



# Development of electrically insulating coatings for service in a lithium environment

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## Abstract

Several experiments were conducted to develop electrically insulating CaO coatings on a V–4Cr–4Ti alloy for application in a Li environment. The coatings were developed by vapor-phase transport external to Li, and also in situ in a Li–Ca environment at elevated temperature. In the vapor-phase study, several geometrical arrangements were examined to obtain a uniform coating of Ca on the specimens, which were typically coupons measuring 5 to 10 × 5 × 1 mm<sup>3</sup>. After Ca deposition from the vapor phase, the specimens were oxidized in a high-purity argon environment at 600°C to convert the deposited metal into oxide. The specimens exhibited insulating characteristics after this oxidation step. Several promising coated specimens were then exposed to high-purity Li at 500°C for 48–68 h to determine coating integrity. Microstructural characteristics of the coatings were evaluated by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis. Electrical resistances of the coatings were measured by a two-probe method between room temperature and 700°C before and after exposure to Li. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Blanket-design studies revealed that electrically insulating duct walls will be required to reduce the magnetohydrodynamic (MHD) pressure drop in liquid-metal-cooled blankets used in high-magnetic-field fusion devices. As a result, development of insulator coatings was recommended as the most appropriate approach for resolving this issue [1]. The major requirements for a viable insulator coating are:

- Chemical compatibility in liquid metal.
- Chemical compatibility with structural metal.
- Adequate electrical insulating characteristics.
- Stability under irradiation environment.
- Long-term stability, including self-healing, under thermal cycling conditions.

Based on a review of available information on electrical resistivity values and lithium compatibility, several oxide and nitride candidate materials have been identified for application as insulator coatings. Oxides were generally considered as the preferred candidates, initially, to meet the specified criteria; however, only a limited number of oxides are stable in Li [2]. Nitrides are generally more stable than the oxides in Li; however, many of the nitrides do not exhibit high electrical resistivity. For example, both VN and TiN are stable in Li but exhibit low resistivity. Similarly, most carbides and silicides do not exhibit adequate resistivity. Therefore, oxides such as CaO, Y<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, and Y<sub>3</sub>Al<sub>2</sub>O<sub>12</sub>, and nitrides such as AlN and BN, were considered as potential candidates primarily because of their thermodynamic considerations and electrical resistivities. The Argonne National Laboratory has been developing CaO and AlN coatings on V-alloy substrates for application in V–Li advanced blanket systems. This paper will discuss the procedures used for CaO coating development, microstructural characteristics of these coatings, and electrical resistivity data for the coatings as a function of temperature. The results will be used to assess the applicability of these coatings in a V–Li self-cooled fusion reactor blanket.

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## 2. Experimental procedure

### 2.1. Thermal/chemical coating process

Experiments were conducted to develop Ca-rich coatings by using a thermal/chemical deposition process [3,4]. V-alloy specimens were exposed 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. The temperature dependence of the vapor pressure of Ca showed that above 700°C, the Ca vapor pressure is >0.1 Torr, 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 10×5×1 mm<sup>3</sup>. The exposure time in the deposition process ranged from 100 to 200 h. Upon deposition of Ca, the specimens were oxidized in an Ar environment to oxidize the Ca deposit. The oxidized specimens exhibited poor adherence of the oxide to the substrate, and the oxide layer was patchy and fairly thin. A two-probe method was used to measure the electrical resistance of these specimens by deposition of Au over 2×2-mm<sup>2</sup> areas and use of Pt wire for the electrical leads. The specimen assembly was inserted in a furnace, and resistance was measured in an Ar environment between room temperature and ≈700°C.

The coated specimens exhibited insulating characteristics after this oxidation step. X-ray diffraction studies on these specimens showed a 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 for 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 the coating thickness and the adhesive bonding of the coating to the substrate after a single deposition/oxidation procedure were not adequate to produce the desired insulating characteristics. 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.

### 2.2. In situ coating development in situ in Li–Ca mixture

In earlier studies, scoping tests were conducted by exposing small coupons of V alloys at various temperatures to Li containing various concentrations (2–50 at.%) of calcium [5,6]. A range of conditions (temperature, oxygen pressure, and time) was investigated to

determine those that provided the best coating characteristics. In initial investigations, ‘CaO’ coatings were obtained by reacting V-alloy coupons in Li–Ca mixtures in small capsules (<0.1 l) at 400–1000°C. CaO coatings ≈10-μm thick were successfully formed on vanadium alloys. In this case, microcracks were observed at room temperature, but spallation of the coating was not observed. Some of the coated specimens from these experiments, even with non-uniform thicknesses and cracks, were used in resistivity measurements to compare the resistances of the in situ coatings with those of the coatings developed by the thermal/chemical process.

