

An In-situ Calcium Oxide Coating on Vanadium Alloys in Liquid Lithium-Calcium*

J.-H. Park, K. Natesan, and D. L. Smith (Argonne National Laboratory)

OBJECTIVE

The objective of this task is to develop in-situ stable coatings at the liquid metal/structural-materials interface in a fusion device, with emphasis on coatings that can be converted to an electrically insulating film to prevent adverse currents generated by the magnetohydrodynamic force from passing through the structural walls. The thermodynamics and kinetics of oxygen and calcium interactions in the vanadium alloy/lithium system are being investigated to define the system parameters required for in-situ formation of a CaO coating on vanadium alloys. In addition, other potential coating candidates, such as Y_2O_3 and AlN, are being examined.

SUMMARY

Calcium oxide coatings were produced on oxygen-charged vanadium alloys (V, V-10Cr, V-1Ti, V-4Cr-4Ti, and V-5Cr-5Ti) by exposure to liquid Li that contained 2.8 at.% Ca. The thickness of in-situ-formed CaO layers was larger in the samples with higher oxygen charging. In the experimental conditions used, the thickness of the grown CaO films was 8-30 μm . For the CaO coating on V-4Cr-4Ti, the measured ex-situ dc-electrical conductivity was 3.0×10^{-10} to 1.0×10^{-8} $\text{ohm}^{-1}\text{cm}^{-1}$ in an Ar environment in the temperature range 200-500°C.

INTRODUCTION

One of the most challenging areas for magnetic fusion reactors (MFR) is developing plasma-facing systems that can withstand high surface heat fluxes and neutron wall loads. Several electrically insulating oxides, such as binary oxides (CaO, BeO, MgO, Y_2O_3), ternary perovskite (CaZrO_3), spinel (MgAl_2O_4), and nitrides (AlN), have promise as coatings on a V alloy for application in liquid-lithium MFR-blanket systems. We have chosen the development of in-situ CaO film deposition on the vanadium alloys for the following reasons: CaO is thermodynamically stable in liquid Li, has the highest electrical resistivity desirable for a thin film, forms in-situ, and has potential for healing of defects (microcracks, open pores, etc.)^{1,2} Based on its high thermodynamic stability, CaO can be formed in-situ to heal most of the defects in the insulator coatings that may arise in service.

The main reaction can be stated as $\text{Ca} + \text{O} = \text{CaO}$, where Ca dissolves in liquid Li and then reacts with O near the surface of V alloys to form CaO. The CaO layer grows based on the inward ambipolar diffusion of Ca^{2+} ion and the two electrons through the CaO layer to react with the O in the V alloys at the CaO/V interface. The O accepts two electrons to form O^{2-} ions, and reacts with Ca^{2+} ions to form CaO. As a result, the CaO layer is dynamically adhesive, and O levels decrease in the V alloys. It is expected that the reaction rate of will increase under neutron fluency. Additionally, CaO has low activation with neutron bombardment. Both Li and Ca-Li as liquid metals do not interact heavily with V alloys.

The present study involves in-situ CaO film fabrication at 600 and 700°C in 2.8 at.% Ca-Li on vanadium metal and the alloys V-10Cr, V-1Ti, V-4Cr-4Ti, and V-5Cr-5Ti. We have investigated step-by-step procedures for O charging and homogenization, and determined O-migration profiles before and after Ca-Li exposure in O-charged V alloys. This reporting period our work focused on the V-4Cr-4Ti alloy with CaO coating.

EXPERIMENTAL DETAILS

Samples of V-4Cr-4Ti were prepared in a rectangular shape (2 x 1 x 0.1 cm) with a 1 mm-diameter hole for the attachment. Samples were vacuum-annealed at 1000°C for 2 h, then heated at 710°C in Ar-O₂ to reach a proper amount of O charge, then O homogenized in a vacuum-sealed (quartz) cell for 17 h at 750°C. Details are given in our previous reports.¹⁻³

