

FORMATION AND SELF-HEALING BEHAVIOR OF CaO INSULATOR COATINGS ON A VANADIUM-BASE ALLOY IN LIQUID LITHIUM*

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OBJECTIVE

Corrosion resistance of structural materials and magnetohydrodynamic (MHD) forces and their influence on thermal hydraulics and corrosion are major concerns in the design of liquid-metal blankets for magnetic fusion reactors. The objective of this study is to develop in situ stable coatings at the liquid-metal/structural-material interface, with emphasis on coatings that can be converted to an electrically insulating film to prevent adverse currents that are generated by MHD forces from passing through the structural walls.^{1,2}

SUMMARY

The electrical resistance of CaO coatings produced on V-5%Cr-5%Ti by exposure of the alloy to liquid Li that contained 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 resistance of the coating layer, which followed insulator behavior. Examination of the specimens after cooling to room temperature revealed no spallation, but homogeneous crazing cracks were present in the CaO coating. In-situ self-healing of the cracks occurred at temperatures $\geq 360^\circ\text{C}$. These results suggest that thin coatings can be produced on variously shaped surfaces by controlling the exposure time, temperature, and composition of the liquid metal.

INTRODUCTION

Electrically insulating and corrosion-resistant coatings are required at the liquid-metal/structural interface in a fusion reactor to minimize magnetohydrodynamic forces and their influence on the 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.² 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 , $\text{Y}_3\text{Al}_2\text{O}_{12}$, 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, i.e., deuterium and tritium.

EXPERIMENTAL PROCEDURE

Various experimental methods have been explored to fabricate and characterize insulator coatings for use in liquid-Li environments: O charging of the near-surface region of V-base alloys in Ar gas and in air, evaluation of liquid-Li compatibility of the O-charged specimens, reaction of the O-enriched V-base alloy with dissolved Ca in Li to form a CaO layer, in-situ electrical resistance measurements of CaO coatings on V-5Cr-5Ti in liquid Li, and characterization of O-charged specimens and insulator coatings by scanning electron microscopy (SEM), 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 relatively low temperatures (320-400°C) has been emphasized.

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RESULTS AND DISCUSSION

Oxygen charging of the surface of V-5Cr-5Ti It is well known that O can be incorporated into the interstitial sublattice of body-centered-cubic (bcc) V and its alloys.⁴ 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 up to several atomic percent of the interstitial sites within the lattice. Oxygen charging of V-5Cr-5Ti was conducted for up to 48 h at temperatures between 500 and 1030°C in flowing high-purity Ar and N₂ (99.999%) that contained O as an impurity. Diffusion coefficients of O and N in V show that diffusion of O in V is 10–1800 times faster than that of N.⁵ This property is very important for in-situ formation of CaO. Oxygen charging in an N₂ atmosphere lowers the diffusion rate ($\approx 5\%$) 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 N₂. If we have metallographic information and weight gain, we can control the depth of the O-charged layer by exposure temperature and time in a flowing Ar atmosphere. 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 $\approx 2\text{--}3\%$, depending on position within the layer and exposure conditions.

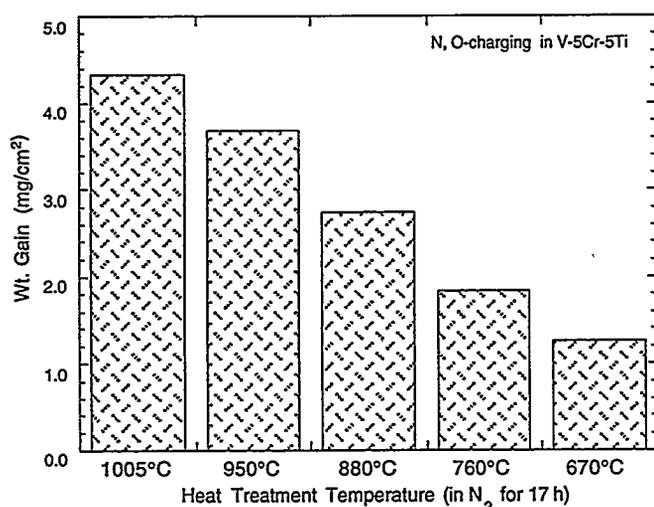


Figure 1.
Weight gain of V-5Cr-5Ti specimens after exposure in 99.999% N₂ for 17 h at several temperatures

Oxygen charging was also performed in air at 400°C to avoid melting of V₂O₅ (690°C) during oxidation. During oxidation in air at 400°C for 20 h, a blue amorphous layer ($\approx 1\ \mu\text{m}$ thick) formed at the surface. Samples charged with O in high-purity Ar or N₂ 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 N₂ showed the same ohmic values before and after O charging. The blue oxide that formed in air at 400°C had a resistance of $\approx 5\ \Omega$, 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., V₂O₃) 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 mg/cm²-h and 0.84 mg/cm²-h, respectively). By 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, Y₂O₃, 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.

