

## CaO INSULATOR COATINGS ON A VANADIUM-BASE ALLOY IN LIQUID 2 at. % CALCIUM-LITHIUM\* J.-H. Park and T. F. Kassner (Argonne National Laboratory)

### OBJECTIVE

In the design of liquid-metal blankets for magnetic fusion reactors, corrosion resistance of structural materials and magnetohydrodynamic (MHD) forces and their influence on thermal hydraulics and corrosion are major concerns. The objective of this study is to develop stable in-situ 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.

### SUMMARY

The electrical resistance of CaO coatings produced on V-4%Cr-4%Ti and V-15%Cr-5%Ti by exposure of the alloy (round bottom samples 6-in. long by 0.25-in. dia.) to liquid lithium that contained 2 at.% dissolved calcium was measured as a function of time at temperatures between 300-464°C. The solute element, calcium in liquid lithium, reacted with the alloy substrate at these temperatures for 17 h to produce a calcium coating  $\approx 7-8 \mu\text{m}$  thick. The calcium-coated vanadium alloy was oxidized to form a CaO coating. Resistance of the coating layer on V-15Cr-5Ti, measured in-situ in liquid lithium that contained 2 at.% calcium, was  $1.0 \times 10^{10} \Omega\text{-cm}^2$  at 300°C and 400 h, and  $0.9 \times 10^{10} \Omega\text{-cm}^2$  at 464°C and 300 h. Thermal cycling between 300 and 464°C changed the resistance of the coating layer, which followed insulator behavior. Examination of the specimen after cooling to room temperature revealed no cracks in the CaO coating. The coatings were evaluated by optical microscopy, scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), and X-ray analysis. Adhesion between CaO and vanadium alloys was enhanced as exposure time increased.

### 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.<sup>1</sup> Vanadium and vanadium-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in fusion reactors.<sup>2</sup> In-situ formation of CaO on V-5Cr-5Ti in liquid lithium was investigated because the electrical resistivity of CaO is very high and also because CaO exhibits a higher thermodynamic stability in liquid lithium than do other potential insulator candidates ( $\text{Y}_2\text{O}_3$ , BeO, MgO,  $\text{MgAl}_2\text{O}_4$ ,  $\text{Y}_3\text{Al}_2\text{O}_{12}$ , etc.).<sup>3</sup> In-situ self-healing behavior of defects (such as cracks in the coating) in liquid-lithium environments<sup>4</sup> 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

V-Ti-Cr alloys in the form of round-bottom pencil-shaped samples (6.35 mm dia x 150 mm long) and flat-tab samples (12.7 x 25.4 x 1.0 mm) were used in this study. Various steps and experimental methods have been explored to fabricate and characterize insulator coatings for use in liquid-lithium environments: as a first step, the near-surface regions of vanadium-base alloys were charged with oxygen by exposure to flowing argon that contained either 10-20 ppm oxygen (i.e., impurity level of commercial 99.999% Ar) or 200 ppm oxygen in argon at 610-658°C for 17-19.5 h. As a second step, the oxygen-

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enriched vanadium-base alloy reacted with dissolved calcium (2 at.%) in lithium for 16-17 h at 300-550°C to form a CaO. During this process in-situ electrical resistance was monitored as a function of time. Subsequently, the samples were raised 10-30 mm above the liquid metal, where they remained for 16-72 h to allow excess molten alloy to drip from the samples. As a third step, the CaO/Ca layer was oxidized in a flowing gas mixture that contained 10-5000 ppm oxygen in argon for 17 h at 450-650°C.

Finally, the samples were examined for coating uniformity, two-point ohmic resistance measurements were made at numerous locations around the CaO-coated rod, and only the samples that showed an infinite ohmic resistance were selected for in-situ resistance measurements during exposure to the same liquid metal at temperatures between 250-500°C for up to 700 h. Samples were evaluated after each step by weighing, optical microscopy, SEM, EDS, and microhardness testing.

## RESULTS AND DISCUSSION

*Oxygen charging of the surface of V-Cr-Ti.* It is well known that oxygen can be incorporated into the interstitial sublattice of body-centered-cubic (bcc) vanadium and its alloys.<sup>5</sup> Detailed information pertaining to oxygen incorporation in the alloys has been reported in Ref. 6. Figure 1 shows thermogravimetric results for the oxygen-charging experiment, and Fig. 2 shows the weight gain for various samples at 650°C after 17 h in argon that contained 10 ppm oxygen. 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  $\approx 1\%$ , within 25  $\mu\text{m}$  of the surface layer.

