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Temperature limits on the compatibility of insulating ceramics in lithium ☆

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Abstract

CaO and AlN are candidates for electrically insulating coatings in a lithium-cooled fusion reactor. Bulk specimens of AlN + 0.04 wt%Y and single-crystal CaO have been exposed to lithium in 1000 h isothermal capsule tests at 500–800 °C to determine the maximum temperature at which acceptable compatibility is likely. A large increase in the amount of mass loss of AlN was observed between 600 and 700 °C. At 700 °C, the amount of dissolution was reduced when a Mo capsule was used instead of a V alloy test capsule. High mass losses for single-crystal specimens of CaO were observed after exposure at 600 °C. In this case, changing to a Mo test capsule or adding Ca or O to the lithium did not consistently show a beneficial effect. At 700 °C, neither doping the Li with Ca or O significantly altered the high mass losses. These results suggest that CaO may be limited to exposure temperatures of less than 600 °C but that AlN may be able to operate above 600 °C. Because some designs call for operating temperatures of 750 °C, other compositions, such as Er_2O_3 and Y_2O_3, also are being evaluated. Preliminary results show promise for these oxides after exposure at 800 °C.

1. Introduction

The most promising blanket concept for a deuterium/tritium fueled fusion reactor with vanadium structural alloys uses liquid lithium because of its excellent tritium breeding ratio but also because of the susceptibility of vanadium alloys to embrittlement by oxygen and hydrogen in other environments such as helium [1–4]. One problem with the vanadium alloy – lithium blanket concept is that, in fusion energy systems where a strong magnetic field is used to contain the fusion plasma, a magneto-hydrodynamic (MHD) pressure drop is developed when the electrically conductive lithium flows across the magnetic field lines. To reduce this problem it is necessary to have an insulating barrier to decouple the lithium and the vanadium alloy structure to minimize the MHD resistance to flow. An acceptable coating must not only be electrically resistant but also must satisfy a variety of requirements such as (1) good adhesion to the vanadium wall, (2) resistance to radiation damage, (3) low thickness to avoid heat transfer and thermal expansion mismatch problems, and (4) compatibility with liquid Li. Whereas some early materials screening tests were conducted at 400–500 °C [5,6], current fusion reactor designs require the coatings to operate at temperatures as high as 700–750 °C in order to obtain economically-viable efficiencies [7,8].

Several studies have shown by experiments and/or theoretical calculations that there are relatively few materials that meet both the Li compatibility and electrical resistance requirements [5,6,9–12]. Two of the most attractive candidates have been CaO and AlN. However, more recent experimental work on bulk ceramic specimens showed that both of these materials exhibited significant dissolution in Li capsule tests at 700 and 800 °C [13]. Bulk specimens were used to verify Li compatibility prior to more-extensive coating development studies and to separate problems associated with

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☆ Dedicated to the memory of J.H. DeVan.

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coating fabrication from the fundamental issue of compatibility in lithium. To follow up on the initial results, additional capsule testing in Li has been conducted on these materials and several new candidates to specify maximum operating temperatures for each material. One objective has been to determine if either doping the Li or changing the capsule material (V–Cr–Ti alloys) would reduce the amount of dissolution. The current results continue to suggest that CaO and AlN have temperature limitations that may require other candidate materials, such as Er_2O_3 and Y_2O_3, to be considered.

2. Experimental procedure

High purity AlN (0.9%O, 0.04%Y) from Tokuyama Corp (Shapal SH-50) was made by nitriding Al_2O_3. (Unless noted, all compositions are given in weight percent.) The AlN specimens measured $2 \times 8 \times 12$ mm^3, had an average grain size of 7–8 μm and a density of 3.25 g/cm^3. Single crystals of CaO, CeO_2 and Y_2O_3 were obtained from Commercial Crystal Laboratories (Naples, FL). To avoid degradation from reaction with moisture, CaO was handled in dry air or in an argon glove box before and after testing. Specimens were cut with a diamond blade into specimens measuring $\approx 2 \times 6 \times 12$ mm^3. Previous work on these compositions also had used AlN with 5%Y_2O_3 and polycrystalline CaO specimens [13]. Specimens of Er_2O_3 were made by conventional powder processing, sintered at 1600 °C and were 85% of theoretical density but with only 1% open porosity. Specimen dimensions and mass were measured before and after exposure. The mass gain accuracy was 0.01 mg/cm^2.

