bowl shaped specimen filled with 0.5 g of Li at temperatures up to 600 °C in an Ar-filled glove box (to minimize Li reaction with O and N). Springs were used to hold the bowl in contact with an alumina disk and a Mo heater [20].

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 (5 g) 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).

3. Results from new coatings

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 >950 K. However, at lower substrate deposition temperatures, additional phases were detected, possibly ErO_6. The first batch of coatings were overlayed with 2 μm vanadium 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 likely not fully dense [17]. Fig. 1 shows the resistivity of an 8 μm EB-PVD Er_2O_3 coating as a function of temperature. The resistivity was higher than the first batch of 12 μm thick EB-PVD Y_2O_3 coatings [16] and well above the minimum MHD coating requirements [9,12]. When a Er_2O_3-coated specimen from this batch was exposed to Li in a capsule test for 1000 h at 800 °C, the coating was severely degraded. Thus, a single layer of Er_2O_3 or Y_2O_3 [16,17] is unlikely to meet the durability goals.

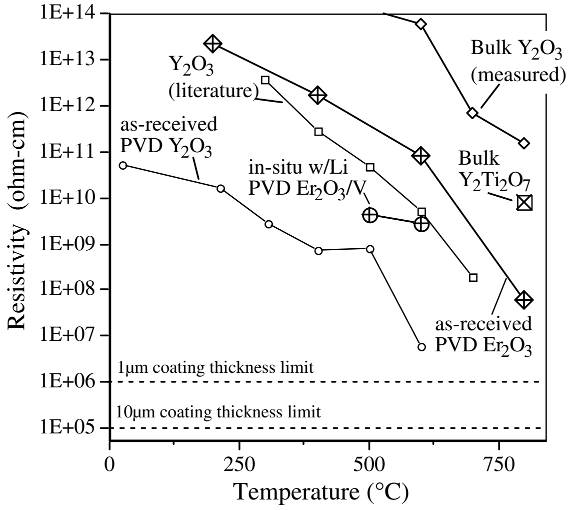

Fig. 1. Resistivity as a function of temperature for as-received EB-PVD Er_2O_3 and Y_2O_3 coatings, in-situ Er_2O_3/V coatings and literature and measured values for bulk Y_2O_3 and bulk $Y_2Ti_2O_7$. Minimum coating values are shown for reference.

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 ~10 μm 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 the as-deposited resistivity should be similar to prior batches. One Y_2O_3/V coated coupon from this batch was exposed to Li in a capsule test for 100 h at 800 °C and survived with a minor mass gain (0.16 mg/cm^2) 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 or etched away in order to isolate it from the V–4Cr–4Ti substrate. This procedure is currently being developed.

For both types of coatings described above, bowl shaped specimens were fabricated for in-situ testing. Previously it was reported that the coatings from the

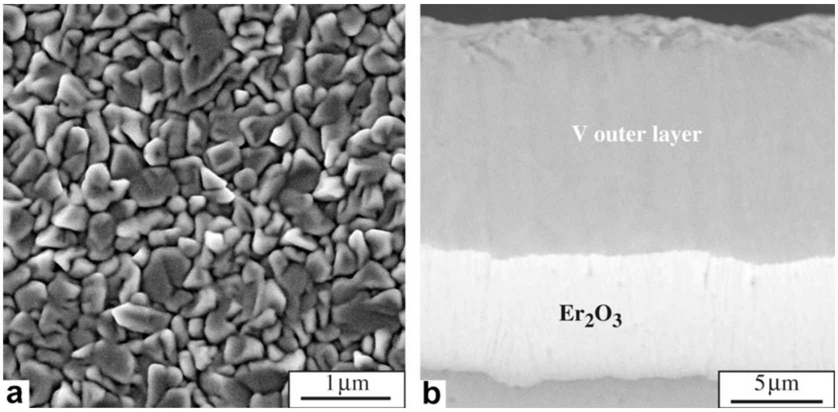

Fig. 2. SEM secondary electron images (a) plan-view of the as-received EB-PVD Y_2O_3/V coating showing the outer V coating morphology and (b) FIB-section of the as-received EB-PVD Er_2O_3/V coating.

