STUDY OF THE LONG-TERM STABILITY OF MULTI-LAYER MHD COATINGS FOR FUSION REACTOR APPLICATIONS—B. A. Pint, J. L. Moser (Oak Ridge National Laboratory), and A. Jankowski (Lawrence Livermore National Laboratory)

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

The Li chemistry before and after a capsule test with V-4Cr-4Ti specimens has been obtained. Although it is difficult to measure low levels of impurities, the analysis has assisted in interpreting the mass change results. Further characterization of recently fabricated, electron beam, physical vapor deposition (EB-PVD) Er_2O_3 coatings indicated that those coated at a low substrate temperature may have contained ErO_6 which made them more susceptible to attack by Li during the in-situ test. New coatings that are fully Er_2O_3 and are protected with a thicker outer vanadium layer have been fabricated.

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 high-resistance ceramic 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 with a dense metallic layer is desired for contact with flowing Li. Vanadium would be the prime metallic coating candidate among refractory metals with good Li compatibility at 700°C. For example, a flow-channel insert could be constructed, Fig. 1, similar in concept to that proposed and tested for a Pb-Li system.[2,3] 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 chemical analysis of the Li before and after a capsule test at 800°C with V-4Cr-4Ti specimens.[4] Also, further analysis of the EB-PVD Er_2O_3 coatings revealed a difference in crystal structure depending on deposition temperature. This may explain the previously reported poor performance of these coatings in the in-situ test.[5,6] New coatings are being fabricated for further testing.

Experimental Procedure

The experimental procedure for the capsule testing has been reported previously.[7] The Li chemical analysis was performed at the Y-12 plant in Oak Ridge, TN and used inductively coupled plasma (metals),

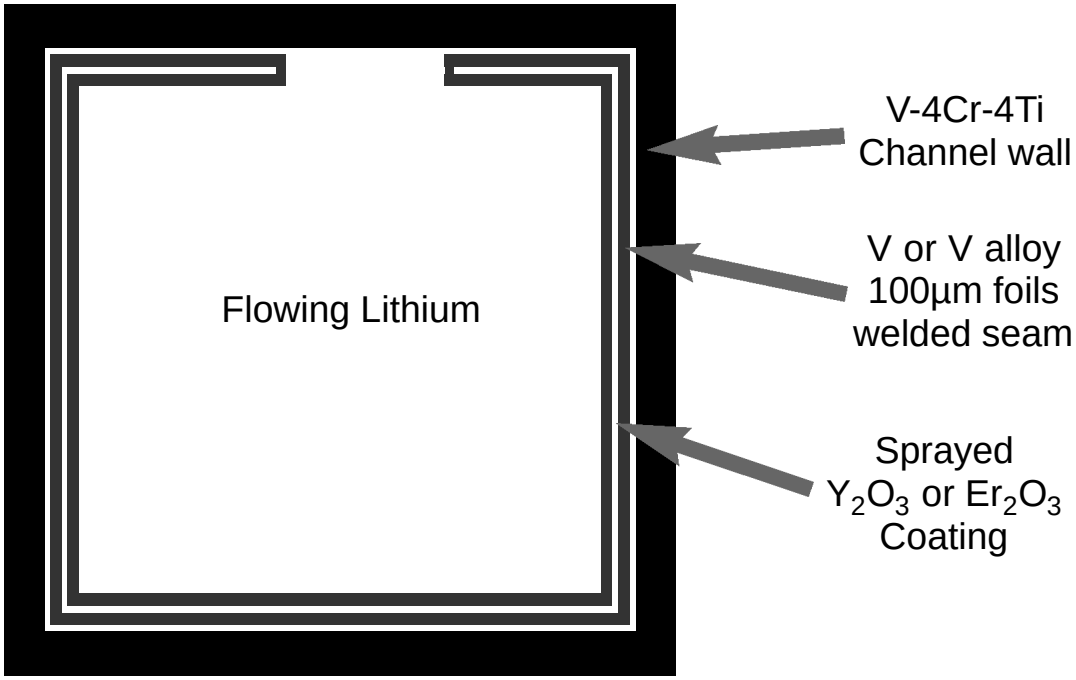

Figure 1. Schematic representation of a flow channel insert made with vanadium foils covering a layer of high resistivity oxide.

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). The Er_2O_3 coatings were fabricated by electron beam physical vapor deposition (EB-PVD) at Lawrence Livermore National Laboratory (LLNL). The in-situ test rig was discussed in the previous report.[3]

Results and Discussion

A recent capsule test using miniature tensile specimens (SS-3 type) of V-4Cr-4Ti in a Mo capsule was conducted and post-test characterization illustrates some of the potential problems in interpreting results. After exposure for 1000h at 800°C and cleaning in methanol for 24h, each of the specimens remained shiny but showed an unexpected mass gain, Figure 2. More importantly, the room temperature ductility dropped from a total elongation of ~30% before the test to 0-5% after exposure, Figure 2. A similar embrittlement was observed after 1050h at 700°C in Nb capsules but the Li contained 2500ppmw N in that case[8]. In Li at this temperature, the V-4Cr-4Ti alloy should getter C and N from the Li and lose O[9,10]. Table 1 provides the chemistry of the Li before and after the test. No dissolution of V, Cr or Ti was detected after the test although an unexpectedly high Mo content was detected and the O content of the Li increased. A mass loss of 0.05mg/cm^2 would be expected if the Li gettered 300ppmw O from each specimen (which has a reported starting O content of 310ppmw[11]). However, if all of the N and C in the Li were absorbed by the three specimens, a 0.14mg/cm^2 mass gain would be expected. The net mass gain of 0.09mg/cm^2 is somewhat consistent with the observations. Unfortunately, the chemical analysis of the Li was not accurate enough to quantify the post-test C and N contents and the specimen masses are not sufficiently large to directly measure the uptake of N, O, C and H (due to cleaning in methanol) after exposure. The N and C uptake could lead to embrittlement due to the formation of internal nitrides or thermodynamically stable X-Li-N compounds[12].

