RECENT PROGRESS IN THE DEVELOPMENT OF ELECTRICALLY INSULATING COATINGS FOR A LIQUID LITHIUM BLANKET—B. A. Pint, P. F. Tortorelli (Oak Ridge National Laboratory, USA), A. Jankowski, J. Hayes (Lawrence Livermore National Laboratory, USA), T. Muroga, A. Suzuki (NIFS, Japan), O. I. Yeliseyeva (G. V. Karpenko Physico-Mechanical Institute NASU, Ukraine), and V. M. Chernov (Bochvar Institute of Inorganic Materials, Russia)

To be published in the Journal of Nuclear Materials as Proceedings of the 11th International Conference on Fusion Reactor Materials, December 2003, Kyoto, Japan.

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. Experimental and theoretical work is being conducted on bulk ceramics to determine resistivity, basic lithium compatibility and maximum-use temperatures of candidate ceramics such as Er_2O_3 and Y_2O_3.

SUMMARY

There are very few candidate MHD coating materials since Li dissolves most oxides and many carbides and nitrides do not have sufficient electrical resistivity for this application. The past few years have seen great changes in the research emphasis and strategy for MHD coatings. Problems with CaO have led to a focus on new candidates with low cation solubility in Li, such as Y_2O_3 and Er_2O_3. Coatings of these materials are being fabricated by a variety of processing techniques and the resistivity and microstructure characterized. Progress is being made in the development of MHD coatings, but as yet no coatings have shown sufficient compatibility with Li. Electrical resistivity results from Y_2O_3 coatings as-deposited and after exposure to Li are presented. Self-healing and in-situ coatings are being investigated based on CaO from Li-Ca and Er_2O_3 from Li-Er. Anticipated problems with defects in ceramic coatings, either as-fabricated or due to tensile cracking, suggests that the most viable coating strategy will have to be multi-layered. An outer metallic layer will prevent Li from wetting cracks in the inner ceramic insulating layer and also limit interaction between the ceramic and Li. Whether the MHD coating is single- or dual-layered, processing issues will need to be addressed before the issue of compatibility can be answered.

PROGRESS AND STATUS

Introduction

In all alloy - liquid metal (e.g. Li and Pb-Li) blanket concepts for a deuterium/tritium fueled fusion reactor where a strong magnetic field is used to contain the fusion plasma, a magnetohydrodynamic (MHD) pressure drop is developed when the electrically conductive lithium flows across the magnetic field lines. To minimize the MHD resistance to flow, it is necessary to have an insulating barrier to decouple the liquid metal and the alloy structure. The coatings must be thin, durable and electrically resistive.[1-3] Perhaps the most difficult material requirement for a Li self-cooled blanket is compatibility with Li at temperatures up to ≈700°C.[4,5] Because of the relative stability of Li_2O, most electrically-resistive oxides readily dissolve in Li.[6,7] Therefore, only a few materials are candidates for this application. Over the past few years, there has been a considerable shift in emphasis in this topic as the underlying compatibility issues have been reevaluated and new candidate materials have been tested in bulk form and fabricated as coatings for further experiments. The development of a viable MHD coating is particularly relevant for

concepts that use vanadium structural alloys because of the good compatibility of vanadium alloys with liquid lithium but their susceptibility to embrittlement by oxygen and hydrogen in other environments such as helium.[8-11]

Shift in Research Emphasis

Both theoretical calculations and experiments over the past 40 years have shown that there are relatively few materials that meet both the Li compatibility and electrical resistance requirements.[1,3,6,7,12-16] Recent reviews have emphasized CaO and AlN as the most attractive candidate materials.[2,3] However, more recent work has shown that the these materials may not be viable.[17,18]

Over the past decade, CaO has been extensively investigated as a candidate coating material.[2,3,14,19] One of its attractive features is its high solubility in Li which suggests that it might be possible to have a self-healing coating. However, thermodynamic calculations and recent experimental work[17] on bulk CaO specimens have proven that CaO cannot perform adequately at 600°-800°C in static Li tests, Figure 1. A mass loss of ≈3mg/cm^2 is equivalent to a 10µm loss of material. Thus, the high mass losses at these temperatures are unacceptably high for a thin coating. An even higher dissolution rate (0.085µm/h) was observed for single crystal CaO in Li-2.8at.%Ca at 600°C.[18] Results for coatings formed on V-4Cr-4Ti with different oxygen preloading showed a lower dissolution rate when tested under the same conditions at 600°C.[18] However, the dissolution rates were sufficient to remove a significant fraction of the coating after 1000h and suggested a coating lifetime of <3000h at 600°C, Figure 2. Because of its poor high temperature compatibility, the CaO coating development program in the U.S. has recently been concluded.