The experimental procedure for exposure to lithium has been outlined elsewhere [13]. High purity solid lithium (starting composition in Table 1) was top loaded into a V alloy or Mo capsule in an argon glove box and the capsules were sealed using gas-tungsten-arc welding. Bulk ceramic specimens were exposed for 1000 h at 500–800 °C in calibrated box furnaces. In some tests, additions of Li_3N, Li_2O or Ca (99.5% purity) granules were made to increase the dopant levels in the lithium to nominally 1000 ppm N, 1000–2000 ppm O or 1–10% 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 reaction with interstitial impurities in the lithium was used for some experiments. Molybdenum is even more resistant than V to dissolution in lithium [14]. 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. For example, cross-sections were made by mounting specimens in epoxy and then cutting and polishing to examine the reaction product. Selected samples of lithium were taken after the exposure for spectrographic chemical analysis at Lockheed Martin Energy Systems, Oak Ridge, TN.

3. Results and discussion

Mass changes for AlN + 0.04%Y after 1000 h exposures to lithium with V alloy capsule walls are shown in Fig. 1. The results for AlN + 0.04%Y are significantly better than those previously reported for AlN + 5%Y_2O_3 [13]. However, a mass loss of ≈3.2 mg/cm^2 corresponds to a uniform 10 μm loss in material thickness (which is also true for CaO with a similar density). Thus, the mass losses above 600 °C are unacceptably high in a V alloy capsule.

Because previous work [13] showed the Al content of the Li increased with exposure temperature but the N content did not, there was some concern that the V alloy capsule was gettering N during the test. When a Mo test capsule was used instead of a V alloy, the results at 700° (2 separate tests) and 800 °C showed only a slight mass loss, Fig. 1. However, these results suggest that all V alloy surfaces exposed to Li at high temperature would have to be coated in order to prevent N gettering from the Li.

In order to increase the initial nitrogen content in the lithium and possibly improve compatibility with AlN, 1000 ppm N was added to the lithium for several tests. With a V capsule, this resulted in an increased mass gain for AlN at 600 °C but only slightly less mass loss at

Table 1
Lithium composition before and after exposure to AlN specimens determined by spectrographic analysis

Conditions	Nitrogen (wppm)	Aluminum (wppm)	Yttrium (wppm)
Starting lithium[a]	140	<0.3	<0.3
500 °C V can	150	1	<0.3
600 °C Mo can	Contaminated	1	<0.4
700 °C V can	Contaminated	110	<0.4
700 °C V can + 1000 ppm N	120	160	<0.4
700 °C Mo can	330	3	<0.4

[a] 40 metallic elements examined, only Cu (15 wppm) was above detectability limit.

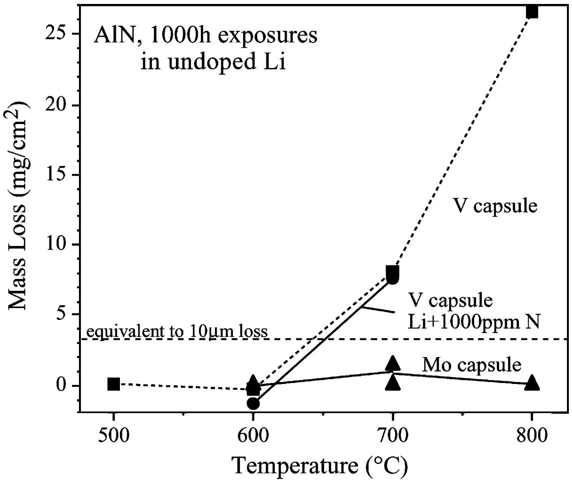

Fig. 1. Mass losses for AlN + 0.04 Y after 1000 h at various temperatures. At 700 °C, switching from a V alloy capsule to a Mo capsule had a more significant effect than the addition of 1000 ppm N to the lithium. A mass loss of ≈3.2 mg/cm^2 corresponds to a 10 μm loss in material thickness.

700 °C, Fig. 1. The AlN 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 a small mass loss with the addition of N, almost identical to the result without a N addition. In terms of reducing the 700 °C dissolution, the addition of N was not as effective as changing to a Mo capsule.

