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CaO INSULATOR COATINGS AND SELF-HEALING OF DEFECTS ON V-Cr-Ti ALLOYS IN LIQUID LITHIUM*

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ABSTRACT

Electrically insulating and corrosion-resistant coatings are required at the liquid metal/structural interface in fusion first-wall/blanket applications. Electrical resistance of CaO coatings that were produced on V-5%Cr-5%Ti by exposure of the alloy to liquid Li containing 0.5-85 wt.% dissolved Ca was measured as a function of time at temperatures between 250 and 600°C. The solute element, Ca in liquid Li, reacted with the alloy substrate at 400-420°C to produce a CaO coating. Resistance of the coating layer measured in-situ in liquid Li was $\approx 10^6\ \Omega$ at 400°C. Thermal cycling between 300 and 700°C changed the coating layer resistance, which followed insulator behavior. These results suggest that thin homogeneous coatings can be produced on variously shaped surfaces by controlling the exposure time, temperature, and composition of the liquid metal. The technique can be applied to various shapes (e.g., inside/outside of tubes, complex geometrical shapes) because the coating is formed by liquid-phase reaction. Examination of the specimens after cooling to room temperature revealed no spallation, but homogeneous crazing cracks were present in the CaO coating. Additional tests to investigate the in-situ self-healing behavior of the cracks indicated that rapid healing occurred at ≥360°C.

INTRODUCTION

Electrically insulating and corrosion-resistant coatings are required at the liquid-metal/structural interface in a magnetic fusion reactor to minimize the magnetohydrodynamic force and its influence on thermal hydraulics of liquid-metal cooling systems [1]. Vanadium and V-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in fusion reactors because

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of their many benefits, including the capability to fabricate ceramic and intermetallic phases on the alloys in a liquid–metal environment [2-4]. In-situ formation of CaO on V-5Cr-5Ti in liquid Li was investigated because the electrical resistivity of CaO is very high and also because CaO exhibits a higher thermodynamic stability in liquid Li than do other potential insulator candidates (Y_2O_3, BeO, MgO, $MgAl_2O_4$, $Y_3Al_2O_{12}$, etc.) [3]. In-situ self-healing behavior of defects (such as cracks in the coating) in liquid-Li environments is also an important consideration. These coatings should be formable on various shapes such as the inside of tubes or irregular configurations. The coatings could also improve general corrosion resistance and act as a diffusion barrier for hydrogen isotopes, viz., deuterium and tritium.

EXPERIMENTAL PROCEDURE

Various experimental methods have been explored to fabricate and characterize insulator coatings for use in liquid–Li environments: (a) oxygen charging of the near–surface region of V–base alloys in Ar gas (O <5 ppm, H_2O < 5 ppm, and total impurity < 20 ppm) and in air, (b) evaluation of liquid-Li compatibility of the O–charged V–base alloy specimens, (c) reaction of the O–enriched V–base alloy surface with dissolved Ca in Li and oxidation of the Ca-Li layer in high purity Ar to form the CaO layer, (d) in-situ electrical resistance measurements of CaO coatings on V-5Cr-5Ti in liquid Li, and (e) characterization of the O–charged specimens and insulator coatings by scanning electron microscopy (SEM) and X-ray diffraction, together with optical examination of the coatings for evidence of surface defects such as spallation or cracks. Thermal cycling tests were also conducted to investigate the integrity of coating layers that formed in–situ. Fabrication of coatings at a relatively low temperature (320-400°C) has been emphasized.

