

## EVALUATING ELECTRICALLY INSULATING FILMS DEPOSITED ON V-4%Cr-4%Ti BY REACTIVE CVD\* J.-H. Park and W. D. Cho (Argonne National Laboratory)

### OBJECTIVE

Corrosion resistance of structural materials and magnetohydrodynamic 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 evaluate electrically insulating films that were deposited on V-4%Cr-4%Ti by a reactive chemical vapor deposition (CVD) method.

### SUMMARY

Previous CaO coatings on V-4%Cr-4%Ti exhibited high-ohmic insulator behavior even though a small amount of vanadium from the alloy was incorporated in the coating. However, when the vanadium concentration in the coating is  $> 15$  wt.%, the coating becomes conductive. When the vanadium concentration is high in localized areas, a calcium vanadate phase that exhibits semiconductor behavior can form. To explore this situation, CaO and Ca-V-O coatings were produced on vanadium alloys by chemical vapor deposition (CVD) and by a metallic-vapor process to investigate the electrical resistance of the coatings. Initially, the vanadium alloy specimens were either charged with oxygen in argon that contained trace levels of oxygen, or oxidized for 1.5-3 h in a 1% CO-CO<sub>2</sub> gas mixture or in air to form vanadium oxide at 625-650°C. Most of the specimens were exposed to calcium vapor at 800-850°C. Initial and final weights were obtained to monitor each step, and surveillance samples were removed for examination by optical and scanning electron microscopy and electron-energy-dispersive and X-ray diffraction analysis; the electrical resistivity was also measured. We found that Ca-V-O films exhibited insulator behavior when the ratio of calcium concentration to vanadium concentration  $R$  in the film was  $> 0.9$ , and semiconductor or conductor behavior for  $R < 0.8$ . However, in some cases, semiconductor behavior was observed when CaO-coated samples with  $R > 0.98$  were exposed in liquid lithium. Based on these studies, we conclude that semiconductor behavior occurs if a conductive calcium vanadate phase is present in localized regions in the CaO coating.

### INTRODUCTION

Corrosion resistance of structural materials and magnetohydrodynamic (MHD) forces and their influence on thermal hydraulics are major concerns in the design of a liquid-metal cooling system for a first-wall/blanket in a magnetic fusion reactor (MFR).<sup>1,2</sup> Vanadium-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in fusion reactors.<sup>3</sup> The objective of this study is to develop stable, corrosion-resistant coatings, as well as insulator coatings, at the liquid-metal/structural-material interface. Previous studies focused on in-situ formation of AlN on as-received and prealuminided vanadium alloys in liquid-lithium environments.<sup>4,5</sup> Subsequent work addressed in-situ formation of CaO in a liquid-lithium environment because the electrical resistivity of CaO is 10,000 times greater than that of AlN, and because, among the available insulator candidates (i.e., CaO, Y<sub>2</sub>O<sub>3</sub>, BeO, MgO, MgAl<sub>2</sub>O<sub>4</sub>, Y<sub>3</sub>Al<sub>2</sub>O<sub>12</sub>, etc.), CaO exhibits high thermodynamic stability in liquid lithium.<sup>5,6</sup>

The coatings should be formable on various shapes, such as the inside of tubes or irregular shapes, to prevent adverse currents generated by MHD forces from passing through the structural walls. The coatings could also improve general corrosion resistance and act as a diffusion barrier for hydrogen isotopes, i.e., deuterium and tritium. Based on our previous work, CaO coatings on V-4%Cr-4%Ti exhibited high-ohmic-insulator characteristics even when a small amount of vanadium was incorporated in the CaO. However, the coating becomes conductive when the vanadium concentration is  $> 15$  wt.%.

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We hypothesize that, despite the highly resistive nature of CaO, when vanadium is incorporated in the material a calcium vanadate phase that exhibits semiconductor behavior forms in local regions. To explore this hypothesis, CaO and Ca-V-O coatings were produced on vanadium-base alloys by chemical vapor deposition (CVD) and metallic-vapor processes to investigate their electrical behavior. In some cases, when CaO-coated samples were exposed in liquid lithium, semiconductor behavior was observed and we sought the reason for this phenomenon.

### Synthesis of Ca-Vanadates by Self-Ignition Reaction

To examine the electrical behavior of CaO-V<sub>x</sub>O<sub>y</sub> specimens, several calcium vanadates were synthesized by a self-reactive method. Calcium and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) were mixed in various proportions (5-90 wt.% of calcium) and allowed to react in vacuo by self-ignition in sealed quartz capsules in response to heating with a hydrogen-flame torch, and in a Type 304 stainless steel (SS) tube in response to heating in a furnace. An exothermic reaction occurred in only ≈2 s. The synthesized samples were examined by scanning electron microscopy/electron dispersive spectroscopy (SEM/EDS), and electrical resistance was determined. All samples fabricated by these methods were conductive and the results were similar to those of F. Iga and Y. Nishihara,<sup>7</sup> except for single-phase CaO, which showed high resistance.<sup>5</sup> The results indicate that calcium vanadates do not provide sufficient electrical resistance for insulator coatings in MFR applications.