Several samples were arrayed together, then dipped into a Ca-Li vessel at 600°C for times between 50 and 747.5 h. The sample tree was raised above the liquid-Ca-Li level and shaken to minimize residual Ca-Li around the samples. The excessive Ca-Li was dissolved in methanol to investigate the surface and cross section by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS). Ex-situ electrical conductivity measurements were performed for the samples exposed in 2.8 at.% Ca-Li after removal of the residual Ca-Li around the sample in the alcohol. For these measurements, metallic gallium was used as electrodes on two platinum discs in the top and bottom positions (see Fig. 1). Liquid gallium on the coating was not wet at room temperature, but the gallium was well adhered on the platinum discs for the electrical conductivity measurement. However, when the CaO-coated V alloys were placed between two gallium electrodes and a spring load applied, the excessive gallium extruded out around the sample-platinum edge. This excess gallium was removed before the entire stack was inserted into the measuring assembly. The electrical conductivity measurements were performed in 99.996% Ar at 25°C ≤ T ≤ 500°C, and the supplied current, *i*, was ≤ 1 x 10⁻⁶ A. Our instrumentation limit was an input impedance of 1 M-ohm and voltage range of 10 V.

DISCUSSION

During O charging, a blue surface layer of thin vanadium oxide appeared. However, with O homogenization, the sample surface became shiny metallic looking. It can be assumed that surface oxygen entered into the V alloy by solid-state diffusion. For the EDS analysis, O in the V-alloy system causes a problem if the vanadium (or Ti and Cr) concentration is too high. Since the oxygen k-energy level and the V-(Cr-Ti) l-energy level are too close for separation in the EDS analysis, determination of O is possible only when the vanadium concentration is low in comparison with oxygen. In the near future, we plan O analysis of the V alloy by secondary ion mass spectroscopy (SIMS).

According to cross-sectional EDS analysis and SEM photomicrographs, the thickness of the adhered CaO layer formed at 600°C for 120 h on V-4Cr-4Ti alloy is 8 μm. The SEM view and back-scattered electron image revealed a uniform thickness of the in-situ-formed CaO film on the V alloy. While performing the EDS analysis, we found that the interface area had a somewhat higher O concentration than that in the overall CaO layer. This higher O concentration is quite understandable because calcium reacts with the oxygen provided by the V alloy. This trend is promising for in-situ formation of CaO layers on the V alloys because the higher O concentrations mean that higher electrical resistivity is expected.

Figure 2 shows the XRD patterns for (a) physical vapor deposition (PVD) of CaO on O-charged V-4Cr-4Ti and in-situ formation of CaO on (b) V-4Cr-4Ti at 700°C for 50 h, (c) V-1Ti at 600°C for 120 h, and (d) V-5Cr-5Ti at 600°C for 120 h, (For items b-d, the O-charged V alloys were exposed to molten 2.8 at.% Ca-Li.) The results indicate that the PVD CaO coating is generally pure CaO, whereas the in-situ CaO coatings are structurally not similar to that developed by PVD, irrespective of the substrate composition. Presumably, an amorphous CaO film was formed in-situ in the liquid Li-Ca environment. Additional ongoing effort will examine the causes for this difference.