RESULTS AND DISCUSSION

Oxygen charging of the surface of V-Cr-Ti Alloys: Figure 1 shows the thermodynamic stability of solid-state oxide phases, as a function of equilibrium partial pressure of oxygen and temperature, that can form when V-Cr-Ti alloys, Li, and Ca are exposed to oxygen–containing environments. It is well known that O can be incorporated into the interstitial sublattice in body-centered-cubic (bcc) V and its alloys. Thus, if O or N is present in the alloy (as a reactant), these elements may have a higher affinity for solutes, such as Ca, Y, or Mg dissolved in

Li, than do the alloy elements. In the bcc lattice of V-5Cr-5Ti, O can occupy interstitial sites within the lattice up to several atomic percent. Oxygen charging of V-5Cr-5Ti was conducted for up to 48 h at temperatures between 500 and 1030°C in flowing high-purity (99.999%) Ar and N_2 that contained O as an impurity. Diffusion coefficients of O and N in V indicate that O diffuses faster than N by factors of 10 to 1800 [5]. This property is very important for in-situ formation of CaO. Oxygen charging in an N_2 atmosphere lowers the diffusion rate (≈5%) because of some participation of N. Figure 1 shows the weight gain per unit area of the alloy at various temperatures after 17 h in N_2. Based on metallographic information and weight gain, we can control the depth of the O-charged layer by exposure temperature and time in flowing Ar or N_2 atmospheres. Oxygen concentration in the near-surface layer was calculated from the weight gain, surface area, and thickness of the hardened region; it ranged from 250 ppm (as-received) to ≈2–3%, depending on position within the layer and exposure conditions.

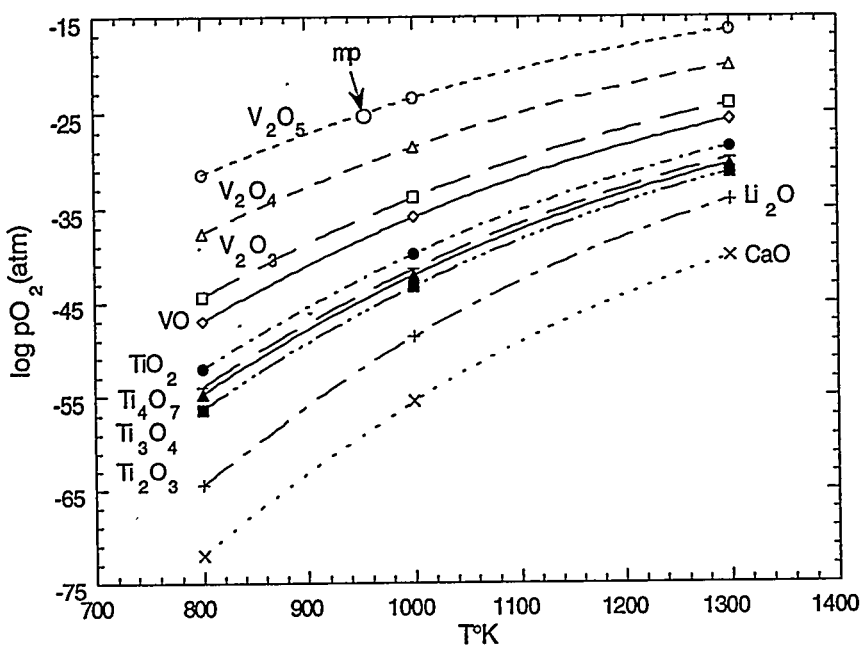

Figure 1. Thermodynamic stability of several possible oxide phases that can form on V-Cr-Ti alloys, Li, and Ca in oxygen-containing environments

Oxygen charging was also performed in air at 400°C to avoid melting of V_2O_5 (690°C) during oxidation. During oxidation in air at 400°C for 20 h, a blue

amorphous layer (≈1 μm thick) formed at the surface. Samples charged with O in high–purity Ar or N_2 atmospheres showed the same X-ray spectra before and after O charging. When we measured ohmic resistance (two–point contact) on the surfaces of heat–treated specimens at room temperature, the specimens charged with O in high–purity Ar or N_2 showed the same ohmic values before and after O charging. The blue oxide that formed in air at 400°C had a resistance of ≈5 Ω, not very high compared to values for most metal oxides. This oxide is not stable in liquid Li.