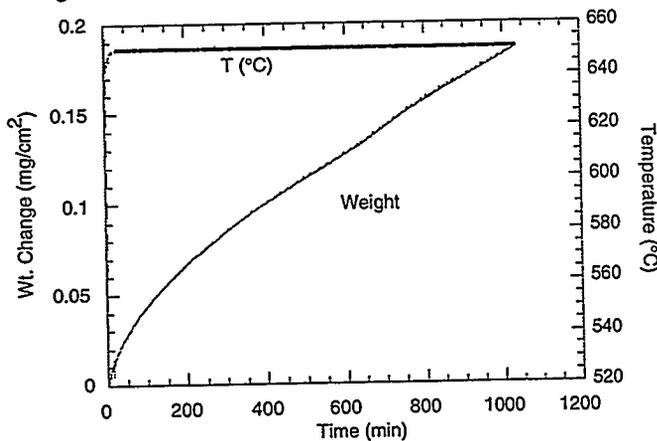


Figure 1. Thermogravimetric results for V-4Cr-4Ti specimens during oxygen charging

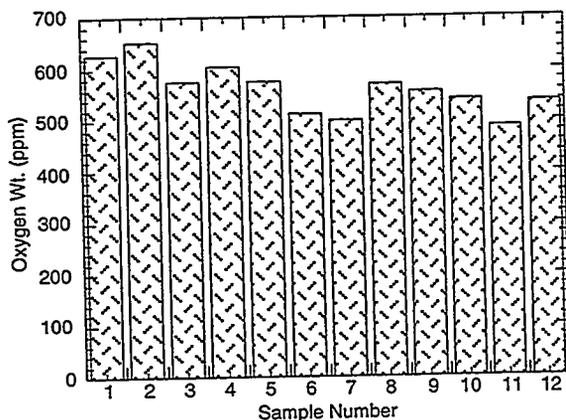


Figure 2. Weight gain of V-4Cr-4Ti tab-shaped specimens after exposure in argon with 10 ppm oxygen for 17 h at 650°C

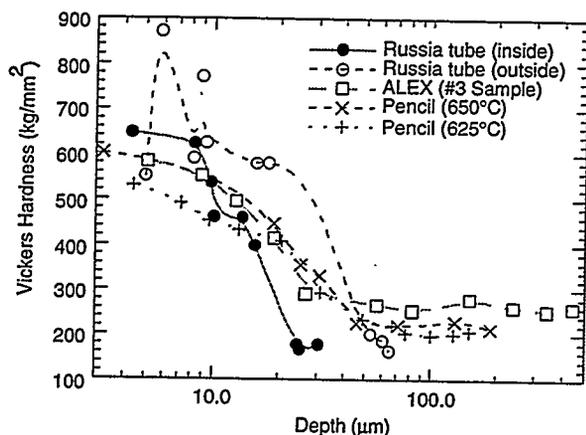


Figure 3.  
Vickers hardness profiles from cross sections of various V-4Cr-4Ti specimens exposed to argon with 10 ppm oxygen for 17 h at 650°C

Figure 3 shows Vickers hardness profiles from cross sections near the surface area of various V-4Cr-4Ti specimens exposed to argon that contained 10 ppm oxygen for 17 h at 650°C. Long pencil-shaped samples placed in a temperature gradient exhibited somewhat lower oxygen uptake in the lower temperature zone. However, a Russian-supplied tube sample showed a higher surface hardness than other samples in this experiment. Oxygen charging was also performed in argon that contained 200 ppm oxygen. However, in this environment, the vanadium alloy surface developed a blue oxide layer over the thin black surface. The ohmic values of specimens before and after oxygen charging were the same. The blue oxide is not stable in liquid lithium.

*Exposure of oxygen-charged V-Cr-Ti samples in 2 at.% Ca-Li.* Figure 4 shows the product of the in-situ ohmic resistance times the liquid-metal contact area of the oxygen-charged samples in 2 at.% Ca-Li at 500°C for 17 h. The R\*A (resistance x area) values for various samples were 20–50  $\Omega\text{-cm}^2$ . Before exposure to the liquid metal, the temperature difference between the samples and the liquid metal was minimized. Typically, at the beginning of the exposure, the resistance is high (~0.2–0.3  $\Omega$ ), but it drops to almost zero within a few seconds, and then the resistance increases to 0.8–2.0  $\Omega$  within 10 min and remains constant for 17 h.