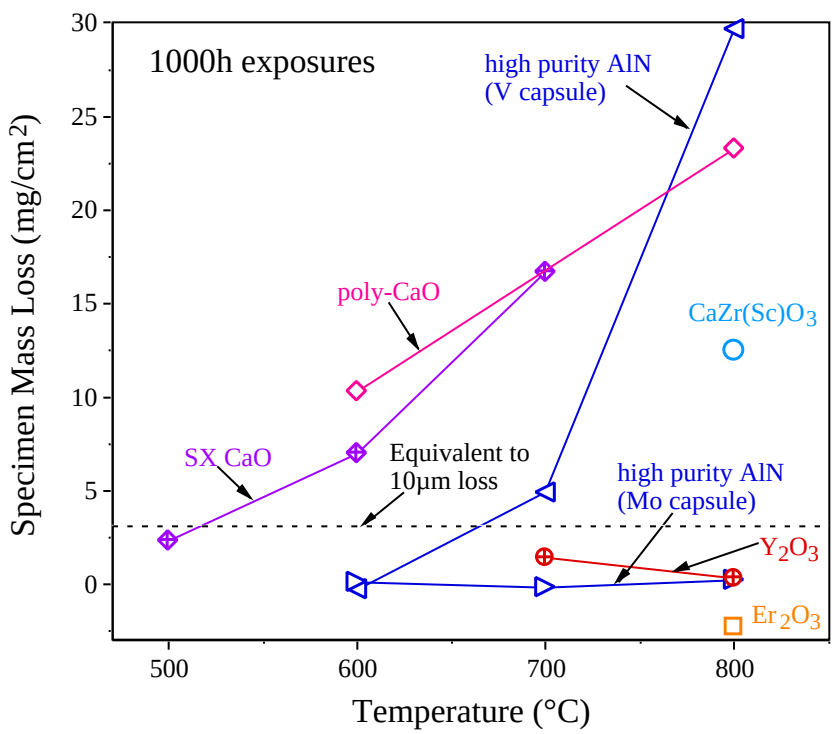

Figure 1. Mass losses for some candidate oxide and nitride materials after 1000h at various temperatures. The results for poly-crystalline and single crystal CaO show severe dissolution above 500°C. The dashed line shows the mass loss associated with the loss of ≈10µm of coating in a 1000h exposure.

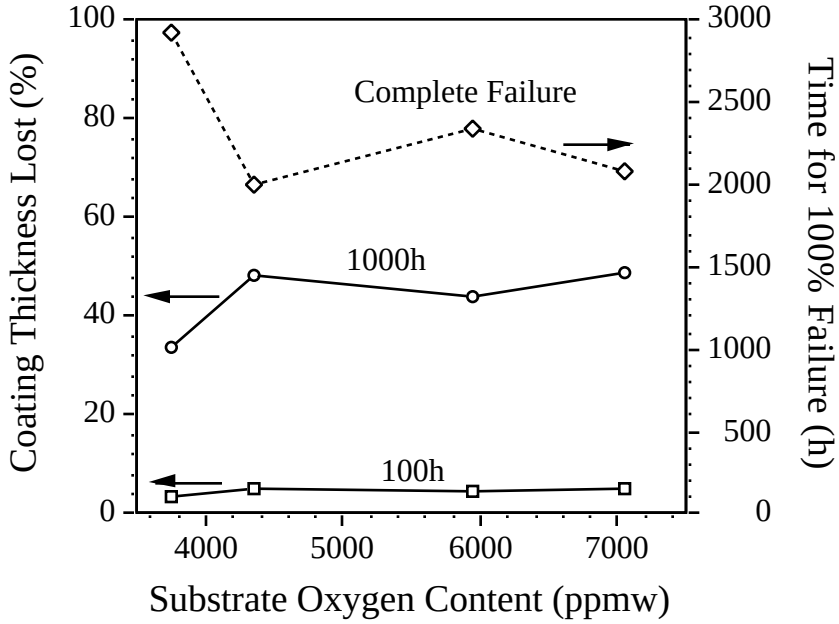

Figure 2. Performance of CaO coatings in Li-2.8at.%Ca at 600°C as a function of oxygen in the V-4Cr-4Ti substrate. Based on the experimentally observed dissolution rate, the percentage of the coating lost with time was calculated as well as the time to complete failure.[18]