Compatibility tests on O-charged V-5Cr-5Ti in liquid Li: Figure 2 shows results of compatibility tests on O–charged samples in flowing liquid Li at 443°C for 298 h. Samples charged with O at 1030 and 1005°C showed the highest weight loss during exposure to liquid Li. Similar results were obtained at 408°C. In general, specimens that exhibit the greatest weight gain during O charging undergo the greatest weight loss during exposure to Li. Presumably, this indicates that an oxide phase (e.g., V_2O_3) that formed during O-charging dissolves in liquid Li. However, weight–loss rates for specimens exposed to Li at 443 and 408°C are virtually the same (i.e., 1.68 $\mu g/cm^2$-h and 0.84 $\mu g/cm^2$-h, respectively). In contrast, if weight loss in short–term corrosion tests was controlled primarily by O diffusion in the alloy, the rates would be expected to be relatively independent of the amount of O charged. This would be applicable to any of the thermodynamically stable oxides in the liquid Li, e.g., BeO, MgO, Y-Al-O garnet, Mg-Al-O spinel, Y_2O_3, and CaO. A similar situation could presumably occur for the formation of nitrides by the reaction of N in the alloy with metallic elements dissolved in Li. Nevertheless, it is important to determine the optimal condition for O-charging of V-5Cr-5Ti; O-charging in 99.999% Ar at 650°C was found to be adequate on the basis of the liquid-Li compatibility tests.

CaO formation on as–received specimens: In-situ formation of CaO on as–received specimens (250 ppm O) has been investigated in liquid Li containing 23 wt.% Ca at 700°C during a 7–day exposure. We believe the reaction that forms CaO occurs at the interface between O at alloy surface and Ca in the liquid metal. The coating did not completely cover the V-5Cr-5Ti surface, but a high ohmic resistance typical of CaO (two–point contact of >20 MΩ at room temperature) was obtained.

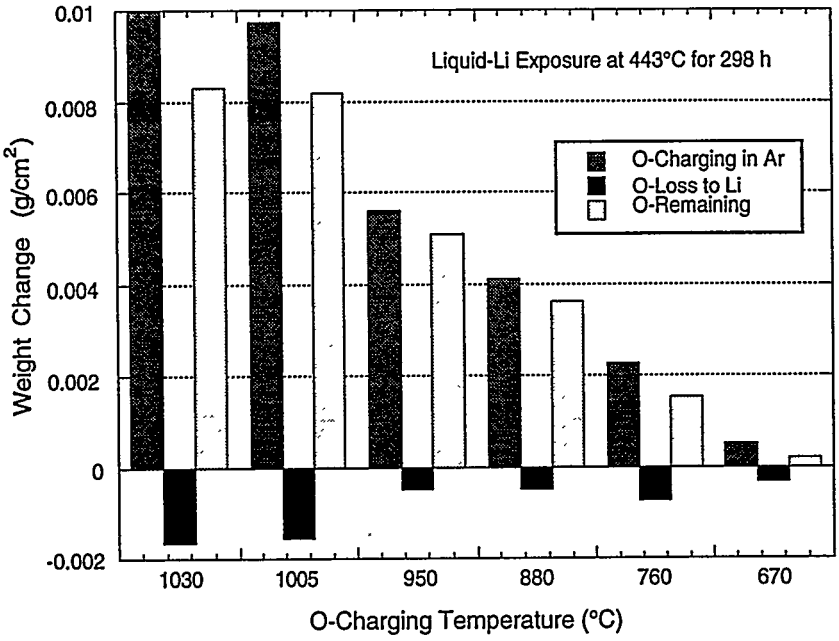

Figure 2. Weight change of V-5Cr-5Ti specimens after O charging in Ar for 40 h at temperatures between 670 and 1030°C and after exposure of O–charged specimens to Li at 443°C for 298 h

<u>*CaO formation on O-charged specimens:*</u> To improve formation of CaO on alloy substrates, O–charged specimens were immersed in Ca-bearing (0.5–85 wt.% Ca) liquid Li for various times and temperatures. This approach was adopted because O in the alloy (as a reactant) may have a higher affinity for a solute such as Ca dissolved in Li than for the alloy elements (V, Cr, and Ti). Several experiments were performed to test this hypothesis. Specimens of V-5Cr-5Ti were heat treated in flowing Ar at 650°C to charge the surface of the alloy with O.

