

DEVELOPMENT OF ELECTRICALLY INSULATING CaOCOATINGS*

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OBJECTIVE

The objectives of this task are to (a) develop electrically insulating coatings with emphasis on basic understanding of the thermodynamic conditions and kinetics of coating development in lithium-calcium mixtures to achieve stable in-situ coatings of CaO in an Li/Li-Ca environment; (b) perform detailed postexposure analysis of the surface layers using several electron-optical techniques to characterize the elemental and phase compositions, quantify stratification in the layers, and establish the role of compositional changes on the coating defect and microstructure; (c) measure the electrical resistance of the coatings, initially external to Li and eventually in situ in an Li environment; and (d) establish optimal procedures from the standpoint of sample preparation, Li chemistry, exposure time and temperature, and sequence of operations to obtain reliable and reproducible coatings with adequate electrical resistance for use in an Li environment.

SUMMARY

A systematic study has been initiated to develop electrically insulating CaO coatings by vapor phase transport and by in-situ formation in a liquid Li environment. Several experiments were conducted in vapor transport studies with variations in process temperature, time, specimen location, specimen surface preparation, and pretreatment. Several of the coatings obtained by this method exhibited Ca concentration in the range of 60-95 wt.% on the surface. However, coating thickness has not been very uniform among several samples exposed in the same run or even within the same sample. The coatings developed in these early tests degraded after 24 h exposure to Li at 500°C. Additional experiments are underway to develop better-adhering and more dense coatings by this method.

A program to develop in-situ CaO coatings in Li has been initiated, and the first set of capsule tests at 800°C in three different Li-Ca mixtures will be completed in early July. Specimens included in the run are bare V-4Cr-4Ti alloy, specimens with a grit-blasted surface and O-precharged in 99.999% Ar, polished specimens precharged in a 99.999% Ar and 5000 ppm O₂-N₂ mixture, and prealuminized V-5Cr-5Ti alloy preoxidized in a 5000 ppm O₂-N₂ mixture. Additional experiments at lower temperatures are planned.

BACKGROUND

The primary mechanism of CaO coating formation involves reactions of oxygen from the V alloy with Ca dissolved in the Li. Several variables in this reaction include temperature, time, O concentration in V alloy, and Ca concentration in Li. Scoping tests were conducted by exposing small coupons of V alloys at several temperatures to Li containing various concentrations of Ca(2-50 at %). Generally, increasing the O concentration in the surface regions of V by exposure to low-pressure O₂ environments before exposure to the Li-Ca alloy produced thicker oxide reaction products, but the results were not conclusive. A range of conditions (temperature, oxygen pressure during preexposure, and time) were investigated to determine which provided the best coating characteristics. In the initial investigations, CaO coatings were obtained by reacting V alloy coupons in Li-Ca in small capsules (<100 cm³) at temperatures of 400-800°C. CaO coatings ≈10 mm thick were successfully formed on V alloys; however, microcracks were observed at room temperature but spallation of the coating was not observed.

Additional tests were conducted to evaluate the effects of thermal cycling/thermal shock resistance of these coatings. Results obtained by thermally cycling the Li-Ca vessel indicated that the ceramic resistivity behavior (increase in resistivity with a decrease in temperature) initially observed was followed by a sharp decrease in resistivity. This decrease was attributed to cracking of the coating. An increase in temperature was followed by an increase in resistance, with a

possibility of self-healing of the cracks. These types of tests were duplicated with similar results. Significant resistances ($R \times A > 1000 \Omega \cdot \text{cm}^2$) were obtained from these "self-healing" experiments; however, the resistance values were typically much lower than the initial high resistance values.

Results obtained in these experiments were considered sufficiently encouraging to initiate tests on a larger scale, i.e., a static test vessel containing ≈ 3 L of Li-Ca alloy. These tests were conducted with rod-type (pencil) specimens with rounded ends in an attempt to minimize adherence of residual liquid metal to the end of the specimens and possible cracking at sharp corners. V-alloy specimens exposed to Li-Ca at temperatures of 400-500°C exhibited a modest increase in resistance with time, indicating formation of a very thin insulating coating.

A range of coating parameters (exposure temperatures and times, Ca content in Li, and pre-oxidation) were investigated. These tests were conducted primarily with only a few percent Ca in Li; however, the general procedure remained the same; viz., oxygenation of the V alloy surface, exposure of the specimen to the Li-Ca alloy, gas-phase oxidation of the Ca coating in most cases, and subsequent compatibility or resistance testing in the Li (usually in Li with low Ca content to ensure self-healing). These tests generally were less successful than the previous tests, typically exhibiting thinner coatings and much lower resistance values from *in-situ* measurements. Resistance measurements by probes indicated high resistance over most of the surface at room temperature, whereas many specimens exhibited very low resistance immediately upon insertion into the liquid. In several cases, relatively high resistance was observed initially, but upon exposure to Li-Ca, electrical shorting (low resistance) occurred after <1 hr exposure.

