STUDY OF THE LONG-TERM STABILITY OF MHD COATINGS FOR FUSION REACTOR APPLICATIONS† -- B. A. Pint, L.D. Chitwood, J. H. DeVan and J. R. DiStefano (Oak Ridge National Laboratory)

† dedicated to the memory of J. H. DeVan

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, magnetohydrodynamic (MHD) coatings on the first wall of magnetic confinement reactors are essential to reduce the MHD force that would otherwise inhibit the flow of the lithium coolant. Initial experimental work is being conducted on bulk ceramics to determine basic lithium compatibility and maximum-use temperatures of candidate ceramics such as AlN and CaO.

SUMMARY

Bulk specimens of two candidate compositions, CaO and AlN, for insulating coatings in a lithium-cooled fusion reactor have been exposed to lithium in 1000h isothermal tests at 500°-800°C to determine the maximum temperature at which acceptable compatibility is likely. Specimens of AlN+0.04Y showed significant mass loss at 700° and 800°C but much less attack at 600°C. For testing at 600°C, changing from a V alloy capsule liner to a Mo liner or adding 1000ppm N to the Li caused only minor differences in the mass change. Polished cross-sections indicated that a reaction layer had formed in each case. Single crystals of CaO showed massive losses at 600° and 700°C similar to results with polycrystalline specimens. With the addition of 1000ppm O to the Li, there was a change in the amount of CaO dissolved during the 1000h exposure suggesting that doping Li may be an avenue for improved compatibility. All of these results are consistent with an analysis of the relevant thermodynamic solubility data.

PROGRESS AND STATUS

Experimental Procedure

Current work focused on two compositions of bulk specimens. High purity AlN (0.9wt%O, 0.04wt% Y) from Tokuyama Corp (Shapal SH-50) was made by nitriding Al_2O_3. The AlN specimens measured 2x8x12mm, had an average grain size of 7-8µm and a density of 3.25g/cm^3. Single crystals of CaO were obtained from Commercial Crystal Laboratories (Naples, FL) and measured ≈2x6x12mm. Previous work on these materials had used AlN with 5wt%Y_2O_3 and polycrystalline CaO specimens.[1] Specimen dimensions and mass were measured before and after exposure. The mass gain accuracy was 0.01mg/cm^2.

The experimental procedure for lithium exposures has been outlined previously[2,3]. Bulk ceramic specimens were exposed for 1000h at 500°-800°C. In some tests, additions of Li_3N, Li_2O or Ca were made to increase the impurity levels in the lithium to nominally 1000ppmw of nitrogen, 1000ppmw oxygen or 1wt%Ca, respectively. In order to explore the effect of the vanadium inner capsule on the experiment, a molybdenum capsule that was expected to be more inert to reactions

of interstitial impurities in the lithium was used for some experiments. After exposure to Li, specimens were distilled in vacuum at 500-550°C to remove any residual Li from the specimen. Additional characterization was performed on selected specimens. In this phase, cross-sections were made by mounting the AlN specimens in epoxy and then cutting and polishing to examine the reaction product.

Results and Discussion

Mass changes after the 1000h exposures to lithium are shown in Table I. Both materials have similar densities; thus a mass loss of ≈3.2 mg/cm^2 corresponds to a 10μm loss in material thickness. The results for AlN+0.04Y are significantly better than those reported for AlN+5wt%Y_2O_3.[1] However, the mass losses were still significant at 700°C. Because previous work[1] showed the Al content of the Li increased with exposure temperature but not the N content, there was some concern that the V alloy capsule was gettering N during the test. Therefore, testing was also performed with Mo capsules. The results at 700°C showed less mass loss with a Mo capsule but at 600°C there was a small mass loss instead of a gain, as with a V alloy capsule.

In order to increase the initial nitrogen content in the lithium and possibly improve compatibility, 1000ppm N was added to the lithium for several tests. With a V capsule, this resulted in an increased mass gain at 600°C and slightly less mass loss at 700°C, Table I. The specimen tested at 600°C appeared to have a thicker residue on the surface that was not removed by distillation. With a Mo capsule at 600°C, there was an increase in the amount of mass loss with the addition of N.

Table I. Mass changes of bulk ceramic specimens after 1000h exposures to lithium in a vanadium alloy capsule at various temperatures.