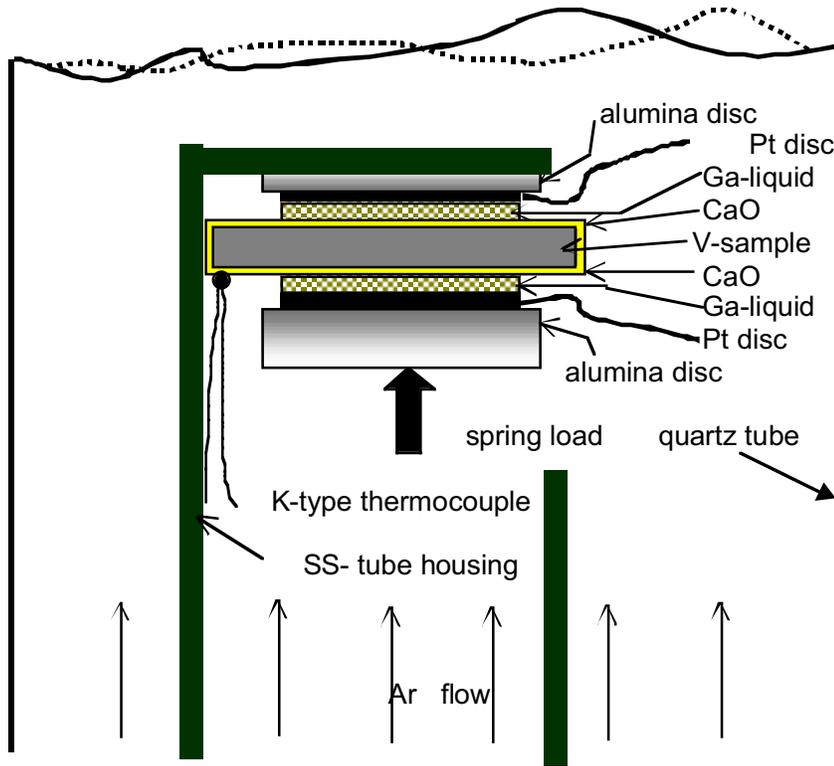


Fig. 1. Experimental setup used for resistance measurements on in-situ CaO coatings.

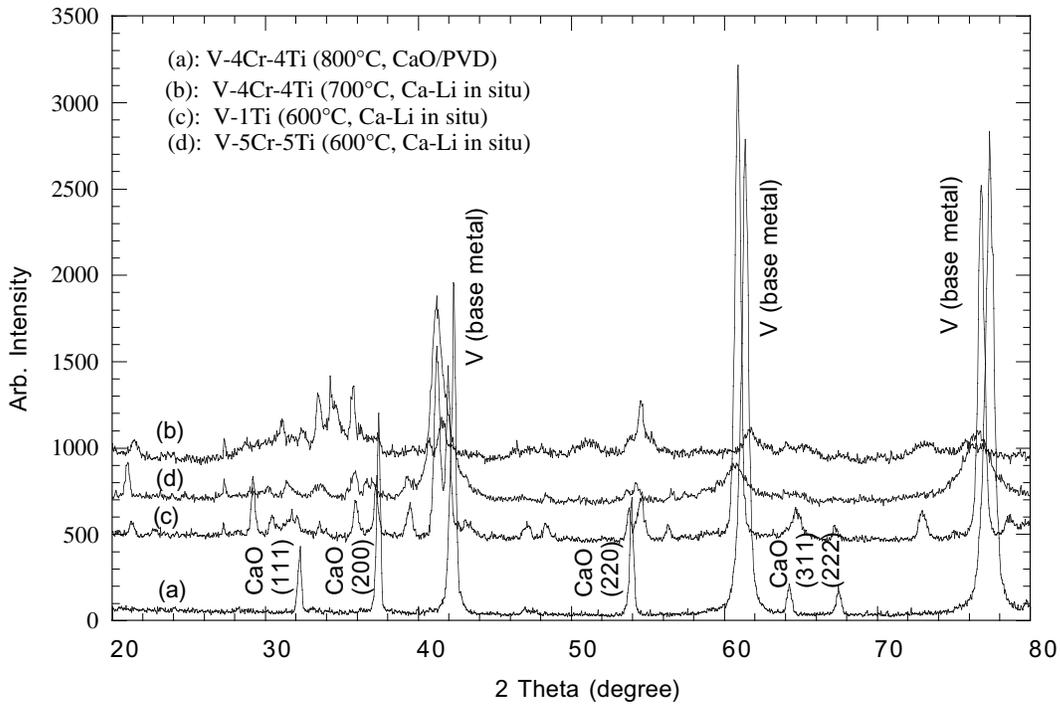


Fig. 2 XRD patterns for (a) PVD/CaO on O-charged V-4Cr-4Ti, and in-situ CaO on (b) V-4Cr-4Ti at 700°C for 50 h, (c) V-1Ti at 600°C for 120 h, and (d) V-5Cr-5Ti at 600°C for 120 h. For patterns b-d, the O-charged V alloys were exposed in-situ to 2.8 at.% Ca-Li.

The in-situ grown film contains Li based on our previous SIMS work. Lithium is oxidized when exposed to oxygen, carbon dioxide, or moisture by the reaction, $2\text{Li} + 1/2 \text{O}_2 = \text{Li}_2\text{O}$, $2\text{Li} + 1/2\text{O}_2 + \text{CO}_2 = \text{Li}_2\text{CO}_3$, or $2\text{Li} + 1/2 \text{O}_2 + \text{H}_2\text{O} = 2\text{LiOH}$, respectively. The generated Li ion is highly mobile in the solid state. Therefore, the Li ion under an electric field becomes very sensitive to field polarity and will be polarized through the film layer. When polarized, the Li makes an open circuit and follows a strong dc dry-battery behavior. Figure 3a shows the polarization behavior for a switching polarity with 10-s intervals. Figure 3b shows the temperature and iR-drop (dc $i = \pm 1 \mu\text{A}$) potential monitored as a function of time during the conductivity measurement of the CaO coating on oxygen-charged V-4Cr-4Ti.