### 2.3. Liquid-metal exposures

Two static liquid–Li systems were used for studies on compatibility of insulator coatings. The systems were filled with ≈15 l of high-purity (99.97 wt%) Li. Concentrations of trace impurities of Na, Ca, K, Fe, Si, and Cl in Li were <50 ppm, and N concentration in the Li was 80 ppm. Coupon specimens of CaO-coated samples were exposed to the liquid Li at 500°C. Weight change was measured to establish corrosion rates for the coatings as a function of time. After exposure, the specimens were examined by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer, and also by X-ray diffraction. The coated specimens were examined to evaluate coating integrity, microstructural changes in coatings, coating/substrate interactions, and electrical insulation characteristics of the coatings.

## 3. Results and discussion

### 3.1. Coatings developed by thermal/chemical process

Fig. 1 shows typical 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 15–30 μm. An EDX analysis of the specimen surfaces showed the coatings to be CaO and also revealed the virtual absence of any elements of the substrate alloy. Fig. 2 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. 3(a) and (b); the profiles indicate coating thicknesses of 16 and 34 μm, respectively. The coating composition in both specimens was predominantly CaO, and negligible amounts of substrate elements were detected in the coating region. The difference in scale thickness between the two specimens is due to the proximity of different specimens in the Ca pack. Both specimens, after

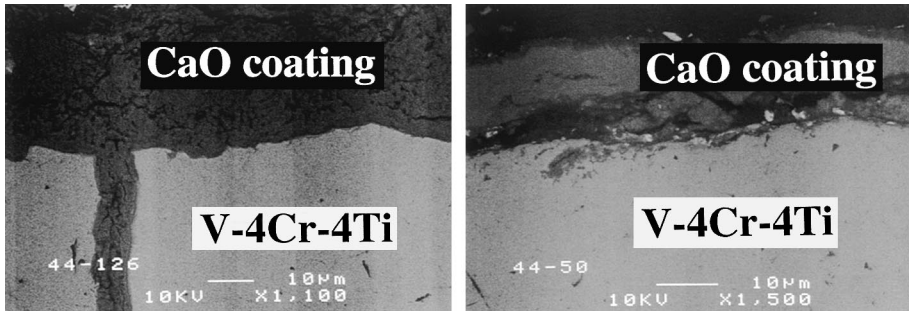


Fig. 1. SEM photomicrographs of cross-sections of two V-4Cr-4Ti alloy specimens after double-Ca deposition/oxidation treatment.

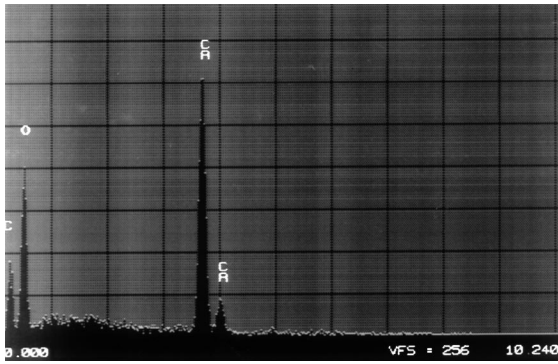


Fig. 2. EDX spectrum of the surface of V-4Cr-4Ti alloy specimen after double-Ca deposition/oxidation treatment.

double Ca and oxidation treatment, were exposed to Li of normal purity at 500°C for 68 h.

The variation in the product of resistance times area (i.e.,  $R \times A$ , which is equivalent to the product of resistivity times coating thickness) 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 [4]. These results showed that the as-coated specimen (with a double Ca and oxidation treatment) had resistance values of  $10^4$  to  $10^5 \Omega \text{ cm}^2$ . In this study, resistance mea-

surements 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. Fig. 4 shows the variation in  $R \times A$  as a function of temperature obtained on a CaO-coated and Li-exposed specimen of V-4Cr-4Ti alloy. The figure shows that  $R \times A$  values are  $>10^7 \Omega \text{ cm}^2$  from room temperature to 200°C; the value gradually decreases to  $\approx 5 \times 10^6 \Omega \text{ cm}^2$  as the temperature is increased from 200°C to 540°C. The specimen was maintained isothermally at  $\approx 540^\circ\text{C}$  for  $\approx 6$  h, after which it was further heated to  $\approx 700^\circ\text{C}$ . Even at 700°C, the specimen exhibited an  $R \times A$  value of  $10^4 \Omega \text{ cm}^2$ , at least two orders of magnitude higher than that required in a fusion device using a Li blanket. Fig. 5 shows the variation in  $R \times A$  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  $R \times A$  values of  $10^5$  and  $10^4 \Omega \text{ cm}^2$  at 541 and 702°C, respectively.