To monitor coating development by measuring electrical resistivity, specimens (0.25 x 1.5 x 0.04 in.) were attached to Type 304 SS lead wires (1.2 mm diameter) by electron–beam welding. The specimens were charged with O in an Ar atmosphere at 650°C for 17-20 h, as described previously. Two specimens were coupled to form one conductivity-measuring unit, as described previously [5]. The specimens were immersed for 17 h at 400°C in a solution of Li containing 85 wt.% Ca, which has a liquidus temperature of ≈380°C. Then the specimens were elevated above the liquid and exposed to an Ar atmosphere

(which contained O as an impurity) at 650°C for 17 h to oxidize the Ca, as done in the O-charging procedure for the V–base alloy. The specimens were immersed in the liquid Li-(0.5 wt.%) Ca alloy again to measure the electrical resistance of CaO films at ≈400°C. Figure 3 shows the cell resistance (9.5 x 10^5 Ω) at a current of 100 nA (10^{-7} A) over a 120–h period at 435°C. An initial iR value (where i = current and R = electrical resistance) was obtained at a current of 1 mA, which was too high and caused polarization of the specimen.

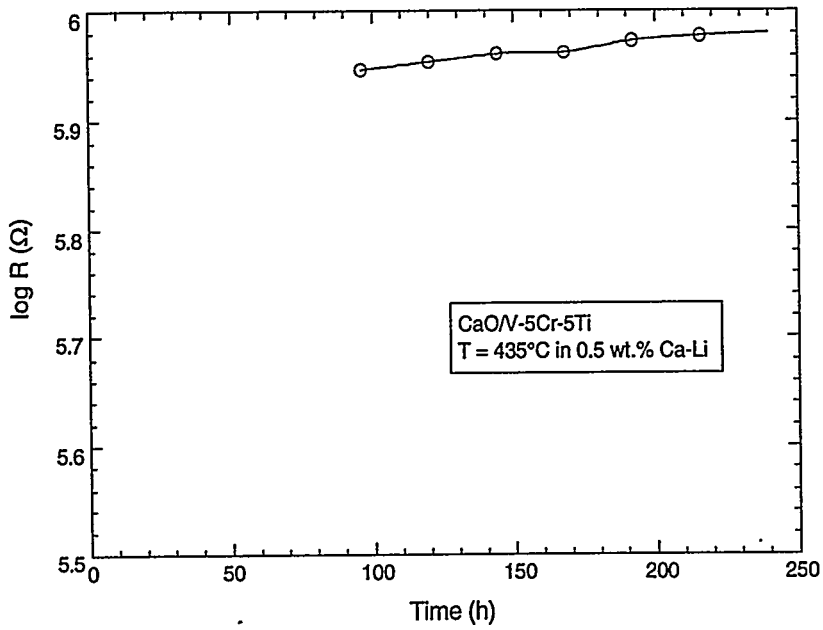

Figure 3. Log R(Ω) vs. time for CaO coating performed in 0.5 wt.% Ca-Li environment. CaO coating fabricated by exposure in 85 wt.% Ca-Li at 400°C and oxidized at 650°C for 17 h in 99.999% Ar.

<u>*Mechanical integrity and self–healing characteristics:*</u> Figure 4 shows SEM photomicrographs of the surface of a CaO coating that contains microcracks. To determine coating thickness, mechanical integrity, and compositional depth profiles in cross section, the specimens were metallographically mounted with an epoxy resin (Fig. 5). As shown in Fig. 5b, depth profiles of the alloy elements near the interface showed that the composition of Ti and Cr remains constant and that only a small amount (1-2%) of the Ca diffused into the V-5Cr-5Ti (1-2 μm depth). From our previous investigation at higher temperatures (≈700°C),

elemental diffusion was more significant and ≥10% V was detected in the CaO layer [6].