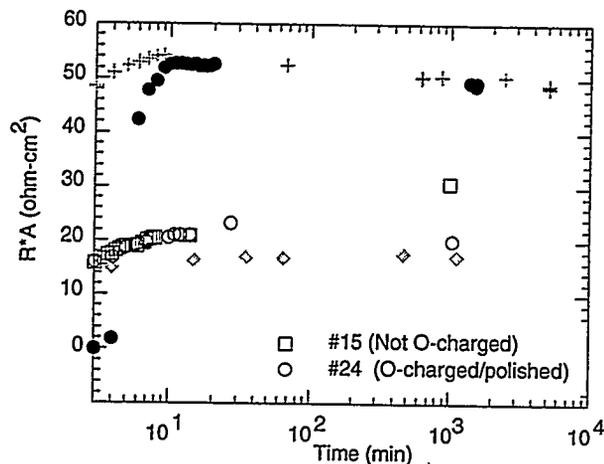


Figure 4.  
R\*A vs. time at 500°C for oxygen-charged V-4Cr-4Ti specimens after exposure in 2 at.% Ca-Li. Cross and diamond symbols denote specimens charged in argon with 10 ppm oxygen, and closed circle denotes specimen charged in argon with 200 ppm oxygen

According to our previous work, we produced in-situ CaO coatings on vanadium-base alloys that contained 250 ppm oxygen during a 7-day exposure in liquid lithium that contained 4 at.% calcium at 700°C.<sup>3</sup> We believe the reaction that forms CaO takes place at the interface between oxygen at the alloy surface and calcium in the liquid metal. The coating did not completely cover the vanadium alloy surface, but a high ohmic resistance, typical of CaO (two-point contact > 20 M $\Omega$  at room temperature), was

obtained. To improve formation of CaO on alloy substrates, oxygen-charged specimens were immersed in calcium-bearing (0.1–50 at.% Ca) liquid lithium for various times at various temperatures. This approach was adopted because oxygen in the alloy (as a reactant) may have a higher affinity for a solute such as calcium dissolved in lithium than for the alloy elements (V, Cr, and Ti). A lower calcium concentration in liquid metal lowers its viscosity.

To confirm the optimal time for calcium deposition at the surface of the oxygen-charged V-4Cr-4Ti specimens in 2 at.%Ca-Li, two samples, i.e., strip samples (140 x 12.7 x 1.0 mm), with and without oxygen-charging, were exposed for 2, 4, 8, and 16 h at 464°C. The sample not charged with oxygen did not form a clear black coating as did the oxygen-charged sample. In the oxygen-charged sample, the black coating layer looked identical for exposures >4 h. This black layer was identified by X-ray diffraction as CaO. In the X-ray spectrum, peaks were mainly attributed to V-4Cr-4Ti, but CaO peaks were also present. In a normal X-ray, beam penetration for CaO and vanadium alloys is  $\approx 40$  and  $\approx 8$   $\mu\text{m}$ , respectively. However, according to the in-situ ohmic resistance (Fig. 4), the thin CaO coating may not be entirely uniform. To conduct gas-phase oxidation, the samples were withdrawn from the liquid and the excess liquid metal was allowed to drip from the samples for 17–72 h.

*CaO coating via gas-phase oxidation.* Liquid-metal exposed samples were oxidized in flowing 200- and 5000-ppm oxygen/argon gas mixtures. To avoid abrupt oxidation during exposure to a high oxygen pressure, high-purity argon gas flowed during heating, and gradually the higher oxygen-bearing argon gas mixture was admitted. Oxidation was conducted at 400 and 650°C for 17 h. A good CaO coating was gray and without cracking or spallation. At room temperature, most samples had infinite ohmic values. X-ray and chemical analyses indicated that the coatings were CaO or Ca-V-O. Currently, we do not have quantitative analytical data for lithium in the CaO layer because of the difficulty in obtaining this information.

*In-situ resistance measurement for CaO coating.* Figure 5 shows in-situ  $R^*A$  vs time for CaO coatings on V-15Cr-5Ti prepared by the present method in lithium that contained 2 at.% calcium, for 700 h at 300–464°C. During in-situ ohmic resistance measurements, we used a DC current of 1–10 nA and observed polarization behavior. When we switch the polarity, the potential drop stabilized within several min at 1 nA, but the response was much faster at 10 nA. The ohmic values were monitored by applying Ohm's law;  $R = V/i$ . When the temperature was increased from 300 to 464°C, the ohmic values decreased only slightly, as shown in Fig. 5. When the sample was removed from the melt after 700 h, we observed a shiny liquid metal coating at the bottom end of the rods, which is indicative of good wetting by the liquid metal. Normally, wetting occurred within  $\approx 2$  min at 250°C.

