

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)

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

Two candidate materials for insulating coatings in a lithium-cooled fusion reactor have been exposed to lithium in 1000h isothermal tests from 400°-800°C to determine their maximum compatibility temperature. Bulk samples of AlN+5wt%Y₂O₃ showed significant mass loss at 600°C and higher temperatures. The amount of attack was reduced when AlN+0.4Y was tested. Characterization by auger spectroscopy of a AlN+0.4Y specimen exposed at 600°C indicated the possibility of a lithium aluminate compound formation. Bulk specimens of CaO (99.9% purity) showed mass losses above 500°C indicating a possible dissolution problem that had not been observed in previous short-term screening tests. Doping of the lithium with oxygen (in the case of CaO) did not appear effective in reducing the attack at 600°C. However, doping with nitrogen (with AlN) did show a possible beneficial effect in conjunction with a Mo capsule. Based on these results, future testing also will consider alternative candidates such as Y₂O₃ and Er₂O₃.

PROGRESS AND STATUS

Experimental Procedure

Two types of aluminum nitride were tested, one with nominally 5wt% Y₂O₃ from Goodfellow Corp. and the other with 400wppm Y and 0.9wt% oxygen from Tokuyama Corp (Shapal SH-50). The AlN+0.4Y material was produced by reducing and nitriding aluminum oxide and had a average grain size of 7-8µm. Both had a density of 3.25g/cm³. Specimens of AlN+Y₂O₃ measured ≈0.6x12x12mm while Y-free AlN measured ≈2x8x12mm. Calcium oxide (99.9% purity) was obtained from Cerac Corp. in the form of a sputtering target that was cut into specimens approximately ≈6x6x13mm. To avoid degradation from reaction with moisture, CaO was cut with a diamond blade and handled in dry air or in an argon glove box before and after testing. Dimensions and mass were measured before and after exposure with an accuracy of 0.02mg/cm².

The experimental procedure for lithium exposures has been outlined previously^{1,2}. Bulk ceramic specimens were exposed for 1000h at 400°-800°C. In three tests, additions of Li₃N and Li₂O were made to increase the impurity levels in the lithium to nominally 1000ppmw of nitrogen or oxygen. In order to explore the effect of the vanadium inner capsule on the experiment, a molybdenum capsule was used for one experiment with Li₃N. In some cases, a final alcohol cleaning of AlN (but not CaO) was done to remove any residual lithium or distillation residue. However, it was

determined that this left a carbon residue on the specimen and inhibited further characterization.

Initial characterization has been performed on selected specimens. In order to detect lithium, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to characterize the specimens after exposure. Because of the heavy attack on many of the specimens, electrical resistance measurements have not yet been made.

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 $\approx 3.2 \text{ mg/cm}^2$ corresponds to a $10 \mu\text{m}$ loss in material thickness. Some of the mass change results were confounded by the inadvertent use of Ni wire (rather than the desired Mo wire) to restrain the specimens in the capsule. This resulted in some nickel being deposited on the surface of the ceramic specimen (determined by AES) due to dissolution of the wire. The amount of deposition appeared to increase with temperature with little Ni observed at 400°C .

At 400°C , the mass changes were slight for all of the materials tested which is in agreement with previous 100h tests at 400°C ³ and 450°C .⁴ As reported previously,^{1,2} AlN with 5wt% Y_2O_3 showed increasing attack over the temperature range 400°C - 700°C , Table I. In order to avoid the complication of the $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) grain boundary phase, additional tests were performed on AlN+0.4Y.

The results for AlN+0.4Y showed mass gains up until 800°C where a large mass loss was measured, Table I. However, the mass gain at 500°C and 700°C was in part due to a visible Ni deposition. Examination of the AlN surface after exposure at 500°C by AES showed 70% of the signal from Ni. A slight mass gain was observed for the AlN+0.4Y at 600°C , rather than the mass loss observed for AlN+5wt% Y_2O_3 . This indicates a beneficial effect of reducing the yttrium content in the AlN.

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

Conditions	AlN+ Y_2O_3		AlN+0.4Y		CaO	
	%	mg/cm ²	%	mg/cm ²	%	mg/cm ²
400°C	-0.18*	-0.17*	+0.1*	+0.23*	+0.08*	+0.22*
500°C	+1.7*	+1.9*	+1.1*	+2.4*	-3.1*	-8.56*
600°C	-1.9	-1.8	+0.1	+0.26	-3.6	-10.3
600°C +1000ppm N			+0.6	+1.36		
600°C +1000ppm N†			-0.1	-0.17		
600°C +1000ppm O					-3.3	-9.51
700°C	specimen broke		+5.4*	+12.5*	-2.7*	-7.18*
800°C	not tested		-8.6	-26.5	-8.0	-23.3

* specimen suspended by Ni wire which dissolved and redeposited on specimen during test

† tested in a Mo capsule

In order to saturate the lithium with nitrogen and possibly improve compatibility, nitrogen was added to the lithium for two tests. A higher mass gain was observed for AlN+0.4Y when 1000ppm nitrogen was added to the lithium (Table I), but the specimen appeared to have a thicker residue on the surface that was not removed by distillation. Previous testing of the lithium after reaction with AlN+5wt%Y₂O₃ showed that, while the Al content of the lithium increased with temperature (i.e. the amount of reaction), the nitrogen content did not. This suggested a possible reaction with the vanadium capsule. Thus, a Mo capsule also was used in one test. In this case, the specimen lost a small amount of weight (0.17mg/cm²). Additional testing and characterization will further explore this result.