Table 1 shows the composition of the lithium after several exposures. Unfortunately, two of the samples were contaminated prior to spectrographic analysis and contained very high N levels. However, the available data supports the hypothesis that N is gettered by a V alloy capsule but not by a Mo capsule. In particular, at 700 °C the post-test N level was only 120 ppm when 1000 ppm N was added prior to the test with a V capsule, Table 1. In contrast, with no added N to a Mo capsule at 700 °C, 330 ppm N was measured in the lithium after exposure. The Al levels likewise reflected the reduced attack at 700°C when a Mo capsule was used. However, the 3 ppm Al detected after the 700 °C exposure in a Mo capsule is much lower than expected.

Because of the small mass changes at 600 °C, cross-sections of the AlN specimens were made to further examine the reaction product. Fig. 2 shows light microscopy images of the polished cross-sections. The cross-sections generally confirm the mass change numbers. For example, the highest mass gain (1.36 mg/cm^2) was with a V capsule and a N addition which also showed the thickest reaction product, Fig. 2(c). The presence of a reaction product when a mass loss was measured (with Mo capsules), Fig. 2(d) and (e) indicated that some AlN dissolved. The roughest interface was observed with a Mo capsule and undoped Li, Fig. 2(d). There also was some indication of attack along grain boundaries in this case (arrows). Previous AES sputter depth profiling of the specimen shown in Fig. 2(b) indicated a lithium aluminate layer at the surface [13]. Further characterization of these specimens was performed by electron probe microanalysis (EPMA). This analysis could not detect Li but an Al and O containing grain boundary phase was observed and was more prominent when the specimen was encapsulated with a V alloy than with Mo. This phase could be a lithium aluminate. For the specimen exposed in a V capsule to undoped Li at 600 °C (Fig. 2(b)), in some areas the oxide grain boundary phase was observed to a depth of 70 μm.

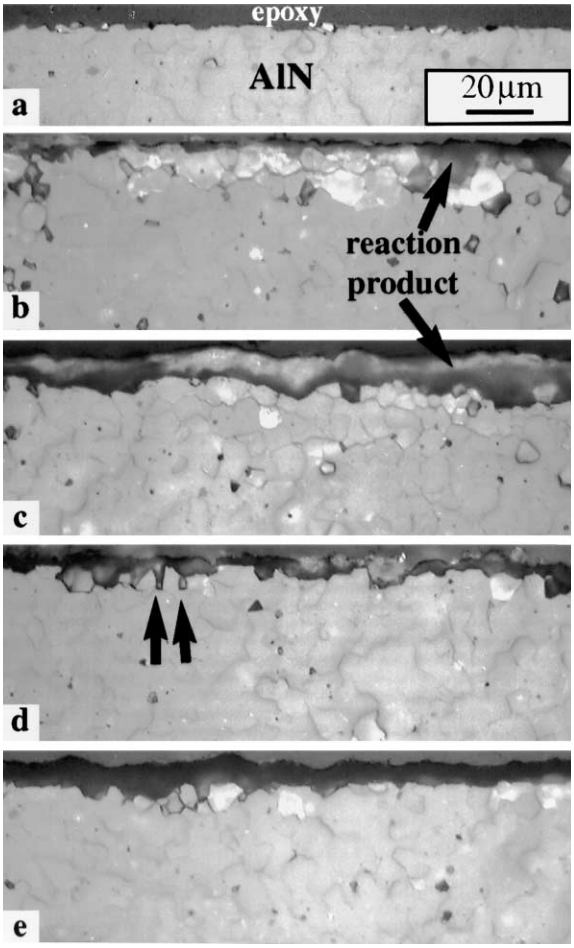

Fig. 2. Light microscopy of polished cross-sections of AlN (a) unexposed and exposed at 600 °C for 100 h, (b) in V capsule with no addition, (c) in V capsule with 1000 ppm N addition, (d) in Mo capsule with no addition, and (e) in Mo capsule with 1000 ppm N addition. Adding N to Li resulted in a thicker reaction layer in both cases. With a Mo capsule, there were slight mass losses instead of slight mass gains with V capsules at 600 °C.

The greater amount of oxide would explain the small mass gain (0.26 mg/cm^2) when a V alloy capsule was used.

For single crystal CaO, relatively high mass losses were observed in undoped Li at 600 and 700 °C, Figs. 3 and 4. In this case, neither V or Mo would be expected to getter O from Li [15]; therefore, no effect of capsule type was expected and virtually none was observed at 600 °C, Fig. 3.

