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SELF-HEALING OF DEFECTS IN CaO COATINGS

ON V-5%Cr-5%Ti IN LIQUID LITHIUM\*

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# SELF-HEALING OF DEFECTS IN CaO COATINGS

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### Abstract

In-situ 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. 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  $\geq 360^\circ\text{C}$ .

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### INTRODUCTION

Corrosion resistance of structural materials, and the MHD force and its influence on thermal hydraulics, are major concerns in the design of liquid-metal cooling systems for fusion first-wall/blanket applications [1]. Vanadium and V-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in fusion reactors [2]. Our recent work has focused on in-situ formation of CaO on V-5Cr-5Ti in liquid Li because CaO exhibits both high electrical resistivity and thermodynamic stability relative to other potential insulator candidates ( $Y_2O_3$ , BeO, MgO,  $MgAl_2O_4$ ,  $Y_3Al_2O_{12}$ , etc.) in liquid Li [3]. The objective of this study is to investigate the in-situ self-healing behavior of the defects, i.e., cracks in the coating, in liquid-Li environments.

### EXPERIMENTAL PROCEDURE

Various experimental methods have been explored to fabricate and characterize insulator coatings for use in liquid-Li environments: exposure of O-enriched V-base alloys in Li containing dissolved Ca to form the CaO layer, in-situ electrical resistance measurements of CaO coatings on V-5Cr-5Ti in liquid Li, characterization of the O-charged specimens and insulator coatings by microhardness measurements and scanning electron microscopy (SEM), and 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

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coating layers that formed in-situ. Fabrication of coatings at a relatively low temperature (320-400°C) has been emphasized.

## RESULTS AND DISCUSSION

*Mechanical integrity and self-healing characteristics:* With regard to microcracks in the coating layer, CaO has a higher coefficient of thermal expansion than that of V-5Cr-5Ti ( $12 \times 10^{-6}$  vs.  $9.2 \times 10^{-6}/K$ ). Therefore, a CaO layer that forms in-situ on a V-alloy will be subjected to a tensile stress during cooling. Based on the photomicrographs in Figs. 1 and 2, CaO coatings on V-5Cr-5Ti have the characteristics described below. The crack pattern consists of regions with diameters of  $\approx 30$ - $40 \mu m$  and crack widths of  $\approx 2000 \text{ \AA}$  over most of the CaO surface, which suggests that the cracks originate by a mismatch of the thermal expansion coefficients during cooling, i.e., "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  $\approx 1 \mu m$  in thickness may have a higher fracture strength and also have a resistance of  $\geq 1 M\Omega$ , which is higher than design requirement for fusion reactors by three to four orders of magnitude.

Liu and Smith [3] 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 criterion 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 shown in Figs. 1 and 2 developed during cooling from 400°C to room temperature. Thermally induced strains are usually calculated by assuming linear thermal expansion, namely

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

$$= 1.13 \times 10^{-3}$$

where  $\alpha_{\text{CaO}}$  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 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  $\geq 360^\circ\text{C}$ , 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  $iR$  (where  $i$  = current and  $R$  = electrical resistance) 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  $\text{Ca (in Li)} + \text{O (in V-5Cr-5Ti)} = \text{CaO}$  accompanied by inward ambipolar diffusion of  $\text{Ca}^{+2}$  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, open voids, microcracks, etc., because the diffusivity of  $\text{Ca}^{+2}$  is much higher than that of  $\text{O}^{-2}$  in CaO and because growth of the CaO layer depends on inward diffusion of  $\text{Ca}^{+2}$ , presumably by a cation vacancy [4] mechanism.

Figure 3 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  $432^\circ\text{C}$  for 50 min stabilized at  $\approx 600 \Omega\cdot\text{cm}^2$ , which is indicative of healing of cracks in the coating. During cooling of the specimen from  $430$  to  $360^\circ\text{C}$ , the specimen initially exhibited ceramic-type behavior, i.e., ohmic value increased to  $\approx 800 \Omega\cdot\text{cm}^2$ , but during further cooling to  $325^\circ\text{C}$ , the ohmic value decreased precipitously to  $\approx 20 \Omega\cdot\text{cm}^2$ , which is indicative of further crack development. During heating of the specimen to  $\approx 450^\circ\text{C}$ , the ohmic value increased to  $\approx 300 \Omega\cdot\text{cm}^2$  and stabilized at that value, which is indicative of self-healing of the defects. However, when the temperature increased to  $490^\circ\text{C}$ , 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  $490^\circ\text{C}$ , 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  $320^\circ\text{C}$ , no new cracks developed and the resistivity once again increased, which is indicative of ceramic-type behavior. During the next  $\approx 100$ -h period at  $320^\circ\text{C}$ , resistivity increased slowly to  $\approx 1200 \Omega\cdot\text{cm}^2$ . 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.

## CONCLUSIONS

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  $740^\circ\text{C}$ . Microcracks develop in the coating layer during cooling from  $>400^\circ\text{C}$  to ambient temperature because of the higher expansion coefficient of CaO. After heating, the cracks exhibit self-healing within a 10-h period at  $360^\circ\text{C}$  and in  $<1$  h at  $500^\circ\text{C}$ , 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  $\text{Ca}^{+2}$  ion and electrons.