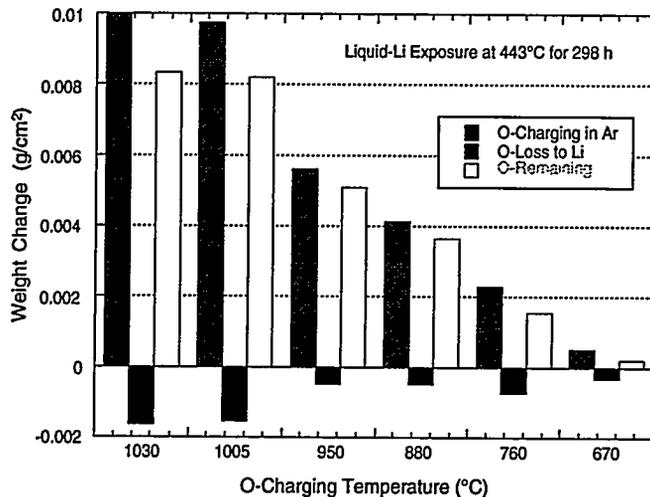


Figure 2. Weight change of V-5Cr-5Ti specimens after O charging in Ar for 40 h at temperatures between 670 and 1030°C and after exposure of O-charged specimens to Li at 443°C for 298 h

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 takes place at the interface between O at the 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.

CaO formation on O-charged specimens 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 at various 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 electrical resistivity measurements, specimens (6.35 x 38 x 1.0 mm.) 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 and two specimens were coupled to form one conductivity-measuring unit, as described previously.³ 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 and then elevated above the liquid and exposed to an Ar atmosphere at 400°C to oxidize the Ca, in a manner similar to the O-charging procedure for the V-base alloy. The specimens were again immersed in the liquid Li-(0.5 wt.% Ca) alloy to measure the electrical resistance of CaO films at 400°C. Figure 3 shows the cell resistance ($9.5 \times 10^5 \Omega$) at a current of 100 nA (10^{-7} A) over a 120-h period at ≈400°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.

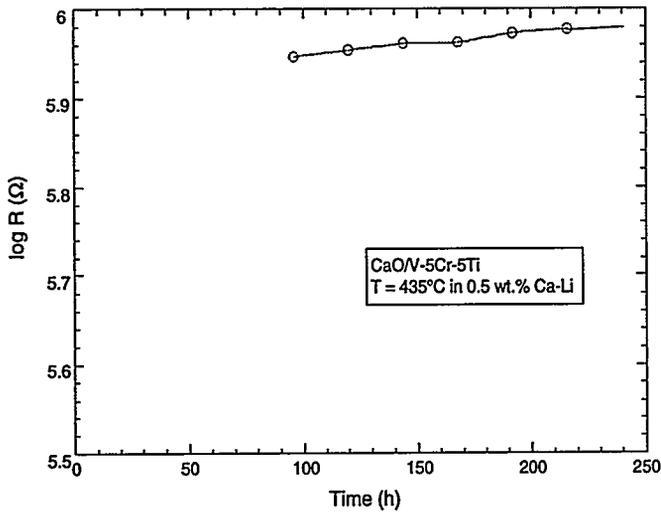


Figure 3.
Log R(Ω) vs. time of CaO coating fabricated by exposure of V-5Cr-5Ti to Ar (99.999%) at 650°C for 17 h and to 85 wt.% Ca-Li at 400°C for 17 h. Resistance measured in 0.5 wt.% Ca-Li at 435°C

Mechanical integrity and self-healing characteristics 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. 5a). 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 ($\approx 700^\circ\text{C}$), elemental diffusion was more significant and $\geq 10\%$ V was detected in the CaO layer.⁵