These mass losses for CaO single crystals are contrary to its anticipated compatibility with Li. The 400–450 °C experimental results [5,6] and thermodynamic calculations [9,10,12] indicate CaO should be have acceptable compatibility. However, no other experimental results have been reported in undoped Li for 1000 h at 600–700 °C and several of the previous thermodynamic calculations only considered the Gibbs free energies of formation. Rather than compare the reaction energy for

$$\mathrm{CaO} + 2\mathrm{Li} \leftrightarrow \mathrm{Ca} + \mathrm{Li_2O} \tag{1}$$

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

$$\mathrm{CaO} = \mathrm{Ca(Li)} + \mathrm{O(Li)} \tag{2}$$

or

$$\mathrm{AlN} = \mathrm{Al(Li)} + \mathrm{N(Li)}. \tag{3}$$

Thus, for CaO the relevant thermodynamic equations are:

$$k_r = a_{\mathrm{Ca}} a_{\mathrm{O}} \tag{4}$$

and

$$\Delta G = RT \ln k_r. \tag{5}$$

Calculations using ThermoCalc software, Fig. 5, provide equilibrium values for Ca(Li) and O(Li) for three different assumptions: (1) fixed Ca level of 5% in the lithium, (2) fixed O level of 500 ppm in the lithium 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. Similar calculations were made for Al and N in lithium over the same temperature range, Fig. 6. In this case, assuming 300 ppm N in the lithium, the equilibrium values for Al are orders of magnitude lower, e.g. <15 ppm at 700 °C, than those for Ca. This may explain why the mass losses at 600 °C were significantly lower for AlN compared to CaO. The calculations also indicate that corrosion control likely will depend upon maintaining the proper levels of corrosion product in the lithium. While intuition from metals compatibility is that pure lithium results in lower corrosion rates, these calculations suggest that, rather than purifying the lithium, adding Ca and O or Al and N to the lithium should lower the rate of corrosion.

Based on these thermodynamic calculations, additions of Ca or O were made to the lithium in an effort to improve performance at 600 and 700 °C. Fig. 3 summarizes the results for various test conditions at 600 °C.

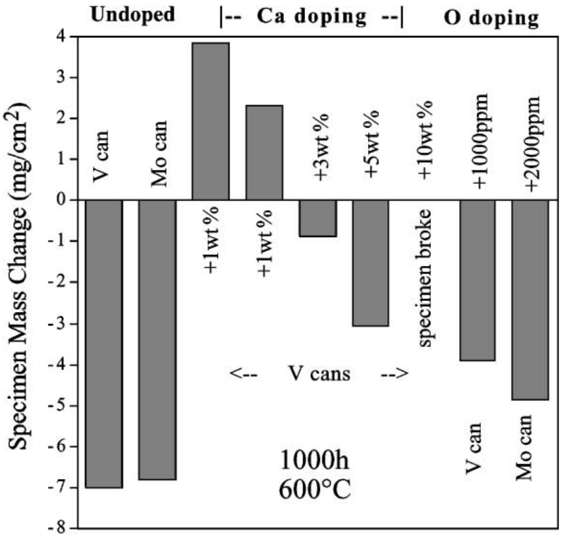

Fig. 3. Mass changes for single crystal CaO after 1000 h at 600 °C with various additives to the lithium and both V and Mo capsules. A mass loss of ≈3.2 mg/cm^2 corresponds to a 10 μm loss in material thickness.

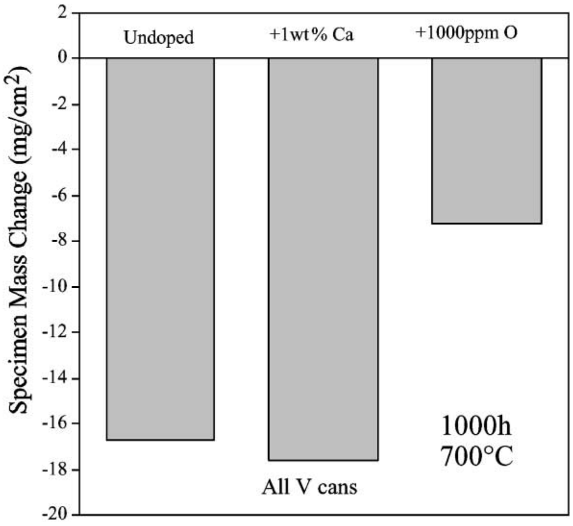

Fig. 4. Mass changes for single crystal CaO after 1000 h at 700 °C with lithium and lithium doped with Ca or O. Neither addition prevented very high levels of dissolution at this temperature.