Screenings studies initially indicated that CaO was a promising candidate. However, the thermodynamic calculations examined the reaction:

$$CaO + 2Li \leftrightarrow Ca + Li_2O \qquad [1]$$

and assumed that the Li was saturated with oxygen. Because CaO has a lower free energy of formation than Li_2O, CaO should be stable in Li under these conditions. However, in a flowing system with a temperature gradient this is an unrealistic assumption as the saturation concentration varies considerably with temperature[17] such that if the lithium were saturated at the highest temperature, Li_2O would precipitate out at the lowest temperature and the lithium would no longer be saturated at the highest temperature. A more relevant reaction is for dissolution of the components into lithium until the following equilibrium is reached in solution:

$$CaO = Ca(Li) + O(Li) \qquad [2]$$

Theoretical calculations showed that the equilibrium solubility of Ca in Li increased dramatically with temperature,[17] which was consistent with the high dissolution rates observed experimentally.

The other candidate that has been extensively studied as a coating is AlN.[2,3,20-23] Nitrides are generally more compatible with Li because nitrides of Li are far less stable than Li_2O. However, AlN is one of only a few nitrides with high electrical resistivity. A number of experiments have shown good Li compatibility up to 600°C. However, in higher temperatures capsule tests,[17,23] the behavior was very sensitive to the capsule material, Figure 1. With a Mo capsule, very little mass change was noted after 1000h at 800°C. When a vanadium alloy capsule was used, the mass losses were much higher, Figure 1. The same behavior was observed for high purity (0.04%Y) and ultra-high purity AlN.[17,23] The effect can be understood based on the dissolution equilibrium equation for AlN:

$$AlN = Al(Li) + N(Li) \qquad [3]$$

The vanadium alloy capsule getters N from the Li during the exposure preventing the Li from becoming saturated with N and thus stopping the dissolution. With capsule made from Mo, which does not form a stable nitride, the Li becomes saturated with N and the dissolution stops. Thus, the use of AlN appears problematic because uncoated vanadium alloy channel walls could getter N from the Li. A further complication is that it is extremely difficult to make AlN without oxygen contamination. Any Al_2O_3 formed during coating fabrication would be readily dissolved by Li. Initial Li exposures of AlN coatings at 500°C have shown poor performance.[21]

This combination of experimental results and thermodynamic analyses suggests a new strategy for selecting possible MHD coating materials. Since elements (e.g. Ca) which are highly soluble in Li may be more susceptible to dissolution at high temperature, oxides with cations that have a low solubility in Li will likely have better compatibility. Therefore, more emphasis is now being placed on Y_2O_3 and Er_2O_3 as candidate materials for coating development.

In-situ Coatings

Despite the observed problems with CaO compatibility at higher temperatures, the concept of a self-healing coating is still attractive. An in-situ technique would more easily allow coating of complex components. Therefore, the Li-CaO concept as well as Li-Er_2O_3 are currently being examined to develop an understanding of the issues related to the processing and use of in-situ coatings. Based on earlier experimental work for vanadium alloys exposed to Li-0.5%Ca at 700°C,[24] the process of CaO formation and degradation on vanadium alloys is being modeled.[25] According to the in-situ model in Figure 3, oxygen from the substrate can react with Ca in the Li to form a CaO outer layer. However, this requires balanced fluxes of Ca in the metal and O from the metal which are difficult to achieve. As oxygen is removed from the substrate, Ti-rich oxide particles dissolve. Eventually, some Ca and Li becomes incorporated into the metal while V and Ti can become incorporated into the oxide. This process degrades the coating and the metal. Another scenario involves the deposition of a CaO layer before exposure to Li-