Conditions	AlN+0.04Y		poly xtal CaO		single xtal CaO	
	%	mg/cm^2	%	mg/cm^2	%	mg/cm^2
500°C	-0.06	-0.15			specimen broke	
600°C	+0.1	+0.26	-3.6	-10.3	-3.0	-7.0
600°C†	-0.04	-0.10				
600°C+1000ppm N	+0.6	+1.36				
600°C+1000ppm N†	-0.07	-0.17				
600°C+1000ppm O			-3.3	-9.51	-1.6	-3.9
600°C+1wt%Ca					+2.0	+3.9
700°C	-3.37	-8.16			-9.1	-16.7
700°C†	-0.65	-1.56				
700°C+1000ppm N	-3.20	-7.66				
700°C+1000ppm O					-2.3	-7.2
700°C+1wt%Ca					-6.9	-17.6
800°C	-8.6	-26.5	-8.0	-23.3		

† tested in a Mo capsule

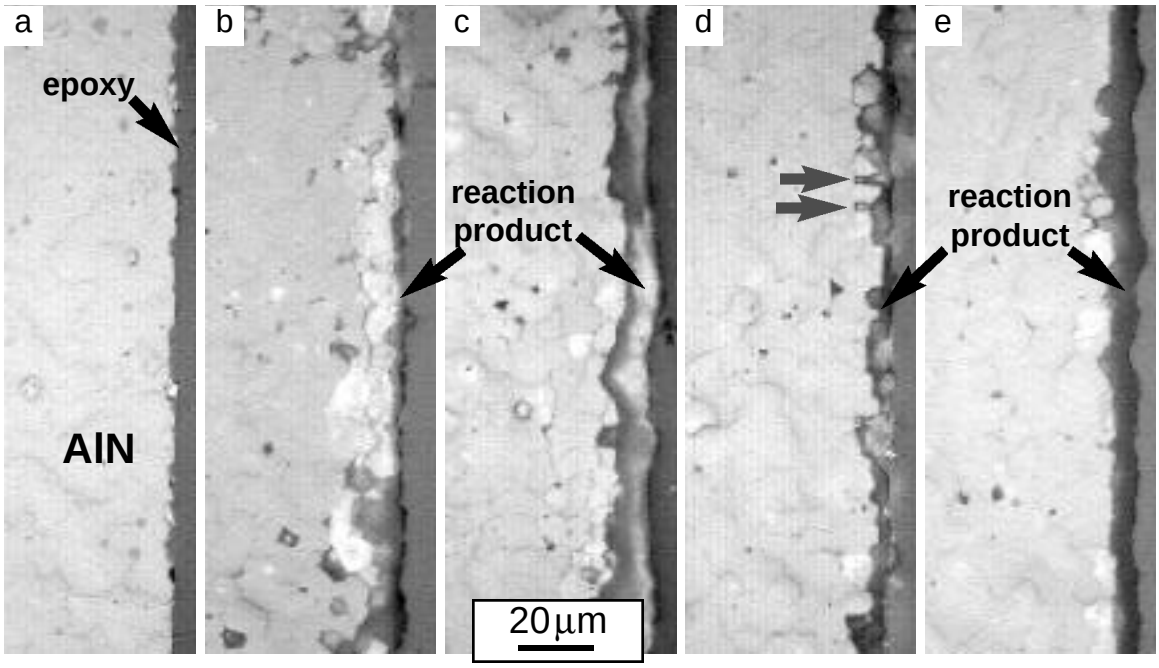

Figure 1. Light microscopy of polished cross-sections of AlN with (a) no exposure, and after 1000h at 600°C in (b) V capsule and undoped Li, (c) V capsule and Li + 1000ppm N, (d) Mo capsule and undoped Li, and (e) Mo capsule and 1000ppm N.

Because of the small mass changes at 600°C, cross-sections of the AlN specimens were made to further examine the reaction product. Figure 1 shows light microscopy images of the polished cross-sections. The cross-sections generally confirm the mass change numbers. For example, the highest mass gain was with a V capsule and a N addition which also showed the thickest reaction product, Figure 1c. The presence of a reaction product when a mass loss was measured (with Mo capsules), Figures 1d and 1e indicated that some AlN dissolved. The roughest interface was observed with a Mo capsule and undoped Li, Figure 1d. There also was some indication of attack along grain boundaries in this case (arrows). Further characterization of these specimens will be performed by Auger electron spectroscopy (AES) or by microprobe. Previous AES sputter depth profiling of the specimen shown in Figure 1b indicated a lithium aluminate layer at the surface.[1,3] Thus, it is necessary to confirm if the layers observed in cross-section also are oxides.

At 600°-800°C, significant mass losses were recorded for both polycrystalline and single crystal CaO, Table I. For either type of specimen, there was no indication of the specimen breaking or chipping and the amount of dissolution increased with test temperature. It is possible that the results for polycrystalline CaO (99.9% purity) reflected grain boundary attack or accelerated attack because the materials was only ≈95% dense. However, the similar results for single crystal CaO suggest that there was significant dissolution of CaO in undoped Li over this temperature range.