Another source of mass gain could be from mass transfer of Mo from the capsule wall to the specimen,

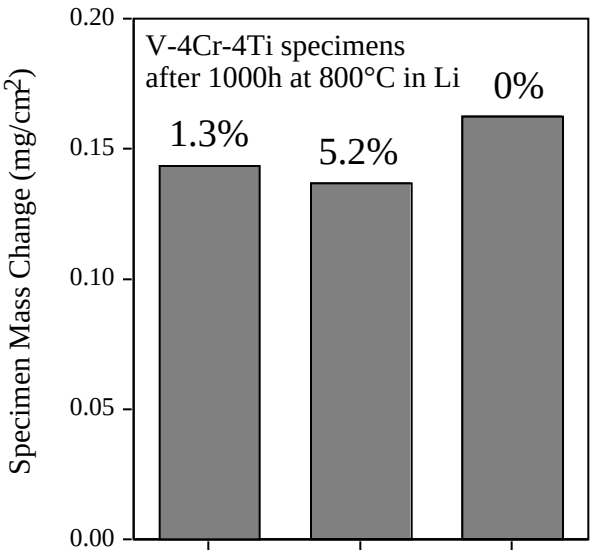

Figure 2. Specimen mass gains for three V-4Cr-4Ti tensile specimens exposed to Li for 1000h at 800°C in a Mo capsule and the total elongation at room temperature after exposure.

as suggested by the Mo detected in the Li after the test. However, as reported previously,[4,13] AES analysis of one specimen after exposure showed no significant Mo or Li on the specimen surface. A non-uniform distribution of Ca was found on the surface in the form of a Ca-V-O layer, approximately 5-10nm thick. A significant mass gain from Ca is not supported by the Li chemical analysis where the Ca content did not decrease after testing, Table 1. Additional capsule testing with larger specimen masses are needed to better understand the interaction of V-4Cr-4Ti and Mo with Li.

Er_2O_3 Coatings. Recently, some initial testing was conducted on EB-PVD Er_2O_3 coatings on V-4Cr-4Ti substrates. X-ray diffraction of the as-deposited coatings 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 ~8µm coatings deposited on bowl-shaped V-4Cr-4Ti specimens for the in-situ test[5] were deposited at 910-25K. After heating to 500°C and cleaning the residual Li with methanol the coating appeared to be completely removed This was confirmed by Auger electron spectroscopy (AES). This behavior may reflect the presence of less-stable sub-oxides, such as ErO_6. A second bowl experiment had ~11µm erbia and a 2µm V layer. However, this layer was not thick enough to be dense and protective on the rough underlying erbia coating. Thus, new coatings with higher substrate deposition temperatures and thicker outer V layers have been 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

References

[1] B. A. Pint, P. F. Tortorelli, A. Jankowski, J. Hays, T. Muroga, A. Suzuki, O. I. Yeliseyeva, and V. M. Chernov, J. Nucl. Mater. 329-333 (2004) 119.
[2] I. Cook et al., Fus. Sci. Technol. 47 (2005) 384.
[3] L. Barleon, V. Casal, and L. Lenhart, Fusion Eng. Des. 14 (1991) 401.
[4] B. A. Pint, P. F. Tortorelli, L. D. Chitwood, H. M. Meyer, and M. Fujiwara, DOE-ER-0313/36 (2004) 76.
[5] B. A. Pint, K. L. More, J. L. Moser, A. Jankowski, and A. Suzuki, DOE-ER-0313/37 (2005) 101.
[6] B. A. Pint, J. L. Moser, and P. F. Tortorelli, Fusion Science and Technology (in press).
[7] B. A. Pint, L. D. Chitwood, and J. R. DiStefano, J. Nucl. Mater. 289 (2001) 52.
[8] V. A. Evtikhin, I. E. Lyublinski, V. Y. Pankratov, and L. P. Zavyalski, J. Nucl. Mater. 191-194 (1992) 924.
[9] O. K. Chopra and A. B. Hull, Fus. Technol. 15 (1989) 309.
[10] J. R. DiStefano, Oak Ridge National Laboratory report #3551, Oak Ridge, Tenn. (1964).
[11] D. L. Smith, H. M. Chung, B. A. Loomis, and H.-C. Tsai, J. Nucl. Mater. 233-237 (1996) 356.
[12] P. Hubberstey and P. G. Roberts, J. Nucl. Mater. 155-157 (1988) 694.
[13] B. A. Pint, K. L. More, H. M. Meyer, and J. R. DiStefano, Fus. Sci. Technol. 47 (2005) 851.