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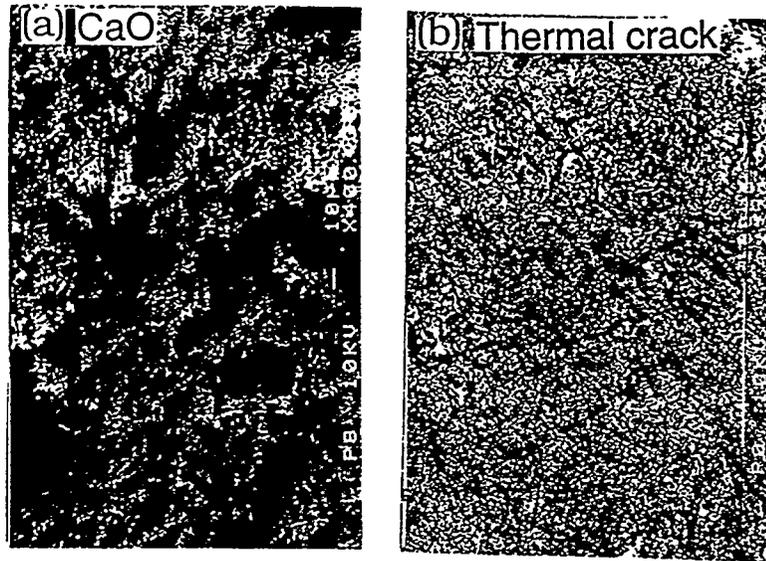


Figure 1. (a) SEM photomicrograph of surface of CaO coating, and (b) microcracks in coating in (a).

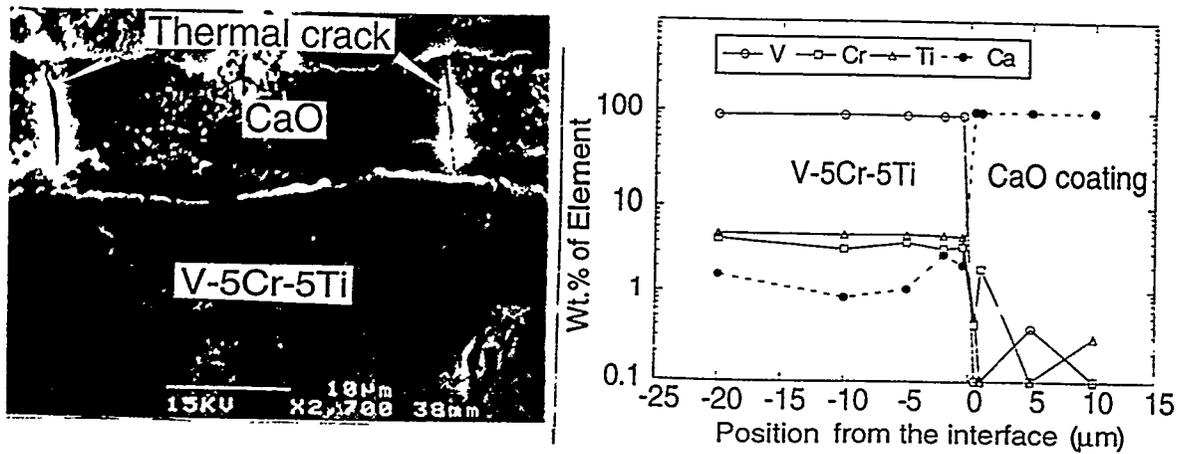


Figure 2. SEM photomicrograph of cross section and EDS depth profiles of V, Cr, Ti, and Ca at CaO/V-5Cr-5Ti interface of a coating formed at 400°C.

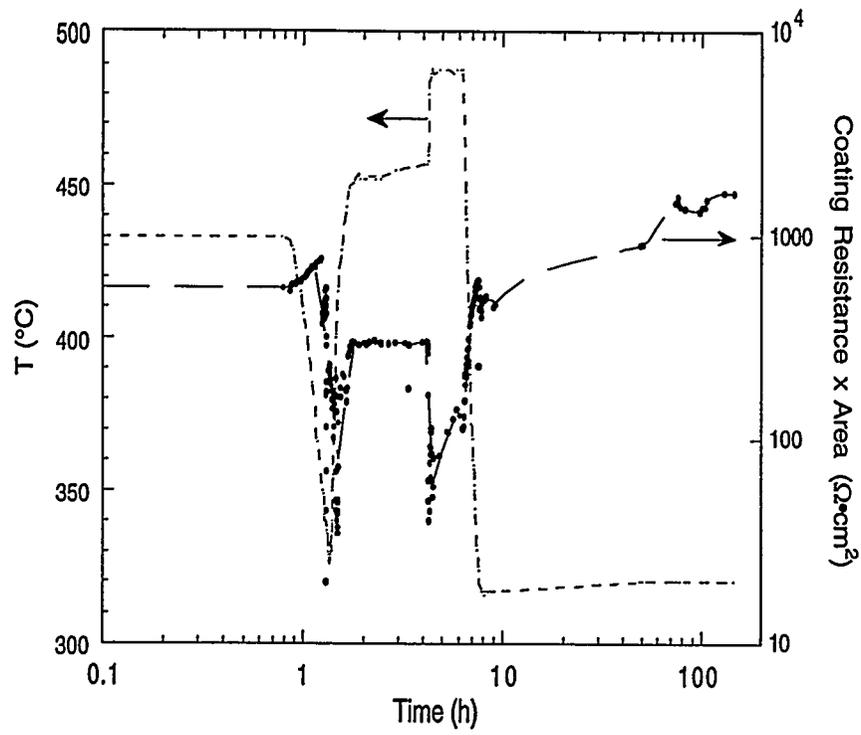


Figure 3. Temperature and ohmic resistance  $\times$  area ( $R \times A$ ) vs. time during thermal cycling.