Six months later, we conducted a similar experiment in the same apparatus. The calcium-lithium alloy was heated above its melting point and then cooled to ambient temperature. The cooling curve had two arrests at 176 and 146°C, which indicate that the dissolved calcium concentration in lithium decreased from 2.0 to 1.4 at.%, based on our previous study.<sup>7</sup> This decrease is caused by oxidation of calcium by impurity oxygen in the argon cover gas and by interaction of calcium with the vanadium-base alloy to form CaO in the previous experiment. Figure 6 shows  $R^*A$  vs. time at 300°C for an oxygen-charged V-4Cr-4Ti specimen and a specimen that was coated previously at 500°C in the liquid metal that contained 2 at.% calcium. After  $\approx 3$  h, the previously coated specimen that exhibited a high ohmic value became conductive because either the concentration of calcium in the liquid metal was too low or the initial CaO layer was too thin ( $\approx 3$   $\mu\text{m}$ ).

*Microstructural analysis.* The specimens were removed from the melt, cleaned in absolute ethanol, and examined by X-ray diffraction and SEM/EDS. Figure 7 shows the concentration of calcium, vanadium,

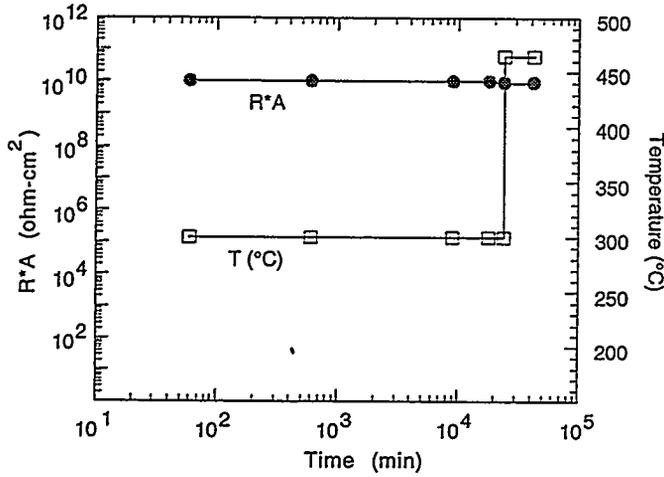


Figure 5. In-situ R\*A (solid symbol) and temperature (open symbol) vs. time for CaO coating on V-15Cr-5Ti

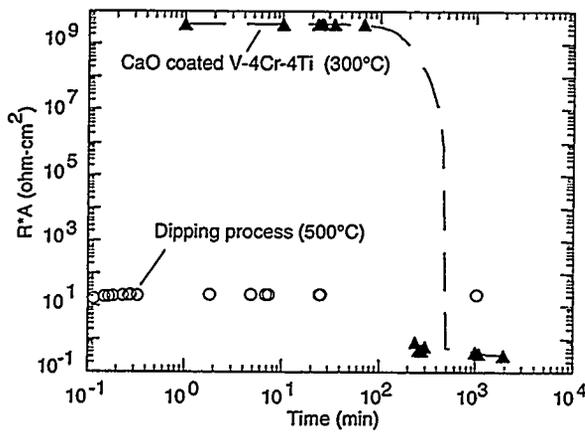


Figure 6. In-situ R\*A vs. time for oxygen-charged (open symbol) and previously coated (closed symbol) V-4Cr-4Ti specimens in lithium with 2 at.% calcium at 300°C

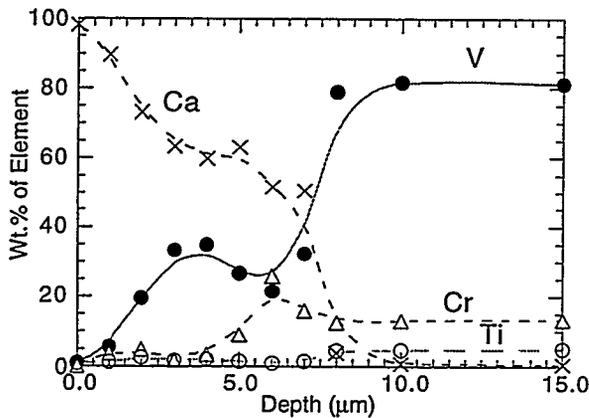


Figure 7. Chemical composition from EDS analysis vs. depth for CaO/V-15Cr-5Ti specimen after exposure to lithium with 2 at.% calcium for 700 h at 300-464°C

titanium, and chromium as a function of depth from the liquid/alloy interface obtained by EDS analysis of the cross section of a CaO-coated V-15Cr-5Ti specimen after exposure to lithium that contained 2 at.% calcium, for 700 h at 300-464°C. SEM photomicrographs of the cross section revealed a crack-free layer 7-8 μm thick. Table 1 shows the characteristics of this coating and a coating produced in lithium that contained 50 at.% calcium.