In an attempt to slow the rate of dissolution, Ca (1wt%) and O (1000ppmw) were added to the Li. While the addition of O did not change the mass loss for polycrystalline CaO, it did appear to reduce the mass loss for single crystal CaO at 600°C and 700°C, Table I. However, the amount of mass loss after 1000h at 600°C was still the equivalent of more than 10µm of lost material and, at 700°C, the equivalent of more than 20µm was lost.

The addition of Ca to the lithium had a minimal effect on the mass loss at 700°C but resulted in a mass gain at 600°C, Table I. Prior to exposure, the crystals appear greyish and opaque. After distillation, the specimen exposed to Li+1wt%Ca at 600°C was darker and appeared to have a surface layer which may account for the mass gain. Problems with charging in AES and XPS have prevented further characterization of these specimens. Additional experiments with higher O and Ca levels are presently being conducted.

The 400°C-450°C experimental results[4,5] and thermodynamic calculations[6-8] indicate CaO should be a good candidate material. However, rather than compare the reaction energy:

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

the more relevant reactions are the dissolution reactions for the ceramics and the lithium until equilibrium is reached in solution:

$$CaO = (\underline{Ca})Li + (\underline{O})Li \quad \text{or} \qquad [2]$$
$$AlN = (\underline{Al})Li + (\underline{N})Li \qquad [3]$$

Thus, for CaO the relevant thermodynamic equations are:

$$k_r = a_{Ca} \cdot a_O \quad \text{and} \quad \Delta G = R \cdot T \cdot \ln k_r \qquad [4,5]$$

The reaction of the ceramic with lithium should occur until equilibrium is achieved in solution. Calculations using ThermoCalc software, Figure 2, provide equilibrium values using three different assumptions: (1) fixed Ca level of 5wt% in the lithium, (2) fixed O level of 500ppm in the lithium

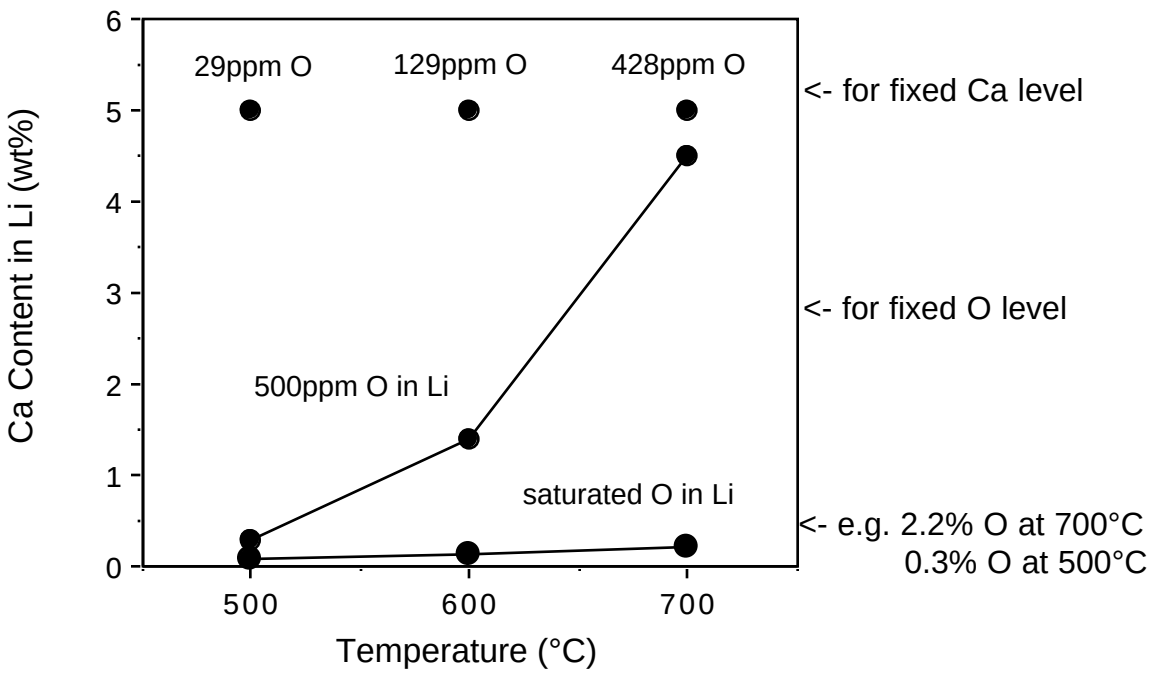

Figure 2. Calculated equilibrium values for Ca and O in Li at 500°-700°C given different assumptions (1) fixed Ca level of 5wt%, (2) fixed O level of 500ppm and (3) Li saturated with O where the saturation value increase from 0.3% at 500°C to 2.2% at 700°C.