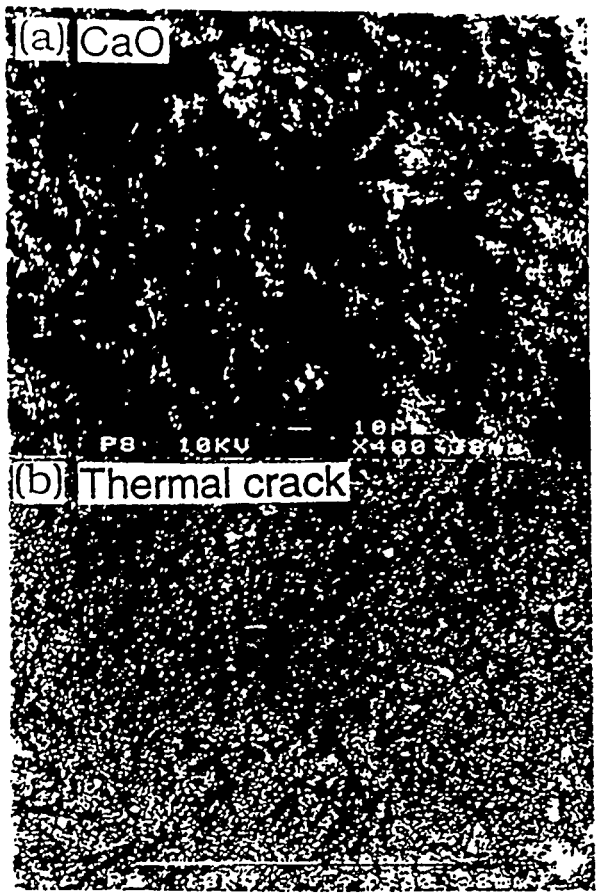

Figure 4. (a) SEM photomicrograph of surface of CaO coating, and (b) microcracks in coating shown in (a)

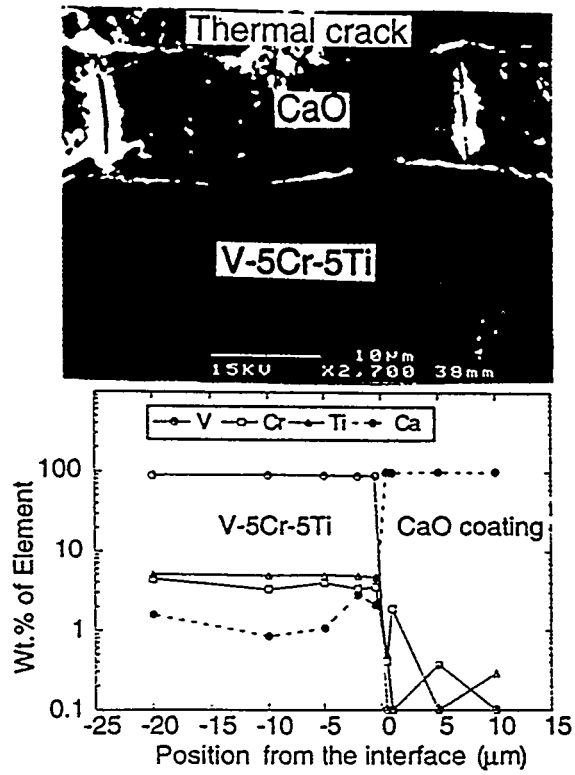

Figure 5. (a) SEM photomicrograph of cross section, and (b) EDS depth profiles of V, Cr, Ti, and Ca at CaO/V-5Cr-5Ti interface of coating formed at 400°C

With regard to microcracks in the coating layer, CaO has a higher coefficient of thermal expansion than that of V-5Cr-5Ti (12×10^{-6} vs. 9.2×10^{-6}/K). Therefore, a CaO layer that forms in-situ on a V-alloy will be subjected to a tensile stress during cooling. Based on the photomicrograph shown in Figs. 4 and 5, CaO coatings on V-5Cr-5Ti have the characteristics described below. The crack pattern consists of regions with diameters of ≈30-40 μm and crack widths of ≈2000 Å over most of the CaO surface, which suggests that the cracks

originate by a mismatch of the thermal expansion coefficients during cooling, i.e., they are "crazing cracks." Adhesion of the CaO film to the V-5Cr-5Ti substrate appears to be quite good. One approach to minimize microcracking would be to decrease the thickness of the CaO film to better match its mechanical strength with that of the V-5Cr-5Ti substrate. For example, a CaO film ≈1 μm in thickness may have a higher fracture strength and also have a resistance of ≥1 MΩ, which is higher than design requirement for fusion reactors by three to four orders of magnitude.