Table 1. Characteristics of CaO coatings produced on V-(4, 5, and 15)Cr-(4 and 5)Ti in liquid lithium that contained 2 and 50 at.% calcium

Liquid metal composition	2 at.% Ca-Li	50 at.% Ca-Li <sup>a</sup>
Microcracks in CaO layer	None	Crazing cracks
V concentration in CaO layer	≈35 at.% (center)	<2 at. %
Thickness of CaO layer	7-8 μm (2 at.% Ca); 3 μm (1.4 at.% Ca)	10-14 μm
Stability of CaO layer in liquid Li	Good, ≈8 μm Poor, ≈4 μm	Good

<sup>a</sup>Data from Ref. 6.

Figure 8 shows the Vickers hardness as a function of depth for a CaO/V-15Cr-5Ti specimen. The CaO layer on the oxygen-charged specimen is much harder ( $\sim 780 \text{ kg/mm}^2$ ) than the surface region of several V-4Cr-4Ti specimens that were exposed to argon containing 10 ppm oxygen for 17 h at 650°C (Fig. 3). Visual examination of the surface of the CaO coating indicated no microcracks or spallation of the layer.

The coefficient of thermal expansion of CaO is higher than that of V-Cr-Ti alloys ( $12 \times 10^{-6}$  vs.  $9.2 \times 10^{-6}/\text{K}$ ). Therefore, a CaO layer that forms in-situ on a vanadium alloy will be subjected to a tensile stress during cooling. Photomicrographs of CaO coatings on V-15Cr-5Ti did not show any cracks. However, CaO coatings that were produced in lithium containing higher calcium concentrations revealed a network of microcracks that consisted of regions  $\approx 30\text{--}40 \text{ μm}$  in diameter separated by narrow cracks,  $\approx 2000 \text{ Å}$  in width, over most of the CaO surface. This suggests that the cracks originate from a mismatch of the thermal expansion coefficients during cooling, i.e., they are "crazing cracks." 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-Cr-Ti alloy substrates. However, if the coating is too thin, it may not be stable in liquid lithium containing 2 at.% calcium. In this study, the incorporation of vanadium in the CaO layer produces a somewhat thicker but adherent coating.

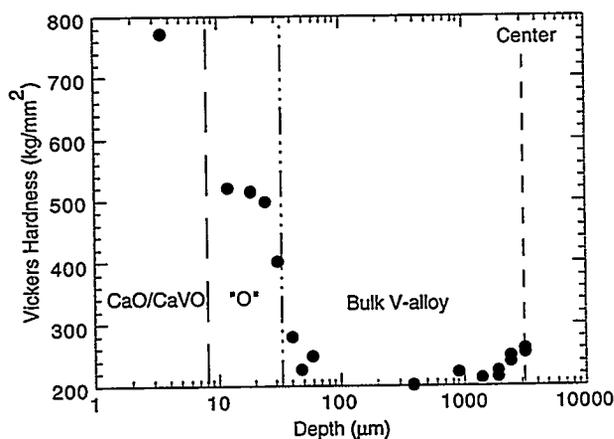


Figure 8.  
Vickers hardness vs. depth for CaO/V-15Cr-5Ti specimen after exposure to lithium with 2 at.% calcium for 700 h at 300-464°C

## FUTURE WORK

The performance of a CaO coating on the inner surface of a vanadium alloy tube will be evaluated after an MHD pressure-drop test on the tube.

## 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, *Fusion Engineering and Design* 27 (1995) 682-695.
- [4] J.-H. Park and T. F. Kassner, CaO Insulator Coating and Self-Healing of Defects on a V-Cr-Ti Alloys in Liquid Lithium System, *J. Nucl. Mater.*, to be published (1996).
- [5] A. U. Seybolt and H. T. Sumsion, Vanadium-Oxygen Solid Solutions, *Met. Trans. AIME*, 292-299 (1953).
- [6] J.-H. Park, D. Kupperman, and E. T. Park, Mechanical Properties of V-Cr-Ti-(O and N) Solid Solutions, Submitted to *Acta Materialia* (1996).
- [7] J.-H. Park and T. F. Kassner, Selection of a Liquid Calcium-Lithium Alloy for Fabricating CaO Insulator Coatings on V-5%Cr-5%Ti, Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1995, DOE/ER-0313/18, pp. 347-351 (July 1995).