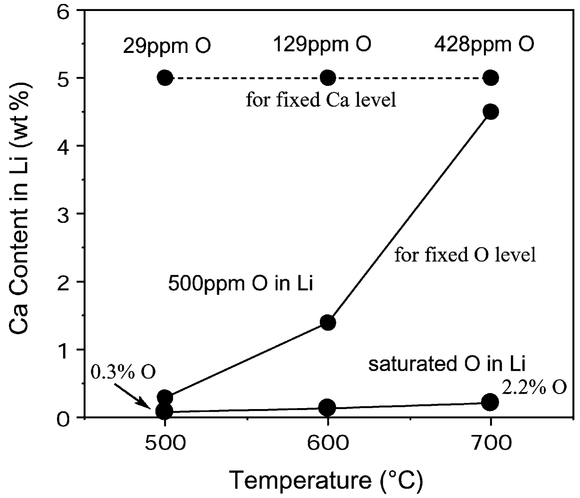

Fig. 5. Calculated equilibrium values for Ca and O in Li at 500–700 °C given different assumptions: (1) fixed Ca level of 5%, (2) fixed O level of 500 ppm and (3) Li saturated with O where the saturation value increase from 0.3% at 500 °C to 2.2% at 700 °C.

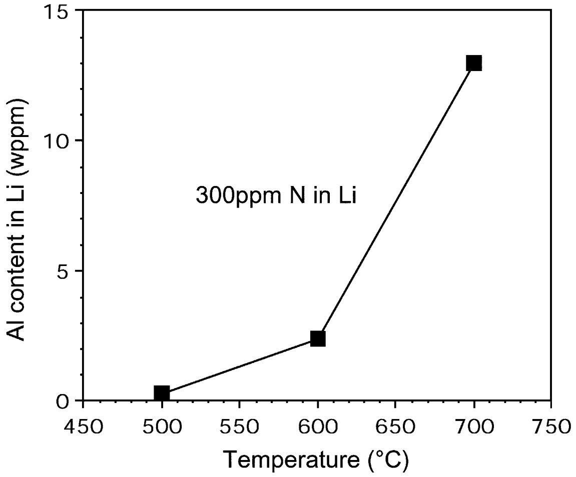

Fig. 6. Calculated equilibrium values for Al in Li at 500–700 °C given a fixed N level of 300 ppm. Note that the equilibrium Al levels are in wppm compared to up to 5% for Ca.

The addition of 1000 or 2000 ppm O resulted in a modest reduction in the amount of dissolution. However, the mass losses were still equivalent to more than a 10 μm loss in material after 1000 h. An addition of 1% Ca in two separate tests resulted in a mass gain rather than a mass loss without Ca. The reason for the mass gain is not known but may be the result of Ca remaining on the specimen after distillation of the lithium after the test. Prior to exposure, the crystals appear greyish and opaque. After distillation, the specimen exposed to Li + 1% Ca at 600 °C was darker and appeared to have a surface layer which may account for the mass gain. Unexpectedly, the addition of more Ca (3% and 5%) resulted in specimen mass losses, Fig. 3. The specimen broke after exposure to Li + 10% Ca preventing an accurate mass change measurement.

These results with higher Ca levels suggest that very high Ca doping levels may be required to improve the compatibility. The major problem with this doping strategy is that for Ca-doped Li the solubility of O will change radically from the hot leg (e.g. with 5% Ca, 428 ppm at 700 °C) to the cold leg (e.g. 29 ppm at 600 °C) of the flowing Li system, Fig. 5. This change in solubility would likely result in mass transfer of oxygen 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 temperature) could restrict the Li flow. A second concern is that the breeding efficiency of the lithium would be negatively affected if a significant amount of Ca or O were added to the lithium [18].

Similar doping tests also were performed at 700 °C. In this case, pronounced mass losses were observed even with a 1% Ca addition, Fig. 4. An addition of 1000 ppm O reduced the mass loss compared to undoped Li but a significant amount of material was still lost during the 1000 h exposure. Problems with charging in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy have prevented further characterization of these specimens. In the previous study [13], it was suggested that the mass losses for polycrystalline CaO (99.9% purity) specimens might reflect grain boundary attack or accelerated attack because the material was only ≈95% dense. However, a comparison of the single- and poly-crystalline specimen mass losses in Fig. 7 shows that nearly identical mass losses were observed and the amount of dissolution increased with test temperature.