### 3.2. Coatings developed in situ

Specimens of V-4Cr-4Ti alloy with a coating of CaO developed in situ in a Li-Ca environment were examined to characterize the microstructure and coating resistance. Fig. 6 is a SEM photomicrograph of the surface of a 'CaO'-coated V-4Cr-4Ti alloy specimen after ex-

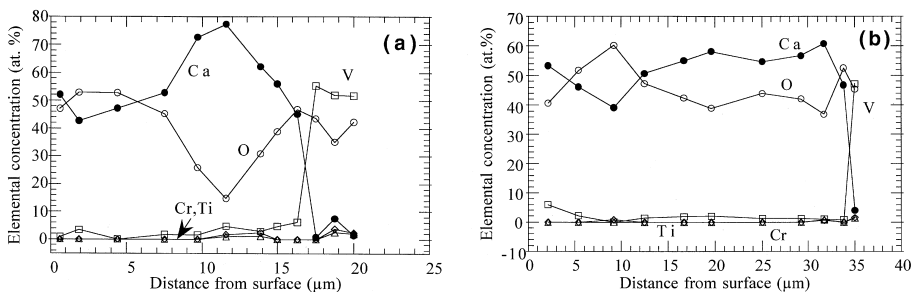


Fig. 3. Elemental concentrations as a function of coating thickness for V-4Cr-4Ti alloy specimens after double-Ca deposition/oxidation treatment: (a) coating thickness = 16 μm; (b) coating thickness = 34 μm.

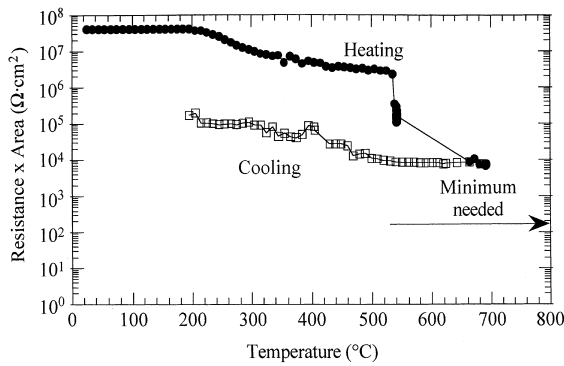


Fig. 4. Product of resistance times area as a function of temperature for V-4Cr-4Ti alloy with double-Ca deposition/oxidation after 68-h exposure in Li environment at 500°C.

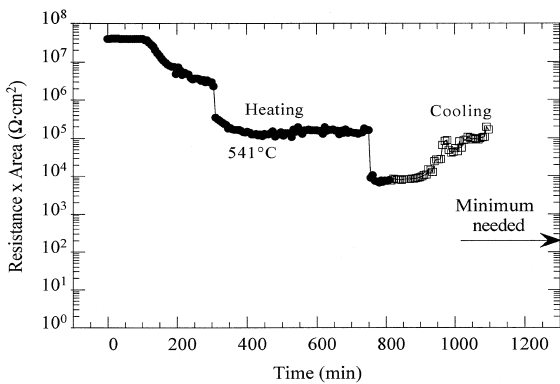


Fig. 5. Product of resistance times area as a function of time for V-4Cr-4Ti alloy with double-Ca deposition/oxidation after 68-h exposure in Li environment at 500°C.

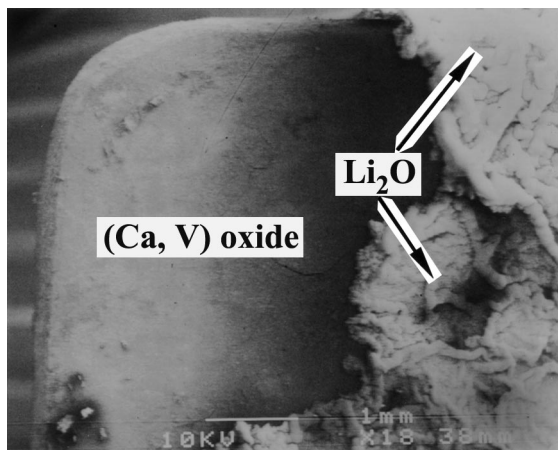


Fig. 6. SEM photomicrograph of the surface of V-4Cr-4Ti alloy specimen with 'CaO' coating developed in situ in Li-Ca mixture.