The AlN+0.4Y specimen exposed to lithium at 600°C (followed by distillation at 500-600°C) was sputter depth profiled by AES in order to characterize the reaction product. Figure 2 shows a complex distribution of elements to a depth of almost 2µm below which there appeared to be largely Al and N present. There appeared to be an outer layer (labeled I) of mainly Li and O and a second layer (II) where there were large amounts of Li, Al and O above the substrate (III). This indicates that there is probably a reaction where the AlN is transforming to an oxide, such as lithium aluminate. The specimen exposed at 800°C showed a surface composition of 42at.%O-32%Al-12%Li-14%C beneath a patchy layer of Li-C-O which appeared to spall off of some areas. (Lithium exposed to air will readily form a carbonate.) In this case, it was believed that the oxygen-rich layer was too thick to be sputtered through by AES. The presence of an aluminate reaction product could degrade the electrical properties of the coating and lithium aluminate is not stable in Li at 450°C.⁴

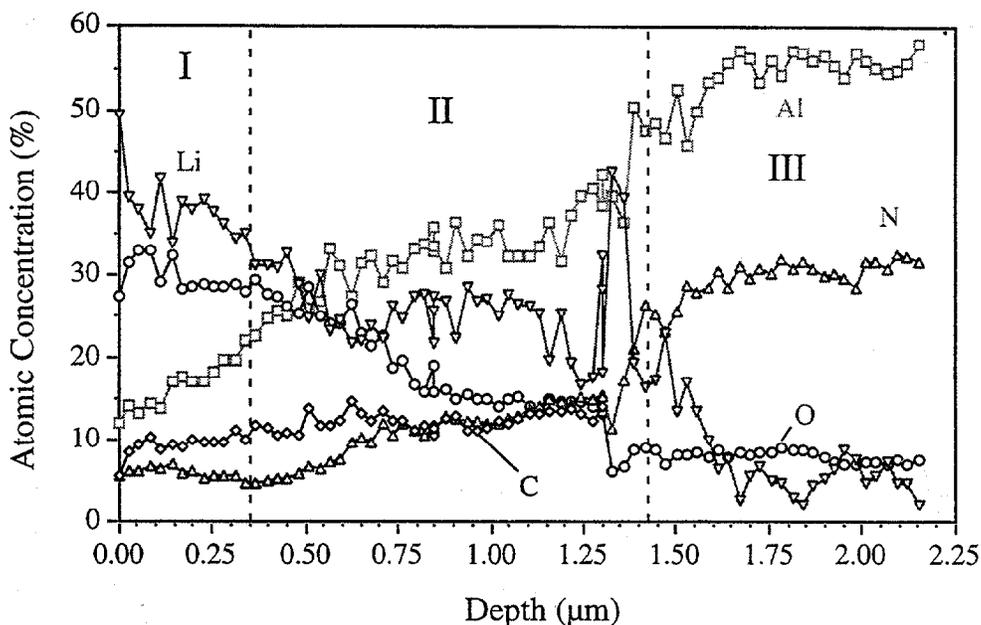


Figure 2. Sputter depth profile from the surface of AlN+0.4Y after 1000h at 600°C determined by Auger electron spectroscopy. A layer of largely Li and O (I) was observed above a layer with large amounts of Li, Al and O (II). Further sputtering appeared to reveal the substrate (III).

The source of the oxygen in the Li-containing reaction layer (Figure 2) could be the AlN-0.4Y material (0.9wt%), impurities in the lithium or the vanadium walls. In the presence of lithium, any oxygen in the V-4Cr-4Ti is likely to diffuse out. However, this process would be relatively slow at temperatures below 600°C. More testing is required to confirm this behavior over the temperature range 500°-700°C and additional characterization by x-ray diffraction is warranted. These results suggest that a thin AlN MHD coating may be substantially attacked by a similar process in a flowing lithium system. The change in electrical properties of AlN after exposure to lithium may indicate the severity of this problem. The presence of oxygen in the outer layer indicates that the lithium may need to be further purified in order to avoid oxidation of AlN. Neither alumina³ or LiAlO₂⁴ is compatible with lithium.

At 500°-800°C, significant mass losses were recorded for CaO that generally increased with temperature. These specimens were very brittle and some mass loss may have resulted from small pieces breaking off. However, the consistency of the losses and similar general appearance of the specimens after testing suggested that these results are accurate and that substantial dissolution occurred at higher temperatures. An attempt was made to saturate the lithium with oxygen in order to slow the rate of dissolution. However, the addition of 1000ppm O to the lithium showed little change in reaction rate and did not appear to affect the reaction. Due to charging problems, CaO specimens could not be analyzed by AES. XPS was used to detect Li on the surface but it could not be determined if it was residual Li not removed during distillation. The 400°C-450°C experimental results^{3,4} and thermodynamic calculations⁵⁻⁷ indicate CaO should be a good candidate material. However, based on these results, CaO does not appear to be a viable candidate material for the higher temperature range desired.

In general, the results are not promising for CaO or AlN+5wt%Y₂O₃ at 600°-800°C; however, more work is required to better characterize the performance of AlN+0.4Y in this temperature range and further investigate the effect of N doping in conjunction with a Mo capsule. Future work also will focus on single crystals of CaO in attempt to further confirm these results for its long-term, high temperature compatibility. Single crystals will eliminate issues such as accelerated grain boundary attack or the role of porosity on these tests. Also single crystals of other oxides such as Sc₂O₃, Y₂O₃ and Er₂O₃, which have similar stabilities as CaO,⁸ will be considered. Recent work suggests that oxides such as these may be stable in lithium in this temperature range.⁹

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