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 an 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 in progress 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, several specimens were prepared with a coating of CaO by thermal/chemical deposition and measurements were made of the electrical resistance of several CaO-coated specimens before and after exposure to an Li environment.

EXPERIMENTAL PROGRAM

Experiments were conducted to develop Ca-rich coatings by using the thermal/chemical deposition 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 hung above the pack material in a static Ar environment. Figure 1 shows the temperature dependence of the vapor pressure of Ca. Above 700°C, the vapor pressure of Ca is >0.1 torr and 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 to 10 x 5 x 1 mm. Effort during this period concentrated on developing procedures to develop a thick adherent coating of CaO on a V-4Cr-4Ti alloy substrate and on measuring the electrical resistance of the coated specimens as a function of temperature up to ≈710°C.

RESULTS AND DISCUSSION

In previous reports, we discussed the procedure for the deposition of Ca and subsequent oxidation to convert the Ca into CaO.[1,2] The coated specimens exhibited insulating characteristics after this oxidation step. X-ray diffraction studies on these specimens showed good correlation between high resistance values at room temperature and a high concentration of Ca in oxide form. Calcium concentrations in the range of 60-80 wt.% were obtained in several specimens. However, coating thickness in a given specimen or among various specimens was not uniform; in some specimens, coating spallation was noted. The results also showed that Ca deposition via vapor phase transport is possible but that the coating thickness and the adhesive bonding of the coating to the substrate after a single deposition/oxidation procedure was not adequate to produce the desired insulating characteristics.

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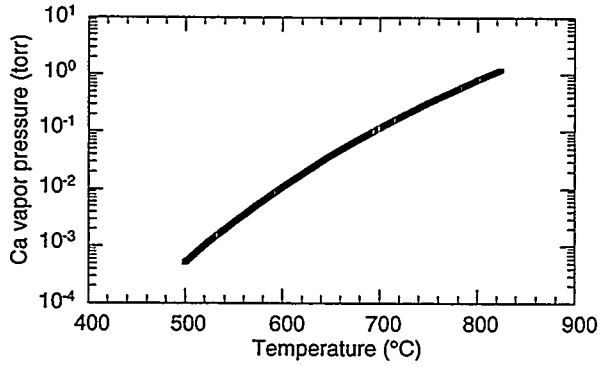

Fig. 1. Temperature dependence of Ca vapor pressure.

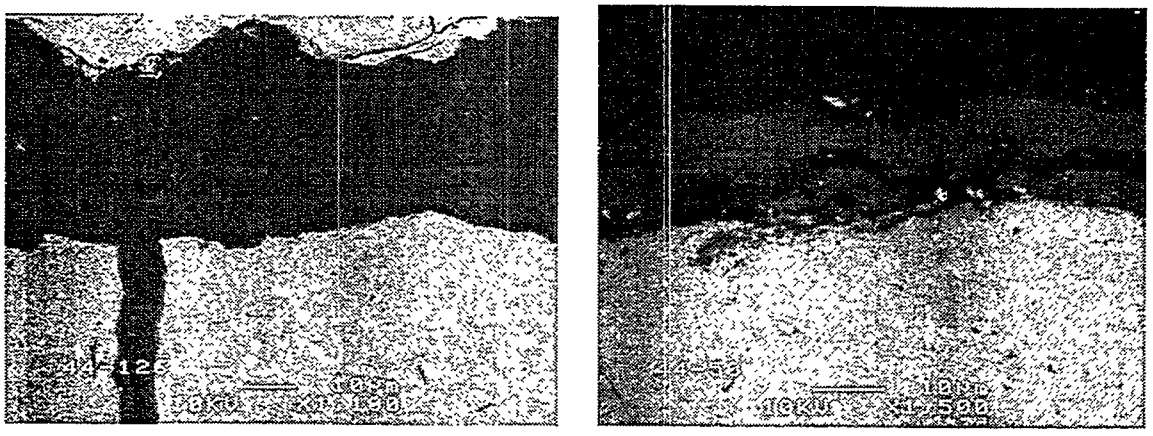

Fig. 2. SEM photomicrographs of cross sections of two V-4Cr-4Ti alloy specimens after double Ca deposition/oxidation treatment.