An important result obtained in the analysis of the coatings involved the composition, in particular the amount of V in the insulator coating. High resistivity was observed at Ca/V ratios above 4, whereas significantly lower resistivities were obtained when V concentration in the coatings significantly exceeded 20% of the total cation concentration.

In general, the CaO coatings developed on pencil samples exhibited several microscopic and macroscopic defects upon reexposure to Li, and *in-situ* resistance measurements of these specimens showed significant decreases to values corresponding to those of uncoated specimens within a few minutes of exposure. Several specimens were examined for defects by masking different regions of specimens with Ga; resistance measurements were conducted on the masked specimens. The results showed high resistance at several locations, indicating that the specimens develop some type of layer with high resistance but that this layer is neither uniform nor defect-free.

Several of these specimens were also examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques, both radially at a given elevation of the specimen and axially at various elevations. Results indicated that the innermost region, adjacent to the V alloy, consisted of V, Ca, and O (and probably Li, which was removed during the alcohol wash). Away from this region and toward the Li side of the interface, the specimens exhibited a higher Ca content and lower V content than in the interior. It is possible that this layer consisted of Li, Ca, and O. Based on the results for the microstructures and elemental compositions of several of the pencil specimens, we concluded that the specimens develop layers that contain Ca and have high resistance at several locations within a specimen. Such a layer does not consist of CaO alone, but displays a gradation in composition with high V/low Ca at the specimen surface and high Ca/low V at the Li side of the interface. We also concluded that the thickness of the coating is an important variable and that initially a high-V layer develops over which a high-Ca layer (which imparts high resistance) develops. It appears that coating thicknesses in excess of 5 μm may be needed to obtain high resistance values and to ensure adequate coverage in all areas.

In addition to evaluating the coatings developed on the pencil specimens, several coupon specimens of V alloy were exposed to the same procedure as the pencil specimens, except

that the Ca-deposited specimens were oxidized at 550 or 625°C. The surface layers on these specimens (without cleaning treatment in alcohol and water) were examined by SEM/EDX and X-ray diffraction (XRD). The results showed that at both temperatures, the outer layer consisted of Li_2O , CaO , and Li_3VO_4 , and the inner layer contained CaO and Li_3VO_4 . Only trace amounts of Li_2O and V_4O_9 were detected in the inner layer. SEM analysis of the specimen oxidized at 550°C indicated isolated patches of Ca-rich oxide and V-rich oxide in the innerlayer. Similar analysis of the specimen oxidized at 625°C indicated predominantly a single phase consisting of Ca, V, and O. Of course, some Li might have been present in these regions (since Li could not be detected by EDX) but the amount should be small, based on the XRD results for the inner layers. The results indicate that oxidation at temperatures <550°C may be beneficial in developing Ca-rich oxides.

Several experimental and procedural variables can have a significant effect on the chemical and mechanical integrity of the coating. The key experimental variables are oxygen precharging time, temperature, and oxygen content of the gas phase; time, temperature, composition and concentration of impurities (e.g., H and N) in the Li-Ca mixture used for exposure of oxygen-precharged specimens; and time, temperature, and oxygen content of the gas phase for oxidation of the Ca-rich surface layer. In addition, the procedural variables include removal of Li after exposure to the Li-Ca mixture and before oxidation, method of Li removal (such as alcohol dissolution, vacuum distillation, etc.), time allowed to drip-clean a sample of Li by allowing the sample to remain in the cover-gas environment above the liquid Li, and removal of residual $\text{Li/Li}_2\text{O}$ from the sample after Ca oxidation.

EXPERIMENTAL PROGRAM

In an attempt to gain further fundamental understanding, experiments were conducted to develop Ca-rich coatings by using the pack diffusion process. The experiments involved exposure of specimens of V alloy to a pack of fine pellets of Ca at temperatures of 700-800°C. The specimens were either completely enclosed within the pack or were hung above the pack material in a static Ar environment. The vapor pressure of Ca at 700-800°C is sufficient to deposit a layer of Ca on the specimens. Several geometrical arrangements were examined to obtain a uniform coating of Ca on the specimens, which were typically coupons measuring 5 to 10 x 5 x 1 mm. The alloys included V-4Cr-4Ti and V-5Cr-5Ti with and without prealuminization. In addition, specimens with various surface roughnesses (polished, grit-blasted, etc.) were included in the evaluation. Deposition of Mg at ≈600°C was also attempted.