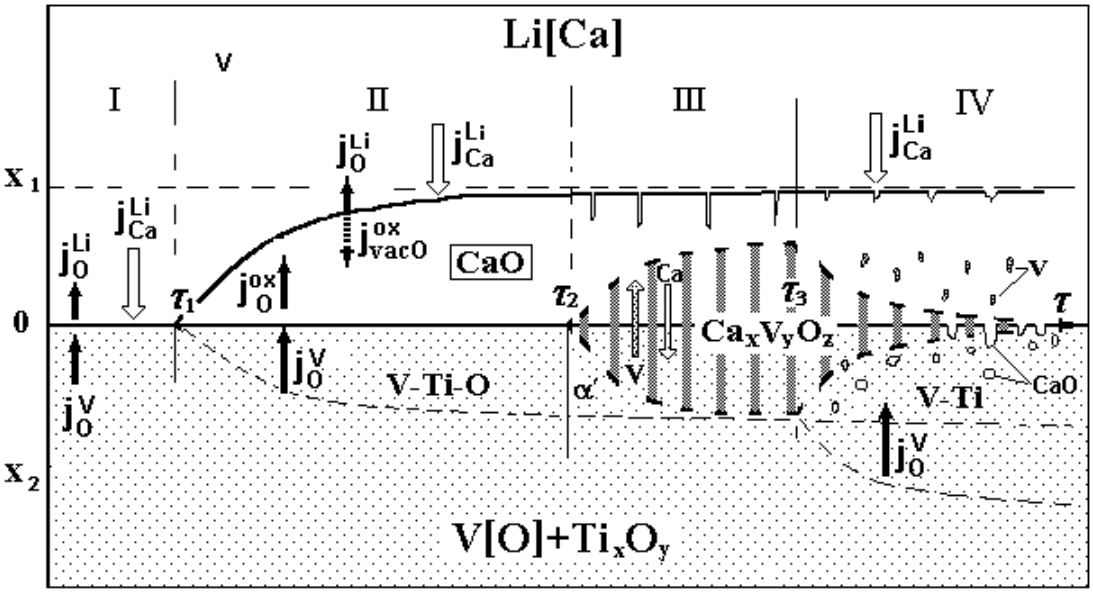

Figure 3. Schematic of the competing processes for the in-situ formation of a CaO layer on a vanadium alloy as a function of time from left to right.[25]

Ca. In this case, similar problems eventually develop as oxygen is removed from the substrate and V and Ti are incorporated into the oxide.

Because of the observed problems with CaO, in-situ Er_2O_3 coatings also are being explored.[26] Vanadium alloys preloaded with oxygen were exposed to Li-0.006at.%Er at 600°C. Figure 4 shows the Er-rich oxide layer formed on the surface. However, the measured O/Er ratio was 2-2.5 due to the incorporation of V, Cr and Ti impurities in the layer. Initial resistance measurements at room temperature showed adequate electrical resistivity when the process was optimized. More work will be required to further optimize this process and characterize the properties and compatibility of coatings made by this process.

Results From New Coatings

Because of the initial positive results on bulk Y_2O_3 and Er_2O_3, the next step was to fabricate coatings of these materials for further characterization and testing. In the U.S., Y_2O_3 coatings were deposited by an electron-beam assisted, physical vapor deposition process (EB-PVD) on V-4Cr-4Ti substrates. The coatings were 12.5µm thick and had a faceted surface microstructure typical of the EB-PVD process, Figure 5a. For coating evaluations, the figure of merit is the change in coating resistivity at 700°C after exposure to Li. The coating must maintain adequate resistivity in order to warrant further testing. In order to avoid oxidation of the vanadium alloy substrate, the electrical resistance was measured in a vacuum. This initial set of coatings showed relatively low resistivity compared to literature values and values measured on a sintered Y_2O_3 specimen using the same equipment, Figure 6. Similar to the testing procedure used for bulk ceramics,[17] the coated specimens were exposed to lithium in sealed vanadium alloy capsules for 100-1,000h at 700° and 800°C. After exposure, performance has varied from little change in resistivity and microstructure to complete loss of the coating. The electrical resistance measured after 3, 100h cycles at 800°C (cooling to room temperature between each cycle) was higher than the as-received coatings. However, after 1000h at 800°C, a degradation in the resistivity was