and (3) Li saturated with O where the calculated saturation value increases from 0.3% at 500°C to 2.2% at 700°C. With the high levels of Ca and O in solution at equilibrium, these thermodynamic calculations suggest that the high dissolution rates of CaO in undoped Li are clearly possible. The calculations also indicate that corrosion control likely will depend upon maintaining the proper levels of corrosion product in the lithium. While it could be argued that pure lithium should result in lower corrosion rates, these calculations suggest that, rather than purifying the lithium, adding Ca and O to the lithium should lower the rate of corrosion. Of course, this hypothesis needs to be experimentally verified. The other concern with heavily doping the lithium is also revealed in Figure 2. If 5wt%Ca were added to Li in order to slow the dissolution of CaO, then the solubility of O will change radically from the hot leg to the cold leg of the system. This change in solubility would likely result in mass transfer by which dissolution would continue in the hot leg and deposition of Li_2O in the cold leg (due to the lower solubility of O at lower temperatures) could clog the Li flow.

Similar calculations were made for Al and N in lithium over the same temperature range, Figure 3. In this case, assuming 300ppm N in the lithium, the equilibrium values for Al are orders of magnitude lower, <15ppm at 700°C. This may explain why the mass losses at 600°C were significantly lower for AlN compared to CaO, Table I.

This combination of experimental results and thermodynamic analysis suggests a new strategy for selecting possible MHD coating materials. Elements which are highly soluble in Li may be more susceptible to dissolution at high temperature. Thus, one selection criteria could be cations which are insoluble in Li. Of course, looking for insoluble cations does not obviate the thermodynamic requirement suggested by Equation 1. As an example, a single crystal of CeO_2 was exposed in lithium for 1000h at 600°C and lost 20.7% of its mass. While Ce is expected to

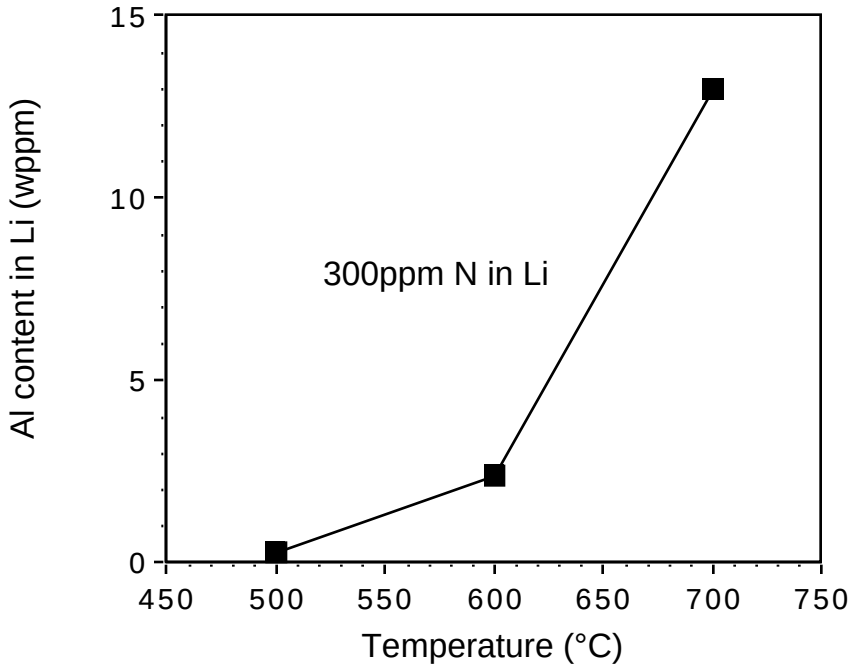

Figure 3. Calculated equilibrium values for Al in Li at 500°-700°C given a fixed N level of 300ppm. Note that the equilibrium Al levels are in wppm compared to up to 5wt% for Ca.

be relatively insoluble in Li, CeO_2 is less stable than Li_2O and thus dissolved during exposure. However, there are other oxides such as Sc_2O_3, Y_2O_3 and Er_2O_3, which have similar stabilities as CaO,[9] but have low solubilities which may make them more attractive candidates. These oxides would not be able to “self-heal” as no supply of cations could be provided in the lithium as is currently envisioned for CaO.[10] However, if the coating has exceptional Li compatibility and adhesion, there would be no need for healing.

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