

DEVELOPMENT OF ELECTRICALLY INSULATING CaO COATINGS*

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OBJECTIVE

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

SUMMARY

A systematic vapor transport study has been initiated to develop electrically insulating CaO coatings that are compatible with use in a liquid Li environment. Several experiments were conducted to study how the deposition of Ca on V-4Cr-4Ti substrate alloys is affected by variations in process temperature and time, and specimen location, surface preparation, and pretreatment. During this reporting period, a setup has been completed to measure the electrical resistivity of the coatings in air or in an inert gas environment as a function of temperature up to 750°C. Some preliminary data are presented.

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 V alloy specimens to a pack of fine Ca pellets at 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 that measured 5-10 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. The effort during this period concentrated on setting up an apparatus for measuring the electrical resistivity of the coated specimens as a function of temperature up to 750°C. The apparatus has been used to measure the resistance of thin coating layers developed by the pack diffusion process.

RESULTS AND DISCUSSION

Coating by Vapor Phase Transport

Twelve runs have been conducted to study the deposition of Ca or Ca/Mg on V alloys.¹ 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 X-ray diffraction studies on these specimens showed good correlation between high resistance values at room temperature and a high concentration of Ca/Mg in oxide form. Calcium concentrations in the range of 60-80 wt.% were obtained in several specimens. However, coating thicknesses in a given specimen or between various specimens were not uniform; in some

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specimens, coating spallation was noted.

The results also showed that Ca and/or Mg deposition via vapor phase transport is possible but that the coating thickness and the adhesive bonding of the coating with the substrate that was obtained by a single deposition/oxidation procedure was not adequate to produce the desired insulating characteristics. Additional experiments, with several procedural modifications, were conducted and, finally, double deposition/oxidation seemed to produce a thicker coating that was more adherent and exhibited adequate insulating characteristics at room temperature. To examine the stability of the coating and its electrical resistivity at elevated temperature, experiments were conducted with some of the coated samples at temperatures up to $\approx 700^{\circ}\text{C}$ in which a two-probe method was used to measure resistance.

Figure 1 shows typical scanning electron microscopy (SEM) photomicrographs of cross sections and surfaces of V-4Cr-4Ti alloy in various stages of coating development, i.e., after Ca deposition, after oxidation of the Ca deposit, and after repeated oxidation of the Ca deposit. The top left photomicrograph shows a cross section of a specimen after Ca deposition by pack diffusion. Even though Ca is the deposited element, some CaO is present in the layer because the low flow rate of 99.999 vol.% Ar used in the experiment contained sufficient oxygen to partially oxidize Ca to CaO. The top right photomicrograph shows the cross section of the specimen after Ca deposition and subsequent oxidation in 99.999% Ar. The average thickness of the coating layer was $\approx 4\ \mu\text{m}$ but the thickness was not uniform. The bottom left photomicrograph shows a cross section of a specimen in which the sequence was Ca deposition, oxidation, and deposition. It is evident that the coating after this sequence is much thicker and denser than the coating observed after single-stage deposition.

The bottom right photomicrograph shows the surface of a specimen after dual deposition/oxidation treatments. The sample was mechanically weak and broke into several pieces, especially after resistance measurements at elevated temperatures in air. The results showed that reaction after long-term exposure at high temperature (especially at anticipated service temperatures) should be one of the criteria for an acceptable coating.

The variation in the product of resistance times area as a function of temperature obtained on specimens of V-4Cr-4Ti alloy with Ca deposition/oxidation and with Ca deposition/oxidation and redeposition of Ca is shown in Figure 2. The specimen with single-step deposition of Ca and oxidation exhibited (see left graph in Figure 2) a low value of $\approx 10\ \Omega\cdot\text{cm}^2$ at room temperature. Upon heating the specimen during the resistance measurement, the value decreased further to as low as $0.5\ \Omega\cdot\text{cm}^2$ at 546°C . The specimen was maintained at 546°C overnight and the resistance gradually increased to a value of $10\ \Omega\cdot\text{cm}^2$; it was then given a second cycle of heating and cooling, as shown in the figure. The resistance during the second heating remained the same as it was during the cooling part of the first cycle. However, a further increase in resistance was observed during the cooling part of the second cycle. The product of the resistance times area still remained in the range of $15\text{-}20\ \Omega\cdot\text{cm}^2$ in a temperature range of $200\text{-}500^{\circ}\text{C}$.