Additional experiments, with several procedural modifications, were conducted and, finally, a double deposition/oxidation treatment seemed to produce a thicker coating that was more adherent and exhibited adequate insulating characteristics at room temperature. Preliminary results on electrical resistance (measured by a two-probe method) of the coatings as a function of temperature up to ≈550°C were described in Ref.2.

During this period, several additional specimens were coated using the double Ca deposition/oxidation treatment, and the microstructural and compositional characteristics of the coatings were evaluated in detail. Figure 2 shows typical scanning electron microscopy (SEM) photomicrographs of cross sections of two V-4Cr-4Ti alloy specimens after a double Ca deposition/oxidation treatment. Coating thicknesses in these specimens were 15 to 30 μm. Energy-dispersive X-ray (EDX) analysis of the specimen surfaces showed the coatings to be CaO and also revealed the virtual absence of any elements from the substrate alloy. Figure 3 shows a typical EDX spectrum of the coating surface and indicates primarily Ca and O peaks. Cross sections of several specimens were analyzed as a function of depth for constituent elements of the coating and substrate. Depth profiles for two of the coated specimens are shown in Figs. 4a and 4b; the profiles in indicate coating thicknesses of 16 and 34 μm, respectively. The coating composition was predominantly CaO in both specimens, and negligible amounts of substrate elements were detected in the coating region. The difference in scale thickness between the two specimens in due to the proximity of different specimens in the Ca pack. Both specimens, after double Ca and oxidation treatment, were exposed to Li of normal purity at 500°C for 68 h.

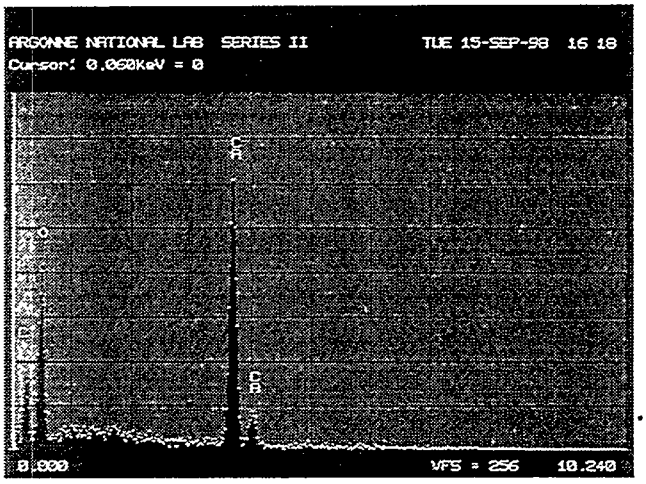

Fig. 3. EDX spectrum of surface of V-4Cr-4Ti alloy specimen after double Ca deposition/oxidation treatment.