Figure 4 shows the electrical conductivity and resistivity vs. reciprocal temperature for the sample prepared initially from oxygen charged V-4Cr-4Ti, followed by exposure to 2.8 at.% Ca-Li at 600°C for 50 h. These measurements were made after the excess Ca-Li had been dissolved from the CaO-coated samples using gallium metallic electrodes supplying a switching polarity of 1 μA (dc) in flowing 99.996% Ar. Figure 5 shows the measured dc-electrical conductivity for the CaO coating along with literature data. The electrical conductivity measured in an Ar environment at temperatures of 200-500°C ranged from 3.0×10^{-10} to $1.0 \times 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ for the in-situ CaO coating on V-4Cr-4Ti, and these values are comparable with earlier data.^{5,6}

FUTURE DIRECTIONS

Planned future activities include the following:

1. In-situ electrical resistance measurements on the in-situ CaO coatings in a Li-Ca environment.
2. Development and characterization of other insulator coating candidates, such as Y_2O_3 , and AlN.

CONCLUSIONS

In-situ CaO coatings were produced on oxygen-charged V-4Cr-4Ti alloy by exposure of the alloy to liquid Li that contained 2.8 at.% Ca. The adhered CaO layer was 8 μm . The dc-electrical conductivity of the coating measured in an Ar environment in the temperature range of 200-500°C was 3.0×10^{-10} to $1.0 \times 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$.

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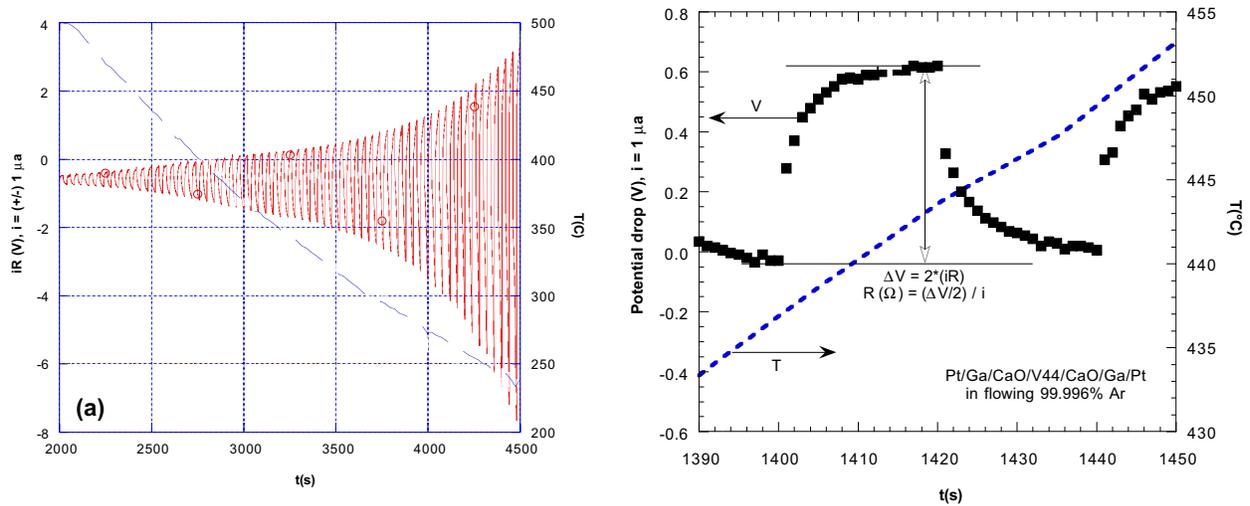


Fig. 3. Temperature and iR-drop potential monitored as a function of time during conductivity measurement for the O-charged V-4Cr-4Ti with CaO coating.