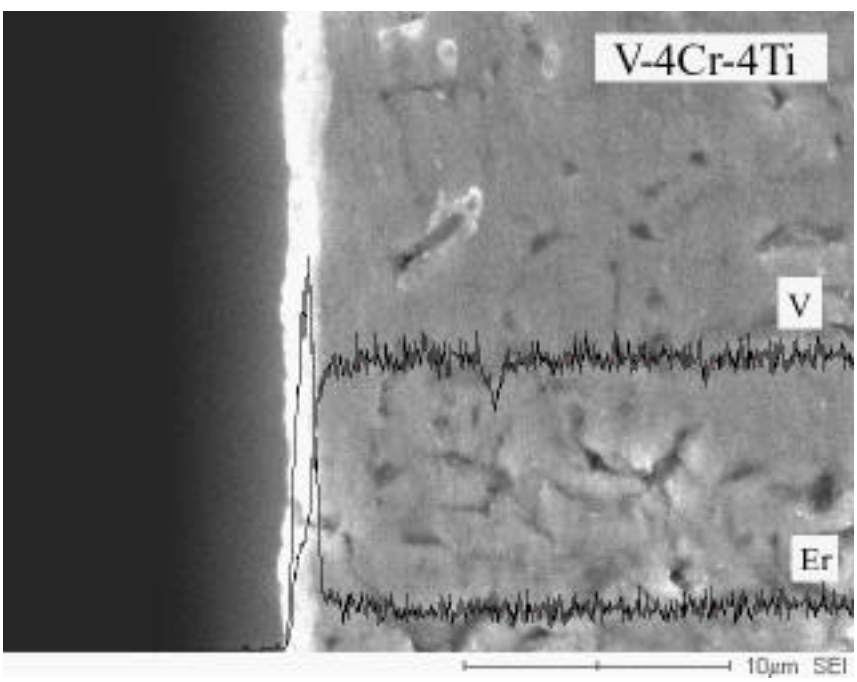

Figure 4. SEM image and EDS line element scan of a cross section of V-4Cr-4Ti oxidized for 6h and annealed for 16h at 700°C, then exposed in Li doped with Er for 300h at 600°C.[26]

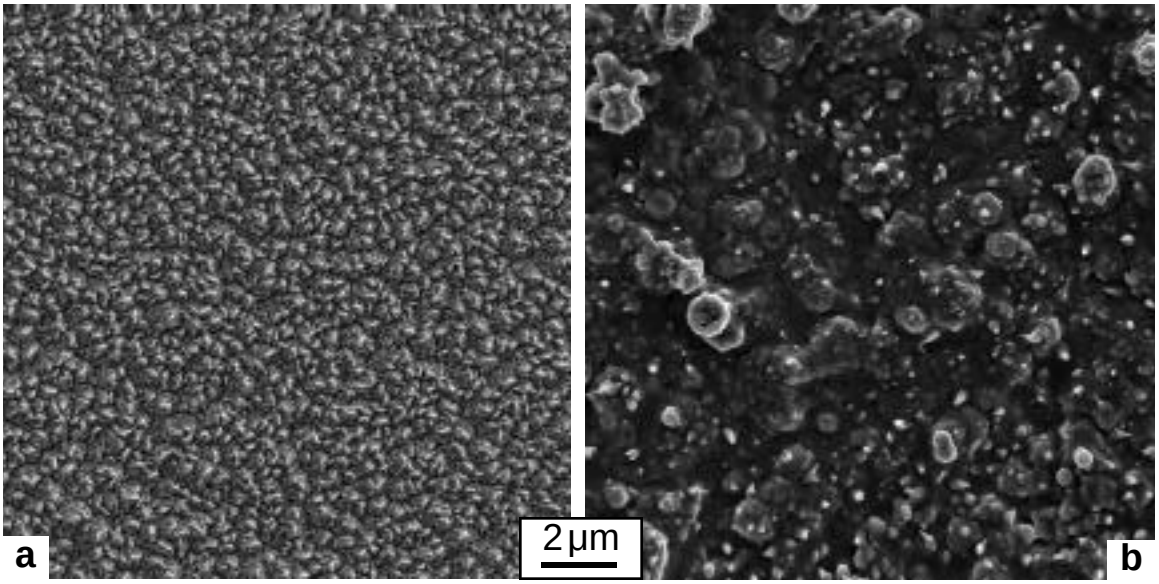

Figure 5. SEM secondary electron plan view images of EB-PVD Y_2O_3 coatings (a) as-received and (b) after exposure to Li at 800°C for 1000h.