Liu and Smith [7] suggest that no coating may be acceptable because calculated stresses are greater than the tensile flexural strengths of most candidate coatings. Therefore, the coatings are subject to cracking in both tension (e.g., CaO) and compression. However, their criteria must be viewed in relationship to the conditions under which the coating is formed (viz., temperature and time), as well as the normal operating temperature. For example, when a CaO film forms at 400°C, no stress develops when the coating operates at 400°C. However, because the fabrication and operating temperatures may differ and the coating will undergo thermal fluctuation during operation, acceptable temperature ranges must be defined to account for these situations. The surface cracks developed during cooling from 400°C to room temperature.

Thermally induced strains are usually calculated by assuming linear thermal expansion, namely $\Delta\varepsilon_{thermal} = (\alpha_{CaO} - \alpha_{V\text{-}5Cr\text{-}5Ti}) \times (T_1 - T_2) = \Delta\alpha \times \Delta T \approx 3 \times 10^{-6} \times 375 = 1.13 \times 10^{-3}$, where α_{CaO} and $\alpha_{V\text{-}5Cr\text{-}5Ti}$ are the coefficients of thermal expansion of CaO and V-5Cr-5Ti, respectively, and T_1 and T_2 are the upper and lower values of the temperature change. Stresses in the CaO coating can be relieved by either plastic deformation (including creep), crack formation (microcracking), or spallation. Plastic deformation is possible only when the stress is below the critical stress for the formation of any type of material separation (e.g., cracking). The CaO layer is subjected to compressive and tensile stress when the temperature is above and below that at which the film formed. When the temperature is cycled slowly, the coating/substrate interface may undergo relaxation such that cracking or spallation does not occur. In any case, because cracking of the CaO layer during cooling is of the greatest concern, it is important for the coating to exhibit self–healing characteristics in a liquid–metal environment.

Preliminary studies have been conducted to explore the self–healing properties of CaO coatings under temperature cycling. Self–healing of CaO was investigated at temperatures between 300 and 740°C. At 300°C, self-healing did not occur in a 10–h period; at ≥360°C, cracks appeared to heal (e.g., at 450°C, resistivity was restored to its initial value within several hours, and at 500°C in <1 h). When a CaO coating was subjected to compressive stress by increasing the temperature in a similar manner, no appreciable cracking was detected. When temperature was increased to accelerate the healing process, we could not assess whether increases in iR values were caused by closing of cracks or by diffusion–related healing behavior. Nevertheless, when the system temperature was raised, the rapid response resembled healing of the cracks.

Preliminary work was conducted to explore the self-healing process in terms of diffusion, thermal expansion, and contraction processes within the CaO layer. In this regard, it is more important to consider reactions that take place at the defect area rather than at the surface region, namely, at the Li-Ca/V-5Cr-5Ti (O) interface. The CaO layer growth mechanism could be as follows; initially a thin CaO forms at the interface by the reaction Ca (in Li) + O (in V-5Cr-5Ti) = CaO accompanied by inward ambipolar diffusion of Ca^{+2} ion and electrons. The spontaneous reaction of Ca^{+2} + 2 e' + O = CaO will take place at the CaO/V-5Cr-5Ti interface, including defect areas such as grain boundaries, dislocations, open voids, and microcracks because the diffusivity of Ca^{+2} is much higher than that of O^{-2} in CaO and because growth of the CaO layer depends on inward diffusion of Ca^{+2}, presumably by a cation vacancy [8] mechanism.