The present work on *in-situ* development of insulator coatings emphasizes a basic understanding of the thermodynamic conditions and kinetics of coating development in Li-Ca mixtures to achieve stable coatings of CaO *in-situ* in a Li/Li-Ca environment. The effort will concentrate on detailed postexposure analysis of the surface layers by using several electron-optical techniques to characterize the elemental and phase compositions, quantify stratification in the layers, and establish the role of compositional changes on coating defects, microstructure, and resistance. Among the key variables that influence coating formation and its chemical and mechanical integrity are test temperature, test time, Li chemistry (including Ca content and trace element concentrations), and alloy chemistry and specimen surface preparation. To ensure flexibility in adjusting the Li-Ca chemistry in these experiments, capsules containing ≈50-60 mL of Li-Ca mixture are used for specimen exposure. The capsules are made of Type 300 series stainless steel with a retractable 0.25-mm-thick liner of V-alloy to avoid Li contact with the steel. The materials to be evaluated include V-4Cr-4Ti in bare and prealuminized conditions with various surface treatments in terms of roughness and precharging of in surface regions with oxygen.

Initially, four exposure temperatures of 800, 700, 600, and 500°C are used for exposure of samples in the Li-Ca mixture. Ca contents of the mixture are 10-90 wt.% and exposure time will be ≈100 h. At Ca contents >30 wt.%, the CaLi_2 phase is expected to deposit as the specimens are cooled, while at a Ca content of 10 wt.%, β -Ca and α -Ca deposits are expected. A furnace has been set up to accommodate at least five capsules simultaneously at a given temperature. The

capsules undergo rocking action to enable mixing of the Ca-Li mixture at elevated temperature. Upon exposure, the capsules will be inverted at temperature to drain the specimens of Li and will then be cooled to room temperature. Subsequently, the capsules will be cut open, the sample holder will be retrieved, and the specimens (without removing the Li) will undergo postexposure examination. Both XRD and SEM with EDX will be the primary modes for analyzing the specimens. After the specimens are examined, they will be oxidized in either air or 99.999% Ar to oxidize the Ca into CaO. The specimens will be reexamined after oxidation to determine the thickness, composition, and morphology of the oxide layer, and its adhesion characteristics with the substrate at room temperature. The results will be correlated with the metallurgical and chemical structures of the coatings and the lithium exposure conditions. These initial capsule experiments will establish the roles of several key variables on coating development.

RESULTS AND DISCUSSION

Coating by Vapor Phase Transport

Figure 1 shows typical photomicrographs of the surface of a Ca-deposited V-4Cr-4Ti specimen and of the surface and cross section of the specimen after oxidation. The layer in the cross-section photograph is $\approx 8\text{-}10\ \mu\text{m}$ thick. EDX analysis of the specimen showed a gradation in composition, with more V in the alloy side of the scale and more Ca in the outer region of the scale. The Ca content range was 0-70 wt.% as a function of depth.

In all, 12 runs were conducted for deposition of Ca or Ca/Mg on V alloys. After deposition, the specimens were oxidized in air at 600°C to convert the deposited metals into their respective oxides. The specimens exhibited insulating characteristics after this oxidation step. Detailed XRD studies on these specimens showed good correlation between high resistance values (at room temperature) and high Ca/Mg concentration in oxide form. Ca concentrations in the range of 60-80 wt.% were obtained in several specimens. However, coating thicknesses in a given specimen or between different specimens were not uniform; in some specimens, coating spallation was noted. Several promising coated specimens were exposed to high-purity Li at 500°C for 24-48 h to examine coating integrity. In some cases, Li-exposed specimens exhibited high resistance but only in isolated locations, indicating that the coating deteriorated during Li exposure. XRD analysis of the Li-exposed specimens showed some indication that locations with high Ca content had high resistance at room temperature. The results also showed that Ca and/or Mg deposition via vapor phase transport is possible but that the thickness of the coating and adhesive bonding of the coating with the substrate produced by this method may need further improvement. Additional experiments with several procedural modifications are currently in progress.

In-Situ Coating Development

Figure 2 shows the specimen assembly used in the capsule experiments in Li. The first capsule experiment at 800°C has been initiated. Three Li-Ca mixtures with Ca contents of 39, 59, and 85 wt.% were used in this run. Specimens included in the run are bare V-4Cr-4Ti alloy, a specimen with a grit-blasted surface and O-precharged in 99.999% Ar, polished specimens precharged in 99.999% Ar and 5000 ppm O₂-N₂ mixture, and a prealuminized V-5Cr-5Ti alloy preoxidized in 5000 ppm O₂-N₂ mixture. The first run is expected to be completed in early July.