observed. X-ray diffraction results showed an exact match with Y_2O_3 for the as-received coatings. With increasing exposure time and temperature, the Y_2O_3 peaks began to disappear and $LiYO_2$ peaks and unidentified peaks were observed. The surface morphology of the coating changed significantly after exposure, for example, Figure 5b. Oxide particles containing Ti and Y were observed on the coating

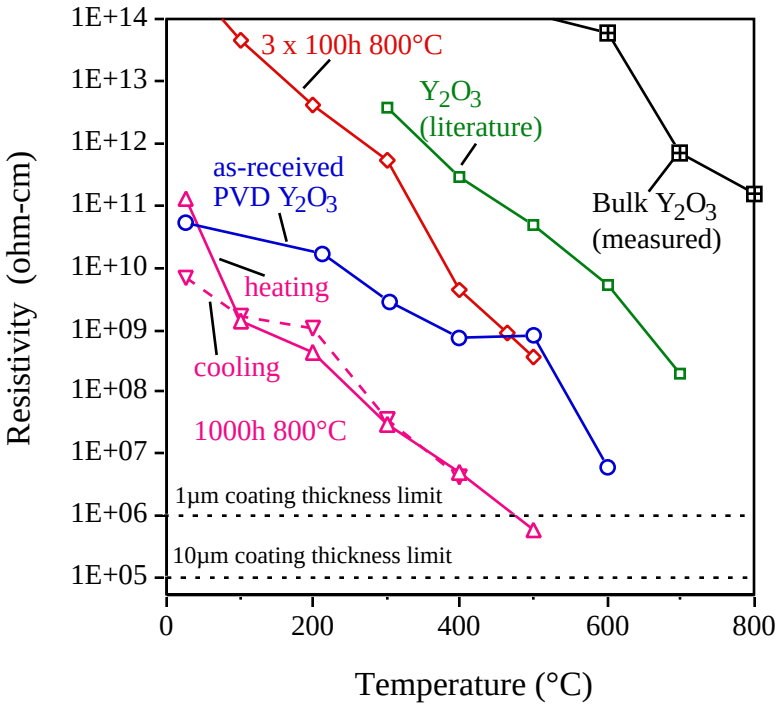

Figure 6. Resistivity as a function of temperature for EB-PVD Y_2O_3 coatings before and after exposure to Li at 800°C. Literature and measured values for bulk Y_2O_3 were much higher.

surface using Auger electron spectroscopy. After a 2000h exposure at 800°C, the coating was destroyed. Exposures at 700°C on a second set of coatings typically showed a complete loss of the coating. Previous work that examined the compatibility of Y_2O_3 and Y_2O_3 coatings in Li found the formation of a $LiYO_2$ layer at the Y_2O_3-Li interface after exposure at 500°C.[27,28] Although the current results on Y_2O_3 coatings show a potential compatibility problem, additional work is needed on coating development to further study the phenomenon as well as the role of coating microstructure on the reaction with Li.

In Japan, research programs are characterizing the properties and microstructure of AlN, Y_2O_3 and Er_2O_3 coatings made by RF sputtering and vacuum arc processes.[29,30] Processing issues need to be separated from those associated with compatibility in Li. Therefore, it is important to have high quality, well characterized coatings prior to testing in Li. For example, the crystallinity and purity of AlN coatings is being characterized.[29] Post-fabrication anneals at 400° and 700°C were used to improve the crystallinity. Annealing lowers the resistivity of the coatings but they retain sufficient resistance for this application. The coatings contain 3-10at.% O which probably contributes to their poor performance in Li at 500°C.[29]

Radiation-induced conductivity effects are being explored using 14MeV neutron irradiation of bulk ceramics specimens and AlN and Y_2O_3 coatings.[30] The increases in conductivity were proportional to the neutron flux but were such that the degradation of the resistivity under irradiation were within allowable limits for the V/Li blanket system.

Coating compatibility testing has not proceeded beyond static capsule-type testing. In order to truly demonstrate compatibility, testing in a thermal gradient will be necessary in order to evaluate the effects of temperature and mass transfer.[31] For example, previous results for Y_2O_3 showed only limited dissolution in static Li testing at 1100°C[12] but complete dissolution in flowing Li in 109h at 1143°C due to mass transfer or erosion.[32] A set of metrics for coating performance has been developed.[33] When coatings are able to meet these metrics in static tests, more extensive thermal convection loop testing will begin.