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 ~180 °C [17]. After the Li was removed by cleaning with ethanol or by vacuum distillation, both coatings degraded and essentially had been removed where the Li was in contact with the coating. This 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 + 14 μm V. The Y_2O_3/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 MΩ). 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 Er_2O_3/V coated bowl showed a resistance of 8 MΩ at 500 °C with no Li. When Li was added, a similar resistance was measured at 500 °C and 600 °C and calculated resistivities are shown in Fig. 1. The resistance dropped from 7.8 to 4.3 MΩ when the bowl was held for 24 h 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 did delaminate after cleaning where it was in contact with Li, Fig. 3.

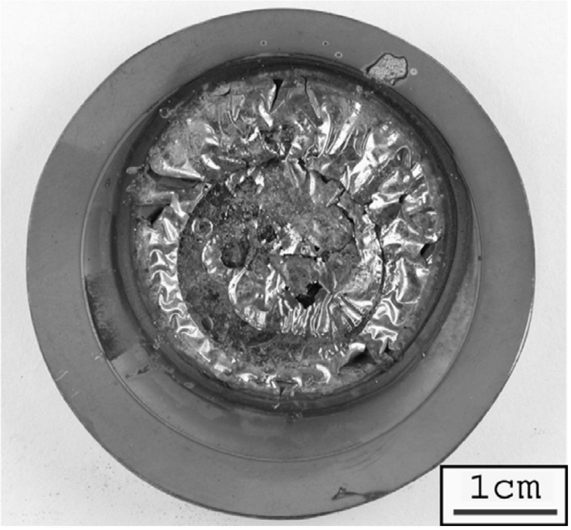

Fig. 3. Photograph of the Er_2O_3/V coated specimen after exposure to Li. A pool of liquid Li was in the center of the bowl at up to 500 °C.

4. Vanadium–lithium compatibility

Both a multi-layer coating or a flow-channel insert [17] rely on excellent long-term compatibility between the vanadium overlayer and Li since this layer would be restricted to <100 μm [21]. A brief summary of the vanadium–lithium compatibility literature [22] showed a wide range of results with no systematic study of the effects or relative importance of alloying elements in vanadium and impurities in Li. Ideally, a monometallic loop with relatively high-purity Li and V or V alloy specimens is needed and this experiment is currently being constructed with V–4Cr–4Ti tubing.

Previous testing of ceramic specimens in Li was conducted with V alloy capsules and no V was

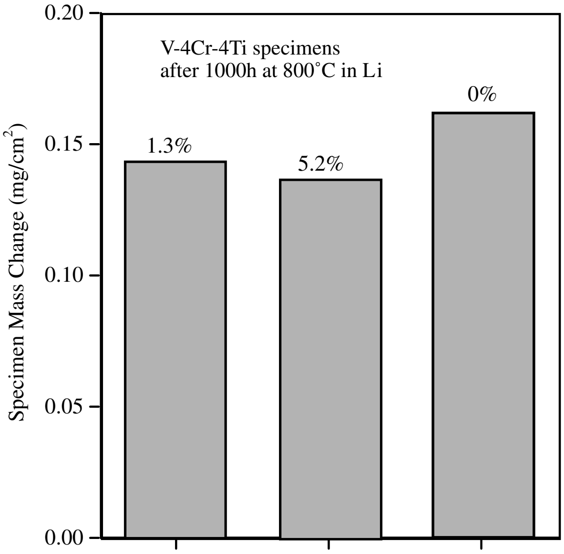

Fig. 4. Specimen mass gains for three V–4Cr–4Ti tensile specimens exposed to Li for 1000 h at 800 °C in a Mo capsule and the total tensile elongation at room temperature after exposure.

detected in the Li after exposures up to 1000 h 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 V–4Cr–4Ti specimen 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 contamination 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 nor 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.

5. New ceramic materials

While Er_2O_3 and Y_2O_3 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 $LiYO_2$ [27] is worth investigating.

Coupons (~1 cm diameter, 3 mm 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 sintered $Y_2Ti_2O_7$ in Li will be examined before coatings are fabricated.

6. Summary

Multi-layer coatings are being investigated as a method to reduce the MHD pressure drop in a lithium-cooled blanket. As fabrication processes are improved, the performances of coatings are 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 1000 h 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 mate-

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 1000 h 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[a]	20	<3	<5	<10	10	<8	65[b]	30	950[a]	<20	<3	<3	4
800 °C	<30	17	<50	30	<3	6	10	<10	89	<100	30	1400	30	<3	<3	6

[a] Average of 5 analyses.

[b] Vendor specification, <100 by analysis.

rials are being investigated with $Y_2Ti_2O_7$ showing some promise for this application.

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