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 Eq. (1). As an example, a single crystal of CeO_2 was exposed in lithium for 1000 h at 600 °C and lost 20.7% of its mass, Fig. 7. While Ce is expected to be relatively insoluble in Li, CeO_2 is less stable than Li_2O (Table 2) 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 (Table 2), but have low solubilities. This may make them more attractive candidates. They also would not disintegrate in ambient air which would eliminate fabrication issues associated with CaO. These oxides would not be able to ‘self-heal’ as no supply of

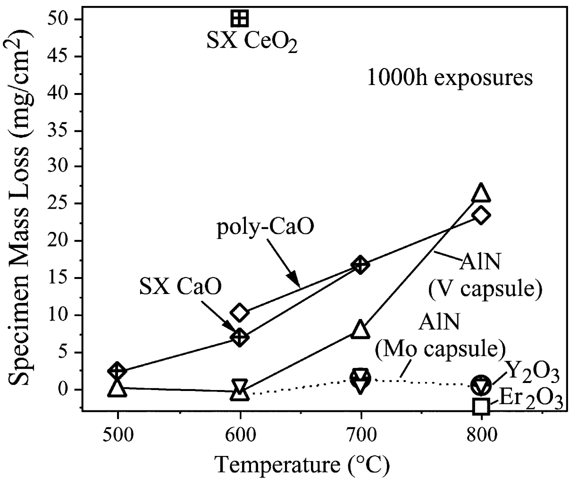

Fig. 7. Mass losses for some other oxide materials compared to the data for AlN and CaO after 1000 h at various temperatures. The results from polycrystalline CaO are from previous work [13].

cations could be provided in the lithium as is currently envisioned for CaO [11]. However, if the coating has exceptional Li compatibility and adhesion, there would be no need for healing.

Initial results at 800 °C for Er_2O_3 and Y_2O_3 are shown in Fig. 7. Compared to AlN and CaO, these oxides showed lower mass changes. The Y_2O_3 specimen lost a small amount of mass while the Er_2O_3 specimen showed a mass gain after exposure. The specimens also changed color from pink for Er_2O_3 and opaque for Y_2O_3 to gray or black after the test, suggesting possible O gettering from the specimen. As with CaO, problems with charging in AES have prevented identification of any residual Li on these specimens. However, because the specimen of Er_2O_3 was not fully dense, penetration of Li may have caused the mass gain and color change. Previous work on Y_2O_3 found the formation of a $YLiO_2$ surface layer [17] which may degrade a thin Y_2O_3 coating.

Table 2
Gibbs free energy of formation for several ceramic materials at room temperature [16]

Materials	$\Delta G_f°$ (kJ/mol O_2)
CeO_2	−1025
Al_2O_3	−1045
Li_2O	−1122
Er_2O_3	−1206
CaO	−1207
Y_2O_3	−1211
Sc_2O_3	−1213

4. Summary

Bulk specimens of two candidate compositions for insulating coatings in a lithium-cooled fusion reactor, CaO and AlN, have been exposed to lithium in 1000 h 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 a thin reaction layer formed at 600 °C. For testing at 700 °C, changing from a V alloy capsule liner to a Mo capsule produced a greater reduction in mass loss than adding 1000 ppm N to the Li in a V alloy capsule test. The maximum use temperature of AlN may be higher than 600 °C, but further testing is necessary to confirm sufficient compatibility at higher temperatures. These results raise concern about the compatibility of AlN with V–4Cr–4Ti, for example, that Ti in the Valloy may getter N from an AlN coating.

Single crystals of CaO showed unacceptably high losses at 600 and 700 °C similar to results with polycrystalline specimens. At 600 °C, additions of O or Ca to the Li reduced the amount of mass loss during the 1000 h exposure suggesting that doping Li may be an avenue for improved compatibility. However at 700 °C, O or Ca additions produced only minor changes to the high mass losses. For exposure to undoped Li, a thin CaO coating would be restricted to temperatures below 600 °C. At 800 °C, Er_2O_3 and Y_2O_3 showed much better compatibility with Li than AlN or CaO. All of these results are consistent with an analysis of the relevant thermodynamic solubility data and the hypothesis that low solubility elements are more promising candidates if a higher temperature MHD coating is needed.

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