Effects of Coating Defects

The required properties and effects of defects in MHD coatings have been considered previously.[34-36] A recent analysis of the minimum properties and maximum defect density allowable[37] has caused a reassessment of the MHD coating strategy. Theoretical calculations suggest that only extremely small defect densities of through thickness defects can be tolerated because Li readily wets oxides in the temperature range of interest.[17] Therefore, it is expected that any crack will fill with Li, greatly increasing the effective conductivity of the coating system. (Even in the absence of a defect, Li has been observed to change the conductivity of oxides by interdiffusion at room temperature.[38]) With MHD coating thicknesses expected to be 5-10µm, it is highly unlikely that coatings could be fabricated with virtually no through thickness cracks. High quality bulk ceramics typically will have defects on the order of 10µm.[39] Even if a coating could be fabricated without cracks, tensile loading of the vanadium alloy substrate will cause cracks to form normal to the stress direction with a uniform spacing[40] that is generally expected to be 10-100 times the coating thickness based on data from the literature for standard properties of oxide films.[41,42] Therefore, unless there are no significant tensile loads on the coated vanadium alloys, through-thickness cracks would be expected every 1mm or less in a 10µm thick MHD coating. These cracks should wet with Li rendering the coating virtually useless.

Current Paradigm

Because of the anticipated defects in the insulating layer, it is suggested that the MHD coating will need to incorporate an outer, protective, metallic layer to prevent Li from entering cracks in the insulating layer.

The potential need for an outer layer has been recognized for some time.[1] Most likely, this layer would be vanadium or a vanadium alloy and could be up to 100µm thick.[43] A dual layer MHD coating system will need to be carefully assessed. Rather than a deposited coating, the outer layer could be free standing. A dual-layer coating will be more difficult to fabricate but will change the necessary compatibility metrics for the ceramic insulating layer. It also may preclude the in-situ or self-healing coating concepts, as lithium will no longer be in direct contact with the ceramic. However, some level of compatibility will be required so that a minor breach in the metallic outer layer will not immediately result in dissolution of the inner layer. For a dual-layer system, Y_2O_3 may be an adequate insulator candidate since the observed degradation was due to a solid state reaction to form $YLiO_2$. The amount of degradation will be limited to the amount of Li able to penetrate the outer layer. A minor leak would only have a limited effect on the ceramic layer.

With a thin metallic layer in contact with Li, there is some concern about the compatibility of vanadium and its alloys with Li. Degradation of the relatively thin outer layer by mass transfer or dissolution would have to be minor. There is some conflict about this issue as some investigators have reported rather high dissolution rates for vanadium alloys in flowing Li.[44,45] However, other work has shown good compatibility and low solubility of vanadium in Li.[46,47] As with a single layer system, this issue will need to be addressed by compatibility studies of a dual-layer system in a temperature gradient.