Figure 6 shows the temperature–and–ohm x area–versus–time response during thermal cycling of a coated specimen in liquid Li. Resistivity of a coated specimen that was cooled to room temperature and then heated to 432°C for 50 min stabilized at ≈600 $\Omega \cdot cm^2$, which is indicative of healing of cracks in the coating. During cooling of the specimen from 430 to 360°C, the specimen initially exhibited ceramic–type behavior, i.e., ohmic value increased to ≈800 $\Omega \cdot cm^2$, but during further cooling to 325°C, the ohmic value decreased precipitously to ≈20 $\Omega \cdot cm^2$, which is indicative of further crack development. During heating of the specimen to ≈450°C, the ohmic value increased to ≈300 $\Omega \cdot cm^2$ and stabilized at that value, which is indicative of self–healing of the defects. However, when the temperature increased to 490°C, the ohmic value dropped immediately because thermal expansion of the liquid caused the meniscus at the liquid/specimen interface to rise and the liquid Li to wet "new" surfaces of

O-charged V-5Cr-5Ti. During a 2-h period at 490°C, the ohmic value increased slowly to the previous value as a CaO coating formed on this region of the specimen. When the specimen was cooled from 490 to 320°C, no new cracks developed and the resistivity once again increased, which is indicative of ceramic-type behavior. During the next ≈100-h period at 320°C, resistivity increased slowly to ≈1200 Ω·cm^2. This could be attributed to further repair of the CaO layer in less protected regions and/or changes in the defect chemistry of CaO when Ca was not present at high concentration in liquid Li. Additional work is required to establish the mechanisms for self-healing of CaO coatings during thermal cycling.

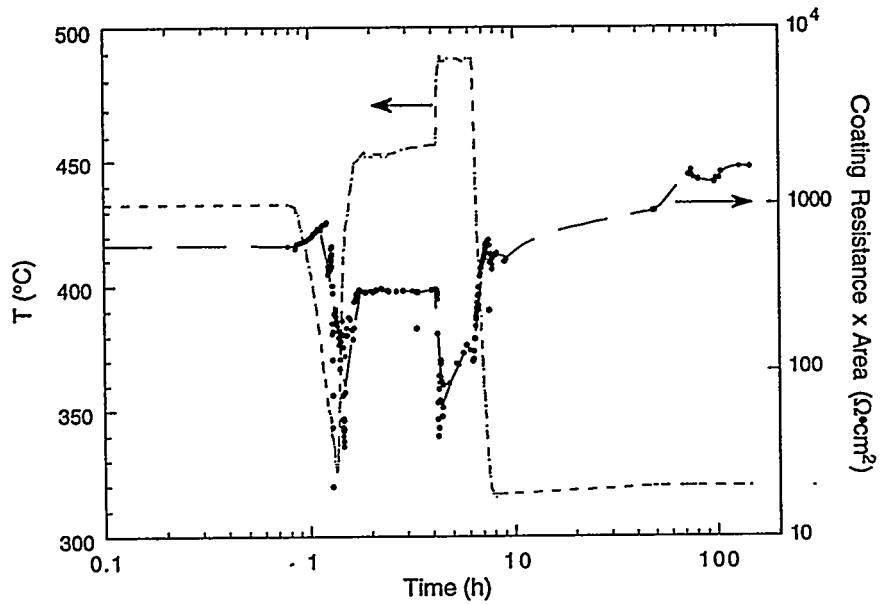

Figure 6. Temperature and ohmic resistance x area (R x A) vs. time during thermal cycling

CONCLUSIONS

A method was developed for in-situ fabrication of an electrically insulating CaO coating on V-5Cr-5Ti in a liquid-Li environment. The process involves reaction of an O-enriched alloy surface with liquid Li containing Ca at 300-400°C. Thermal cycling tests were conducted on CaO coatings that form in-situ on V-5Cr-5Ti in liquid Li containing dissolved Ca at temperatures between 300 and 740°C. Microcracks develop in the coating layer during cooling from >400°C to ambient temperature because of the higher expansion coefficient of CaO. After heating, the cracks exhibit self-healing within a 10-h period at 360°C and in <1 h

at 500°C, as evidenced by restoration of the resistivity to its original value. The layer growth and repair mechanism most likely involves the reaction of Ca (in Li) + O (in V-5Cr-5Ti) to form CaO, accompanied by inward ambipolar diffusion of Ca^{+2} ion and electrons.

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