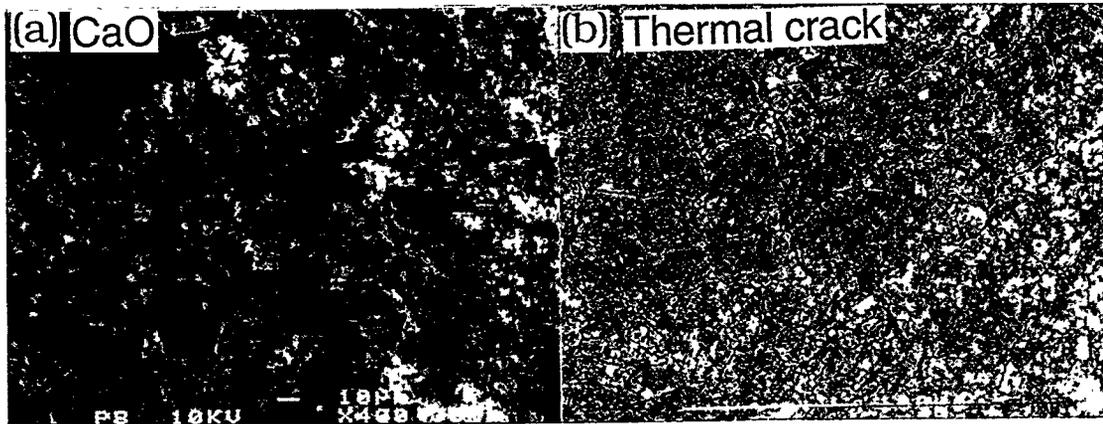


Figure 4. (a) SEM photomicrograph of surface of CaO coating and (b) microcracks in coating shown in (a)

The coefficient of thermal expansion of CaO is higher than that of V-5Cr-5Ti (12×10^{-6} vs. $9.2 \times 10^{-6}/\text{K}$). Therefore, a CaO layer that forms in situ on a V-alloy will be subjected to a tensile stress during cooling. The photomicrographs of CaO coatings on V-5Cr-5Ti shown in Figs. 4 and 5 reveal that the pattern of microcracks consists of regions with diameters of $\approx 30\text{--}40 \mu\text{m}$ and crack widths of $\approx 2000 \text{ \AA}$ over most of the CaO surface, which suggests that the cracks originate from 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 way to minimize microcracking would be to decrease the thickness of the CaO film so that its mechanical strength better matches that of the V-5Cr-5Ti substrate. For

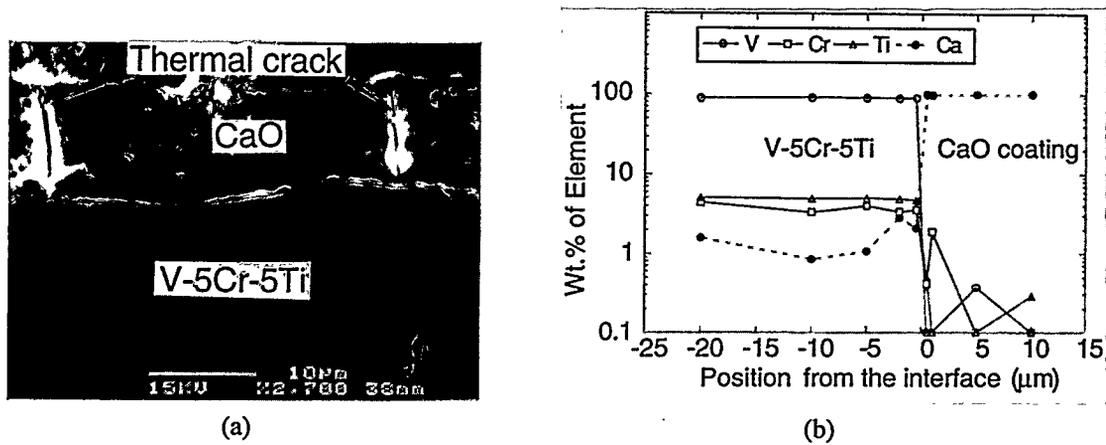


Figure 5. (a) SEM photomicrograph of cross section and (b) EDS depth profiles of V, Cr, Ti, and Ca at CaO/V-5Cr-5Ti interface of coating formed at 400°C

example, a CaO film $\approx 1 \mu\text{m}$ may have a higher fracture strength and also have a resistance $\geq 1 \text{ M}\Omega$, which is higher than design requirement for fusion reactors by three to four orders of magnitude.