References

[1] Y. Y. Liu and D. L. Smith, J. Nucl. Mater. 141-43 (1986) 38.
[2] D. L. Smith, K. Natesan, J. H. Park, C. B. Reed, and R. F. Mattas, Fusion Eng. Design 51-52 (2000) 185.
[3] D. L. Smith, J. Konys, T. Muroga, and V. Evitkhin, J. Nucl. Mater. 307-311 (2002) 1314.
[4] E. E. Bloom, J. Nucl. Mater. 258-263 (1998) 7.
[5] D. L. Smith, M. C. Billone, S. Majumdar, R. F. Mattas, and D.-K. Sze, J. Nucl. Mater. 258-263 (1998) 65.
[6] J. E. Battles, Intern. Mater. Rev. 34 (1989) 1.
[7] R. J. Lauf and J. H. DeVan, J. Electrochem. Soc. 139 (1992) 2087.
[8] H. D. Röhrig, J. R. DiStefano, and L. D. Chitwood, J. Nucl. Mater. 258-63 (1998) 1356.
[9] K. Natesan and W. K. Soppet, J. Nucl. Mater. 283-287 (2000) 1316.
[10] B. A. Pint and J. R. DiStefano, J. Nucl. Mater. 307-311 (2002) 560.
[11] B. A. Pint, J. R. DiStefano, and P. F. Tortorelli, Fusion Sci. Technol. 44 (2003) 433.
[12] D. Elliott, D. Cerini, and L. Hays, Supporting Research and Advanced Development, Space Programs Summary 37-41, Vol. IV, Jet Propulsion Laboratory, Pasadena, CA (Oct. 1966), 124.
[13] R. N. Singh, J. Amer. Ceram. Soc. 59 (1976) 112.
[14] J. H. Park and T. F. Kassner, J. Nucl. Mater. 233-237 (1996) 476.
[15] P. Hubberstey, J. Nucl. Mater. 247 (1997) 208.
[16] P. Hubberstey and T. Sample, J. Nucl. Mater. 248 (1997) 140.
[17] B. A. Pint, J. H. DeVan, and J. R. DiStefano, J. Nucl. Mater. 307-311 (2002) 1344.
[18] J.-H. Park, K. Natesan, and R. Mattas, Argonne National Laboratory, unpublished results from teleconference (Aug. 2002).
[19] K. Natesan, M. Uz, and S. Wieder, J. Nucl. Mater. 283-287 (2000) 1277.
[20] K. Natesan, C. B. Reed, D. L. Rink, and R. C. Haglund, J. Nucl. Mater. 258-263 (1998) 488.
[21] T. Terai, A. Suzuki, T. Yoneoka, and T. Mitsuyama, J. Nucl. Mater. 283-7 (2000) 1322.
[22] T. Yoneoka, T. Sakurai, T. Sato, and S. Tanaka, J. Japan Inst. Metals 66 (2002) 384.
[23] A. Suzuki, T. Muroga, B. A. Pint, T. Yoneoka, and S. Tanaka, Fusion Eng. Design, 69 (2003) 397.
[24] O. I. Yeliseyeva, V. M. Chernov, and T. V. Tsaran, J. Nucl. Mater. 307-311 (2002) 1400.
[25] O. I. Yeliseyeva, V. M. Chernov, T. V. Tsaran, M. M. Potapenko, and D. L. Smith, these proceedings.
[26] Z. Yao, A. Suzuki, T. Muroga, and K. Katahira, these proceedings.

[27] T. Terai, T. Yoneoka, H. Tanaka, A. Suzuki, S. Tanaka, M. Nakamichi, H. Kawamura, K. Miyajima, and Y. Harada, J. Nucl. Mater. 233-237 (1996) 421.
[28] T. Mitsuyama, T. Terai, T. Yoneoka, and S. Tanaka, Fusion Eng. Design 39-40 (1998) 811.
[29] A. Sawada, A. Suzuki, T. Terai, and T. Muroga, these proceedings.
[30] T. Tanaka, A. Suzuki, T. Muroga, F. Sato, T. Iida, and T. Nishitani, these proceedings.
[31] J. H. DeVan, J. Nucl. Mater. 85-86 (1979) 249.
[32] L. Hays, NASA Tech. Report 32-1233, JPL, Pasadena, CA (Dec. 1967).
[33] B. A. Pint and J. R. DiStefano, DOE-ER-0313/32 (2002) 87.
[34] L. Bühler, Fusion Eng. Design 27 (1995) 650.
[35] S. Malang, H. U. Borgstedt, E. H. Farnum, K. Natesan, I. V. Vitkovski, Fusion Eng. Design 27 (1995) 570.
[36] A. Y. Ying and A. A. Gaizer, Fusion Eng. Design 27 (1995) 634.
[37] D.-K. Sze et al., these proceedings.
[38] J. W. Lee and S. I. Pyun, J. Power Sources 119 (2003) 760.
[39] P. F. Becher, private communication (2003).
[40] D. C. Agrawal and R. Raj, Acta Metall. 37 (1989) 1265.
[41] J. R. Nicholls, D. J. Hall, and P. F. Tortorelli, Mater. High Temp. 12 (1994) 141.
[42] M. Schütze, Mater. High Temp. 12 (1994) 237.
[43] D.-K. Sze, private communication (2003).
[44] Ch. Adelhelm, H. U. Borgstedt, and J. Konys, Fusion Tech. 8 (1985) 541.
[45] O. K. Chopra and D. L. Smith, J. Nucl. Mater. 155-157 (1988) 683.
[46] V. A. Evtikhin, I. E. Lyublinski, and A. V. Vertkov, J. Nucl. Mater. 258-263 (1998) 1487.
[47] S. N. Votinov et al., J. Nucl. Mater. 233-237 (1996) 370.