The right-hand graph in Figure 2 shows the variation in values for resistance times area for a specimen that was treated with Ca deposition/oxidation/redeposition of Ca. During the heating cycle, the value ranged between 10^7 to $10^2\ \Omega\cdot\text{cm}^2$ as the temperature increased from room temperature to $\approx 500^{\circ}\text{C}$, with a sharp drop in the temperature range of $200\text{-}500^{\circ}\text{C}$. The specimen was maintained overnight at 546°C in air, during which time the value for resistance times area increased from ≈ 400 to $2 \times 10^5\ \Omega\cdot\text{cm}^2$. Upon cooling, the value showed further increase to $\approx 10^7\ \Omega\cdot\text{cm}^2$ at room temperature. It is evident that the dual treatment of Ca deposition improved the coating from the standpoint of thickness as well as resistance.

The behavior of the coatings of the above two specimens at 546°C as a function of exposure time is shown in Figure 3. At temperature, with a single Ca deposition treatment, the specimen exhibited a gradual increase in resistance to $5\ \Omega\cdot\text{cm}^2$, while the specimen with a double Ca treatment exhibited

values in the range of 10^4 to $10^5 \Omega\text{-cm}^2$. Additional experiments are in progress to evaluate the characteristics of coatings developed on several other specimens. Furthermore, the microstructures of several of these coated specimens will be characterized and compositional gradients will be determined. Also, some of the specimens will be exposed to an Li environment; their resistances will be measured before and after exposure.

