EVALUATION OF THE CHEMICAL COMPATIBILITY OF Y_2O_3 AS AN ELECTRICALLY INSULATING COATING FOR A LIQUID LITHIUM BLANKET—P. F. Tortorelli, B. A. Pint, and T. M. Besmann (Oak Ridge National Laboratory, USA)

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. Thermodynamic modeling is an integral part of this assessment program.

SUMMARY

Modeling of the chemical stability of Y_2O_3 in molten lithium was hampered by the lack of available thermochemical data for mixed oxides of Li-Y and Ti-Y. Nevertheless, this evaluation indicated that Y_2O_3 was not stable in a lithium environment at 600-1000°C. Furthermore, the results indicated that the experimental observations of Y-Ti oxides on Y_2O_3 after exposure to molten lithium in V-4Ti-4Cr capsules was likely due to formation of Li_2TiO_3 and $LiYO_2$.

PROGRESS AND STATUS

Background

Previous work related to the development of electrically insulating coatings to minimize the MHD resistance to lithium flow has shown significant instability issues related to several candidate ceramics (see, for example, [1]). A fundamental problem is that many oxides with sufficient electrical resistivity are reduced by molten lithium.[2,3] Furthermore, ceramics that appear to be stable based on their free energies of formation (ΔG's) with respect to the ΔG of Li_2O (such as CaO) can still decompose due to dissolution of the metallic species when the cation solubility in lithium is appreciable.[4] Therefore, recent efforts have emphasized Y_2O_3 and Er_2O_3 as potential MHD coatings.[1] In this regard, initial fusion-related exposures of bulk Y_2O_3 in static lithium yielded somewhat more promising results[4,5] consistent with some early work on lithium compatibility.[6] However, experiments with Y_2O_3 coatings have shown degradation of the ceramic.[1,7] While some of the incompatibilities can possibly be ascribed to coating defects and/or poor adhesion, chemical interactions of the Y_2O_3 and lithium were noted based on the presence of $LiYO_2$.[1,5,7] This product is electrically conductive and thus compromises the insulating ability of the coating.[1] Furthermore, some evidence of oxide particles containing yttrium and titanium were reported using Auger electron spectroscopy when Y_2O_3 coatings were exposed in V-4Ti-4Cr capsules.[1] Using glancing angle x-ray diffraction, a number of unidentified d peaks were observed but none could be matched to the limited data available from the Y-Ti-O system. In view of these observations, the fundamental chemical stabilities of Y_2O_3 and mixed yttrium-titanium oxides in molten lithium was investigated using equilibrium thermodynamic approaches based on the FACTSage™ databases and codes.[8]

Modeling Results

Based on simple free energy of formation considerations, Y_2O_3 is expected to be stable in molten lithium because the free energy of formation (ΔG) for yttria is significantly more negative than that of Li_2O over the temperature range of interest (see Table 1). In addition, the solubility of yttrium in lithium is expected to be low[9] so, unlike CaO in lithium,[4] cation dissolution should not significantly compromise

Table 1. Calculated free energies of formation per atom of oxygen

Temperature (°C)	**ΔG (kJ/atom of O_2)**		
	Li_2O	**Y_2O_3**	**Li_2TiO_3**
600	-484	-550	-466
700	-470	-541	-456
800	-456	-531	-446
900	-443	-522	-435
1000	-429	-513	-425

compatibility. There are no thermodynamic data available for $LiYO_2$ in the FACTSage™ databases and, consequently, calculation of stable species in the Li-Y-O system does not predict this product. However, given the experimental observations of such,[1,5,7], $LiYO_2$ must be considered a stable product in the subject system.

The observation of Y-Ti-O products after exposure to static lithium[1] suggests the interesting possibility that such mixed oxides may be stable in molten lithium environments. (The titanium must be supplied from the V-Cr-Ti capsule wall or the V-4Cr-4Ti substrates, which were coated on one side only.) Thermodynamic data for Y_2TiO_5 and $Y_2Ti_2O_7$ were not found in any of the available databases. Therefore, to obtain initial thermodynamic values for these compounds, the 298K heats of formation and entropy, and heat capacities for Y_2O_3 and TiO_2 (rutile) were simply added in the appropriate proportions. Then, in order to get the phases to be sufficiently stable to form over the lower end of the temperature range, the binary oxides needed to be somewhat more stable. This was done by making the 298K heats of formation for Y_2TiO_5 and $Y_2Ti_2O_7$ more negative by a minimum of 2 and 3 kJ/mol, respectively.

Using the estimated ΔG's for Y_2TiO_5 and $Y_2Ti_2O_7$, along with existing data for other phases and species in the Li-Y-Ti-O system, the equilibrium composition was calculated assuming one mole each of Y_2O_3, TiO_2, and Li at 800, 900, and 1000°C. In all cases the Li reacted to form complex oxides and reduced TiO_2. The Y_2TiO_5 and $Y_2Ti_2O_7$ phases did not form under these conditions. Interestingly, Li_2TiO_3 was one of the stable products. Its free energy is on the same order as that for Li_2O (see Table I).

To explore the degree of stability needed for Y_2TiO_5 to be present and for Li to remain metallic, the 298K heat of formation for this oxide was systematically made more negative until an equilibrium phase assemblage containing Li only as the metal was obtained. This required that the 298K heat of formation for Y_2TiO_5 be approximately 160 kJ/mol more negative. This is not a reasonable value, and is therefore unlikely. For comparison, the 298K heat for formation reported for the phase $Y_2Zr_2O_5$ is approximately 22 kJ/mol more negative than that calculated by summing the values for Y_2O_3 and ZrO_2 (1:2). This confirms that the Y_2TiO_5 and $Y_2Ti_2O_7$ phases are unlikely to be stable with respect to Li under the conditions of interest.

Based on the thermochemical modeling described above, it appears the experimental finding of Y-Ti oxides on the yttria coating after exposure in molten lithium[1] cannot be explained on the basis of a stable Y_2TiO_5 or $Y_2Ti_2O_7$. However, it is quite possible that a mixture of $LiYO_2$ and Li_2TiO_3 formed and that this is what was observed. The extent of degradation of the Y_2O_3 by formation of these products depends on the respective rate constants, the morphologies of their reaction fronts, and the extent to which the electrical conductivity of the coating is raised by formation of these mixed oxides.

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