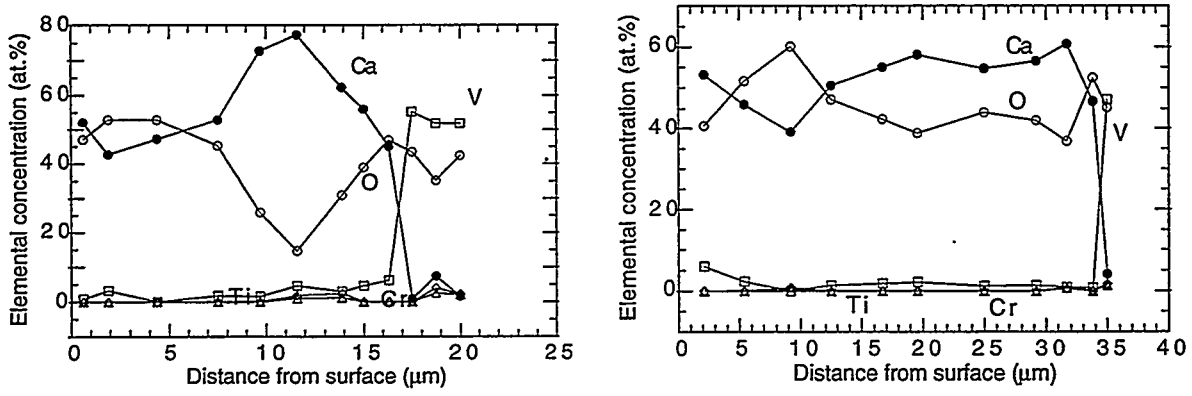

Fig. 4. Elemental concentrations as a function of coating thickness for V-4Cr-4Ti alloy specimens after double Ca deposition/oxidation treatment: (a) coating thickness = 16 μm; (b) coating thickness = 34 μm.

To examine the stability of the coating and its electrical resistivity at elevated temperature, a two-probe method was used to measure resistance in some of the coated specimens at temperatures up to ≈700°C. The variation in the product of resistance times area (R x A) 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 was discussed in Ref.2. Those results showed that the as-coated specimen (with a double Ca and oxidation treatment) had resistance values of 10^4 to 10^5 $\Omega\cdot cm^2$. During this reporting period, resistance measurements were made on specimens that were double Ca/oxidation treated and subsequently exposed to liquid Li of normal purity at 500°C for 68 h. Figure 5 shows the variation in R x A as a function of temperature obtained on a CaO-coated and Li-exposed specimen of V-4Cr-4Ti alloy. The figure shows that R x A values are $>10^7$ $\Omega\cdot cm^2$ from room temperature to 200°C; the value gradually decreases to $\approx 5 \times 10^6$ $\Omega\cdot cm^2$ as temperature is increased from 200 to 540°C. The specimen was maintained isothermally at ≈540°C for ≈6h, after which it was further heated to ≈700°C. Even at 700°C, the specimen exhibited an R x A value of 10^4 $\Omega\cdot cm^2$, at least two orders of magnitude higher than that required in a fusion device using a Li blanket. Figure 6 shows variation in R x A as a function of exposure time obtained on a CaO-coated and Li-exposed specimen of V-4Cr-4Ti alloy. It is evident that the coating had R x A values of 10^5 and 10^4 $\Omega\cdot cm^2$ at 541 and 702°C, respectively.

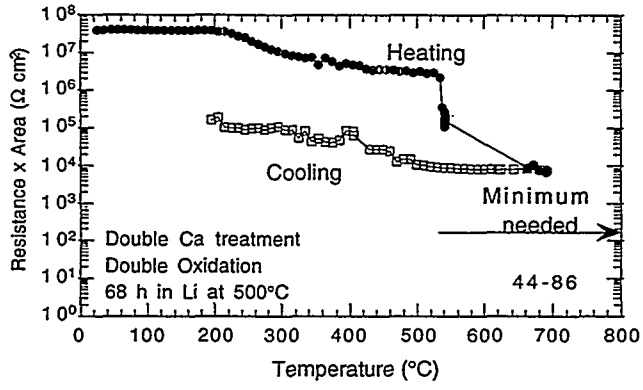

Fig. 5. Product of resistance times area as a function of temperature for V-4Cr-4Ti alloy with double Ca deposition/oxidation after 68-h exposure in Li environment at 500°C.

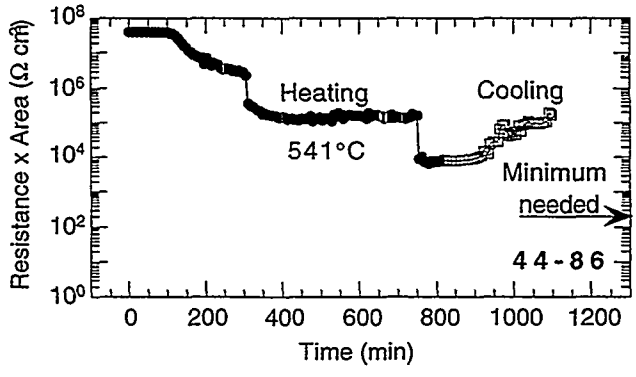

Fig. 6. Product of resistance times area as a function of time for V-4Cr-4Ti alloy with double Ca deposition/oxidation after 68-h exposure in Li environment at 500°C.