Liu and Smith⁶ suggest that no coating³ 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

$$\begin{aligned} \Delta\epsilon_{\text{thermal}} &= (\alpha_{\text{CaO}} - \alpha_{\text{V-5Cr-5Ti}}) \times (T_1 - T_2) \\ &= \Delta\alpha \times \Delta T \approx 3 \times 10^{-6} \times 375 \\ &= 1.13 \times 10^{-3}, \end{aligned} \quad (1)$$

where α_{CaO} and $\alpha_{\text{V-5Cr-5Ti}}$ 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 so 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 temperatures $\geq 360^\circ\text{C}$, 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 growth mechanism of the CaO layer could be as follows; initially a thin CaO forms at the interface by the reaction $\text{Ca (in Li)} + \text{O (in V-5Cr-5Ti)} = \text{CaO}$, accompanied by inward ambipolar diffusion of the Ca^{+2} ion and electrons. The spontaneous reaction of $\text{Ca}^{+2} + 2 e' + \text{O} = \text{CaO}$ will take place at the CaO/V-5Cr-5Ti interface, including defect areas such as grain boundaries, dislocations, and open voids, 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 mechanism.⁷

Figure 6 shows the temperature-and-ohm \times 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 $\approx 600 \Omega\text{-cm}^2$, which is indicative of healing of cracks in the coating. During cooling from 430 to 360°C , the specimen initially exhibited ceramic-type behavior, i.e., the ohmic value increased to $\approx 800 \Omega\text{-cm}^2$, but during further cooling to 325°C , the ohmic value decreased precipitously to $\approx 20 \Omega\text{-cm}^2$, which is indicative of further crack development. During heating of the specimen to $\approx 450^\circ\text{C}$, the ohmic value increased to $\approx 300 \Omega\text{-cm}^2$ and stabilized at that value, which is indicative of self-healing of the defects. However, when the temperature was 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 $\approx 1200 \Omega\text{-cm}^2$. This increase 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 of self-healing of CaO coatings during thermal cycling.

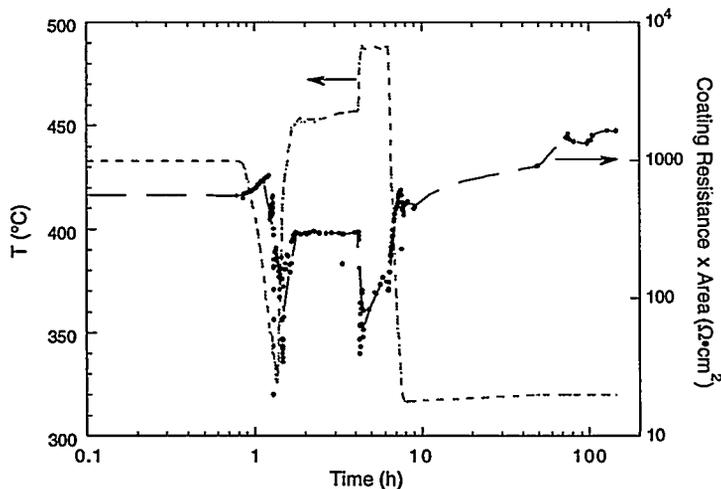


Figure 6.
Temperature and ohmic resistance \times area ($R \times A$) vs. time during thermal cycling

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 that contains 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.

FUTURE WORK

The performance of CaO coatings on V-base alloys in flowing liquid Li will be evaluated in-situ by monitoring induced currents in a magnetic field. Hydrogen permeability measurements will be performed on noncoated and CaO coated V-base alloys.

ACKNOWLEDGMENTS

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REFERENCES

- [1] C. C. Baker et al., *Tokamak Power System Studies FY 1985*, Argonne National Laboratory Report, ANL/FPP-85-2 (Dec. 1985).
- [2] R. F. Mattas, B. A. Loomis, and D. L. Smith, *Vanadium Alloys for Fusion Reactor Applications*, JOM, 44(8), 26 (1992).
- [3] J.-H. Park, T. Domenico, G. Dragel, and R. W. Clark, *Development of Electrical Insulator Coatings for Fusion Power Applications*, submitted to 3rd Intl. Symp. on Fusion Nuclear Technology (ISFNT-3), June 27–July 1, 1994, Los Angeles, CA.
- [4] A. U. Seybolt and H. T. Sumsion, *Vanadium-Oxygen Solid Solutions*, Met. Trans. AIME, 292-299 (1953).
- [5] J.-H. Park, *Intermetallic and Electrical Insulator Coatings on High-Temperature Alloys in Liquid Lithium Environments*, Proc. Symp. on High-Temperature Coatings-I, TMS Fall Meeting, Oct. 2-6, 1994, Rosemont, IL.
- [6] Y. Y. Liu and D. L. Smith, *Ceramic Electrical Insulators for Liquid Metal Blankets*, J. Nucl. Mater., 141-143, 38 (1986).
- [7] V. Kumar and Y. P. Gupta, *Cation Self-diffusion in Single Crystal CaO*, J. Phys. Chem. Solid, 30, 677-685 (1969).