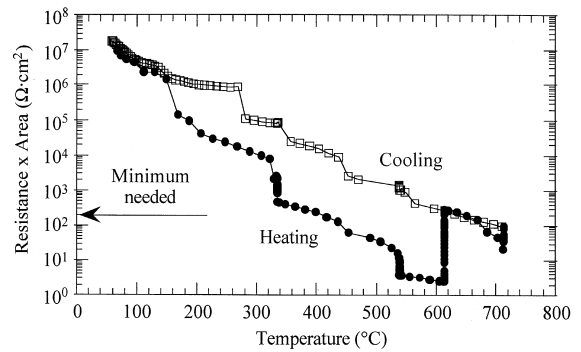


Fig. 7. Product of resistance times area as a function of temperature for V-4Cr-4Ti alloy with 'CaO' coating developed in situ in Li-Ca environment.

posure to a Li environment. The surface region consisted of  $\text{Li}_2\text{O}$  as the outer layer (characterized by a rough, light-toned texture) and a Ca-enriched inner layer (a smooth gray texture). Fig. 7 shows the variation in  $R \times A$  as a function of temperature for this specimen. The value for  $R \times A$  at temperatures up to  $\approx 300^\circ\text{C}$  is more than the minimum needed, but decreases substantially as temperature rises to  $614^\circ\text{C}$ . Maintaining the specimen at  $614^\circ\text{C}$  for extended periods seems to improve the resistance of the coating; a further increase in temperature to  $713^\circ\text{C}$  results in a slight reduction in resistance. In the cooling portion of the cycle, the resistance values are at least two orders of magnitude higher than in the heating portion of the cycle, with a probable inference of coating consolidation/densification and subtle change in the chemistry of the coating during the heating portion of the cycle. Fig. 8 shows the variation in  $R \times A$  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

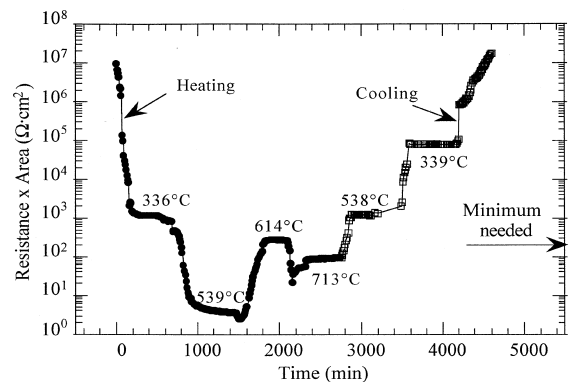


Fig. 8. Product of resistance times area as a function of time for V-4Cr-4Ti alloy with 'CaO' coating developed in situ in Li-Ca environment.

cycle are substantially higher than in the heating portion of the cycle, even though the coating is maintained nominally at the same temperature (e.g., 336°C/339°C and 539°C/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 a heating or cooling cycle. Further, in situ measurement of coating resistance (the next logical step to simultaneously evaluate the coating resistance and Li compatibility) is also planned.

#### 4. Summary

We have developed CaO coatings by a thermal/chemical vapor-deposition process and an in situ approach in a liquid Li–Ca environment. Results showed that thick adherent coatings can be fabricated by thermal/chemical vapor deposition, especially if a double Ca treatment is applied. Coatings were also developed by the in situ approach, but the coatings were much thinner than desired. Furthermore, the coating composition was non-uniform, with significant presence of V in several locations on the coated surface. Extensive microstructural analysis of the coatings developed by the thermal/chemical process showed almost 100% CaO over a coating thickness of 20–30  $\mu\text{m}$ ; electrical resistance (measured by the two-probe method) of the coatings was at least two orders of magnitude higher than the minimum required for blanket application. Electrical resistance of in situ developed coatings was adequate at temperatures up to  $\approx 350^\circ\text{C}$ , but decreased substantially at higher temperatures. The results obtained in this study indicate that CaO is a viable coating for V–Li

advanced blankets, but needs significant additional effort, especially from the standpoint of structure/composition relationship to its electrical resistance. Furthermore, in situ measurement of Li resistance is required to simultaneously evaluate coating integrity, resistance, and Li compatibility.

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