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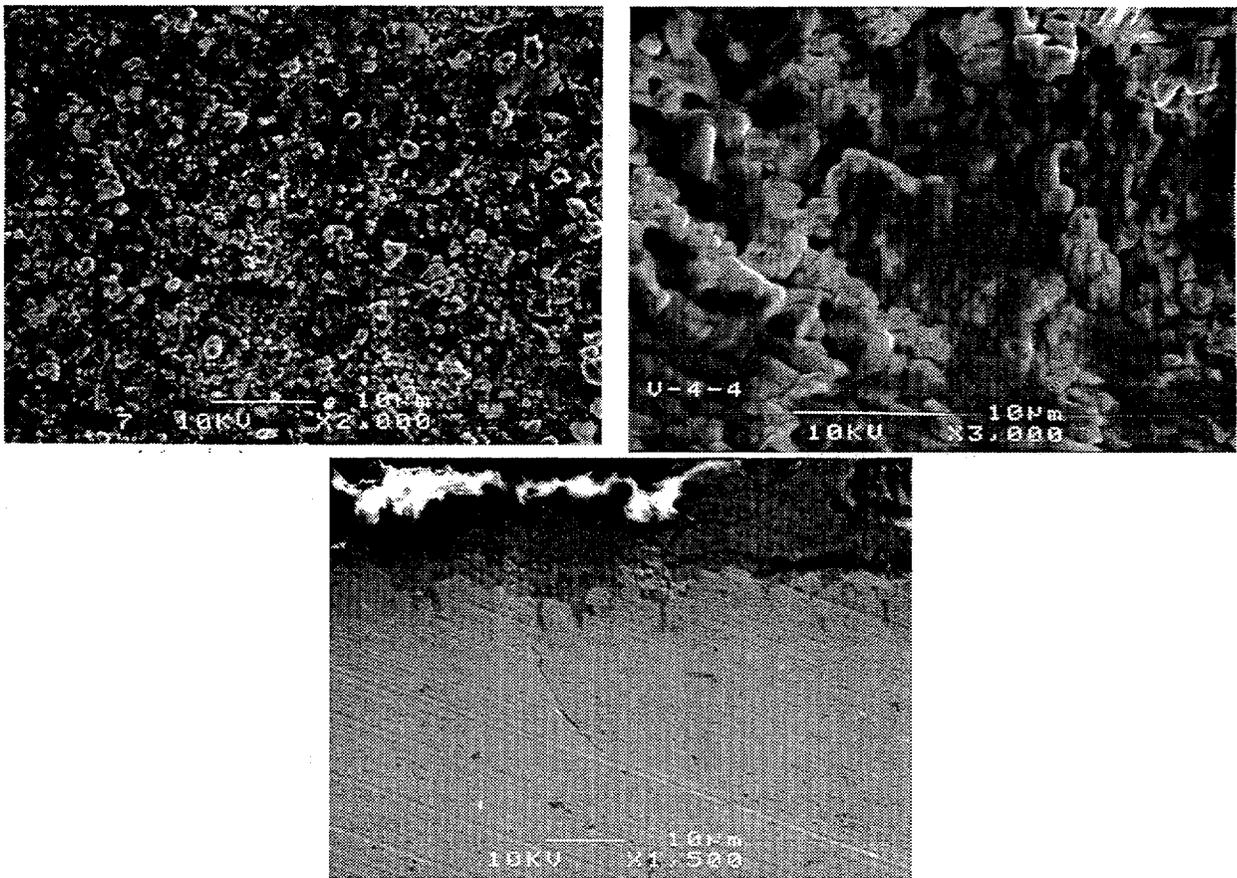


Fig.1. SEM photomicrographs of surface of V-4Cr-4Ti alloy after Ca deposition (top left), after oxidation of Ca deposited specimen (top right), and cross section of oxidized specimen (bottom).

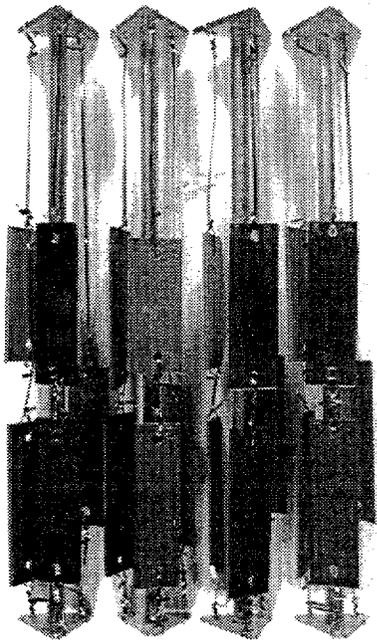


Fig. 2. Macrophotograph of specimen assembly used for in-situ coating development in liquid Li.