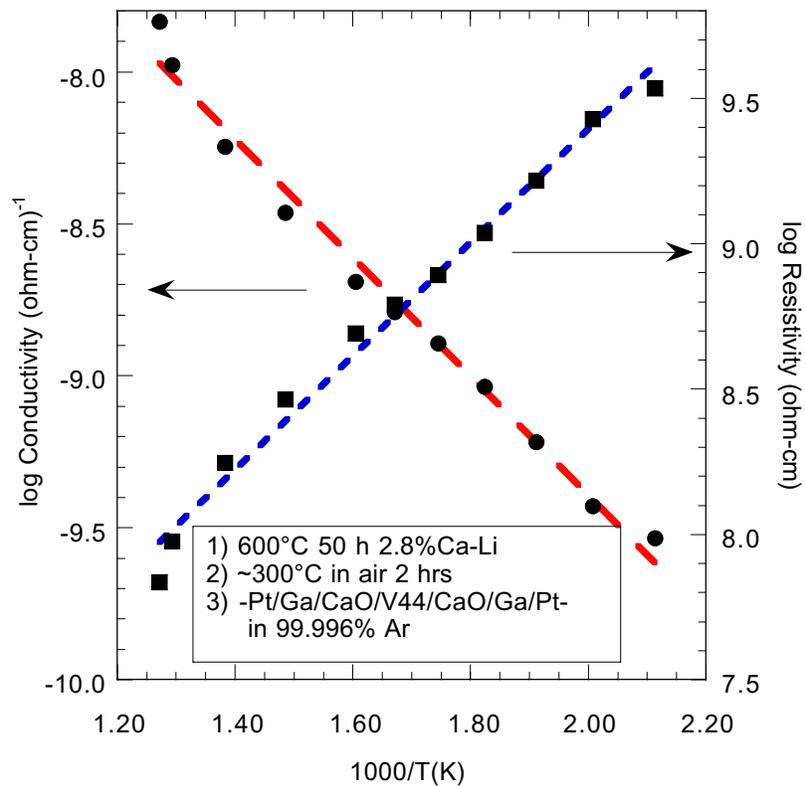


Fig. 4. Electrical conductivity and resistivity vs. $1000/T$ for the O-charged V-4Cr-4Ti after exposure in 2.8 at.% Ca-Li at 600°C for 50 h.

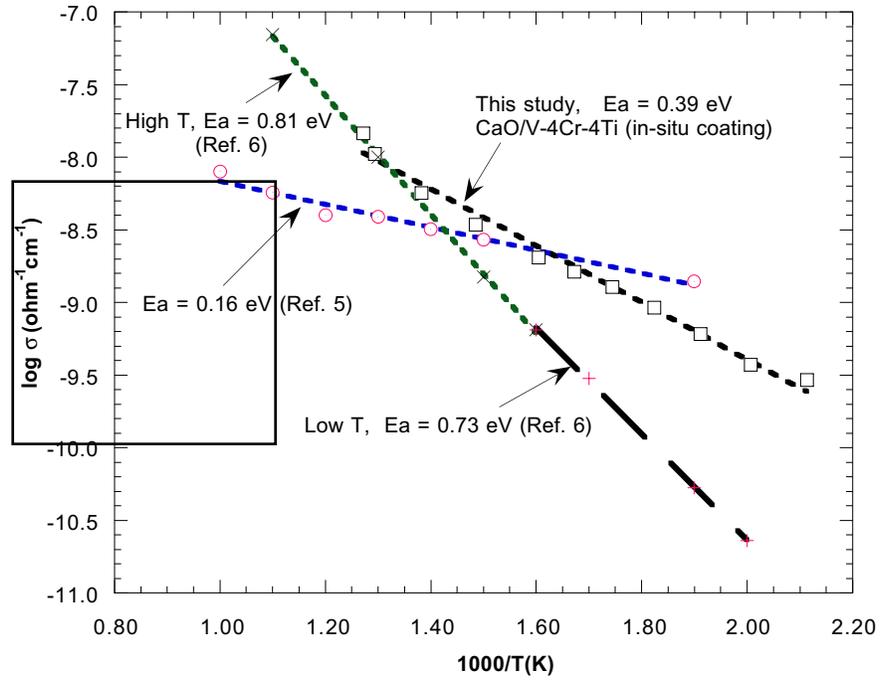


Fig. 5. Temperature dependence of electrical conductivity of in-situ CaO coating along with data on bulk CaO from literature (E_a = activation energy).