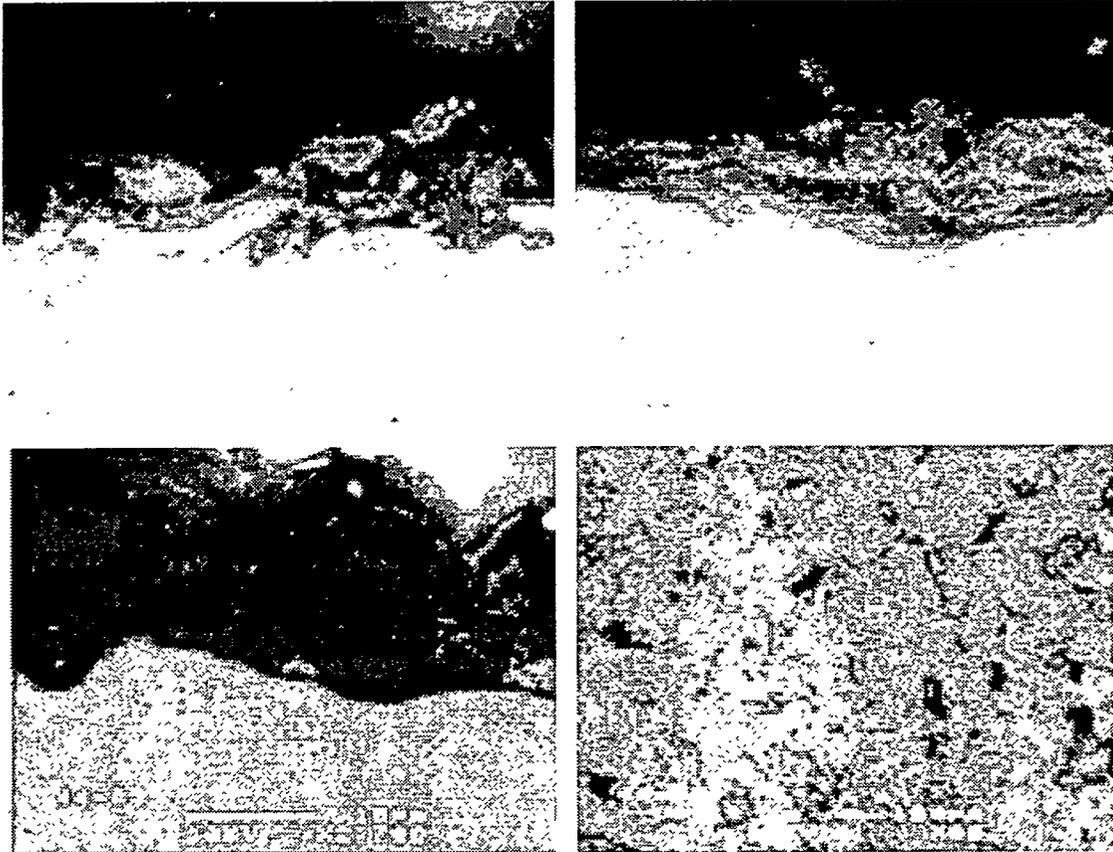


Fig.1. SEM photomicrographs of V-4Cr-4Ti alloy after Ca deposition (top left), after oxidation of Ca deposit (top right), after repeat of Ca deposition (bottom left) and after repeat of oxidation of Ca deposit (bottom right). Bottom right photomicrograph is a surface view, and the others are cross sections.

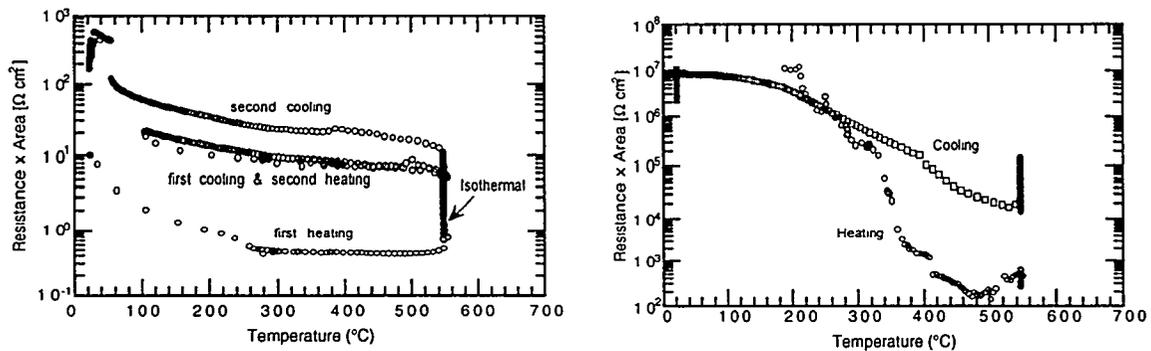


Fig. 2. Product of resistance times area as a function of temperature for V-4Cr-4Ti alloy with (left) Ca deposition/oxidation and (right) Ca deposition/oxidation/Ca deposition.

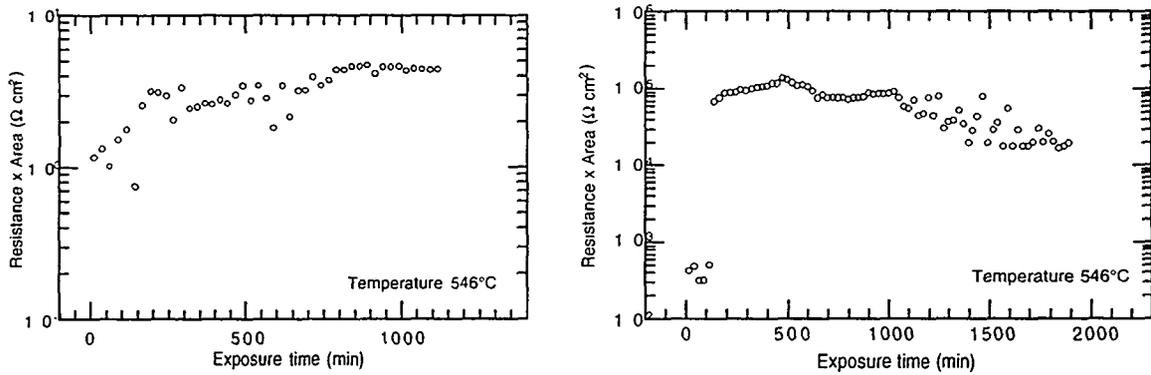


Fig. 3. Product of resistance times area as a function of time at 546°C for V-4Cr-4Ti alloy with (left) Ca deposition/oxidation and (right) Ca deposition/oxidation/Ca deposition.

REFERENCES

1. K. Natesan, C. B. Reed, M. Uz, and D. L. Rink, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending June 30, 1998, Argonne National Laboratory, DOE/ER-0313/24, p. 82, September 1998.