During this period, specimens of V-4Cr-4Ti alloy with a coating of CaO developed in-situ in an Li-Ca environment were examined to characterize the microstructure and coating resistance. Figure 7 shows an SEM photomicrograph of the surface of a "CaO"-coated V-4Cr-4Ti alloy specimen after exposure to an Li environment. The surface region consisted of Li_2O as the outer layer (characterized by a rough, light toned texture) and a Ca-enriched inner layer (a smooth gray texture). Figure 8 shows the variation in R x A as a function of temperature for this specimen. The value for R x A at temperatures up to ≈300°C is more than the minimum needed, but the value decreases substantially as temperature increases to 614°C. Maintaining the specimen at 614°C for extended time periods seems to improve the resistance of the coating; further increase in temperature to 713°C results in a slight reduction in resistance. In the cooling part of the cycle, the resistance values are at least two orders of magnitude higher than in the heating part of the cycle, with a probable inference of coating consolidation/densification and subtle change in chemistry of the coating during the heating part of the cycle. Figure 9 shows the variation in R x A value as a function of time for the same coated specimen. The results indicate that the resistance values for the coating in the cooling part of the cycle are substantially higher than in the heating part of the cycle, even though the coating is maintained nominally at the same temperature (e.g., 336/339 and 539/538°C) during both the heating

and cooling portions of the cycle. Additional experiments are planned in which multiple heating/cooling cycles will be conducted on the same coated sample to evaluate whether the coating characteristics become stabilized and to see whether the coating resistance attains a stable value at each isothermal condition, irrespective of heating or cooling cycle.

Additional experiments are underway 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, planned is the in-situ measurement of the resistance of the coating in a Li environment.

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, Sept.1998.
2. K. Natesan, M. Uz, and S. Wieder, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending December 31, 1998, Argonne National Laboratory, DOE/ER-0313/25, p. 69, April 1999.

Fig. 7. SEM photomicrograph of surface of V-4Cr-4Ti alloy specimen with "CaO" coating developed in-situ in Li-Ca mixture.

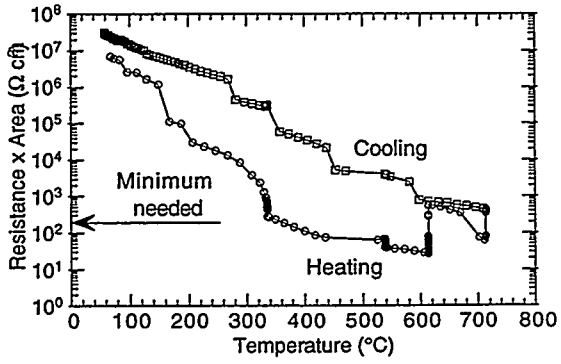

Fig. 8. Product of resistance times area as a function of temperature for V-4Cr-4Ti alloy with "CaO" coating developed in situ in Li-Ca environment

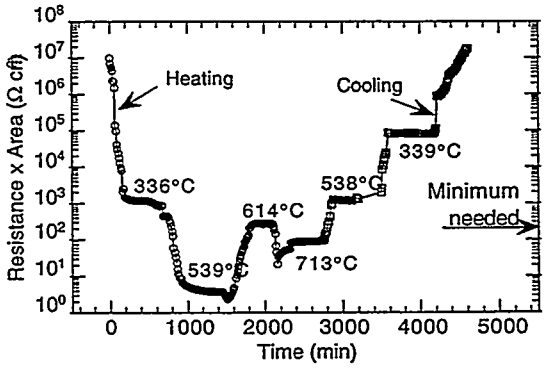

Fig. 9. Product of resistance times area as a function of time for V-4Cr-4Ti alloy with "CaO" coating developed in situ in Li-Ca environment