### High-Temperature Metallic Vapor Deposition of CaO and Calcium Vanadate Coatings

Solid-state interactions between calcium vapor and oxygen-charged V-4%Cr-4%Ti were investigated. An as-received V-4%Cr-4%Ti sheet was cut into 12.7 x 12.7 x 1.0-mm and 9.4 x 9.4 x 1.0-mm specimens and then ultrasonically cleaned in isopropyl alcohol; the specimens were used for electrical resistance and weight-gain measurements, respectively. The near-surface region of the specimens was charged with oxygen by heating the specimens for 2-3 h in argon (99.999% pure with 5-10 ppm oxygen), or in a 1% CO-CO<sub>2</sub> gas mixture or air to form vanadium oxide at 625 to 650°C. The specimens were placed above a calcium vapor source in a Knudsen sublimation cell that was contained in a Type 304 SS chamber surrounded by a furnace (Fig. 1). A detailed description of the apparatus and method of preparation of oxygen-charged vanadium alloys was described in Ref. 8.

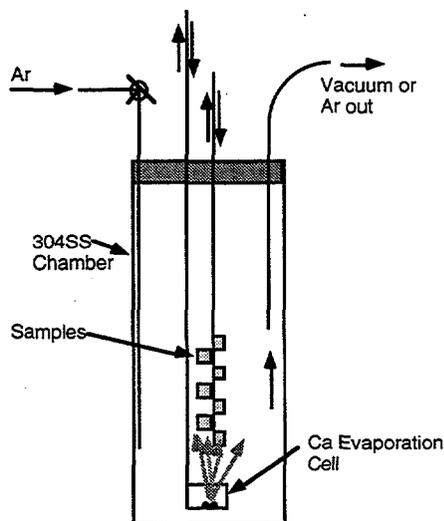


Figure 1.  
Schematic diagram of CVD apparatus

In another apparatus, a Type 304 SS chamber was heated from 25 to 850°C within ≈1 h while purging with 99.999% argon; it was then cooled. Vanadium-alloy samples and a calcium source vessel were then placed

near the bottom and top of the chamber, respectively. The calcium source at the top of the furnace remained at room temperature when the furnace was heated. The vanadium alloy specimens in these experiments were either charged with oxygen for 2–3 h in argon that contained 5–10 ppm oxygen or oxidized in air to form vanadium oxide. Several specimens were retained to quantify oxygen uptake by the specimens during the oxygen-charging step. Subsequently, the stainless steel chamber was evacuated with a vacuum pump and the calcium reservoir was lowered into the hot zone of the furnace to evaporate calcium, which deposited on and reacted with the oxygen-charged and oxidized vanadium alloy surfaces at 800–850°C for 1.5–4 h. The formation of several vanadates ( $\text{Ca-V}_x\text{O}_y$ ) can be predicted from the CaO–vanadium oxide phase diagram.<sup>9</sup> These phase relationships are the basis for the formation of vanadate coatings on vanadium and its alloys. Calcium reacts with the oxygen-precharged surface and diffuses through the CaO or  $\text{Ca-V}_x\text{O}_y$  layer, as shown in Fig. 2. Reactions for the formation of the coatings are



where  $\underline{Q}$  represents the oxygen activity at the interface between CaO and oxygen-charged vanadium alloy. These reactions occur spontaneously, and the rate-determining step most likely is ionic diffusion ( $\text{Ca}^{+2}$ ) through the CaO layer.

EDS analysis of the surface of a CaO coating formed on V-4%Cr-4%Ti at 850°C indicated >97 at.% calcium, and the calcium vanadate coatings contained 15–80 at.% calcium. SEM of CVD coatings on V-4%Cr-4%Ti at 850°C revealed uniform surfaces with grain sizes of 0.7–3  $\mu\text{m}$  for CaO and 3–8  $\mu\text{m}$  for the calcium vanadate coatings. The X-ray diffraction spectrum of the CaO coating on V-4%Cr-4%Ti clearly showed the two sets of peaks for CaO and V-4%Cr-4%Ti and indicated no other phases. The X-ray beam can penetrate  $\approx 40 \mu\text{m}$  into CaO, and into a film thickness of  $\approx 3 \mu\text{m}$ ; the spectrum of the V-4%Cr-4%Ti substrate is also present.

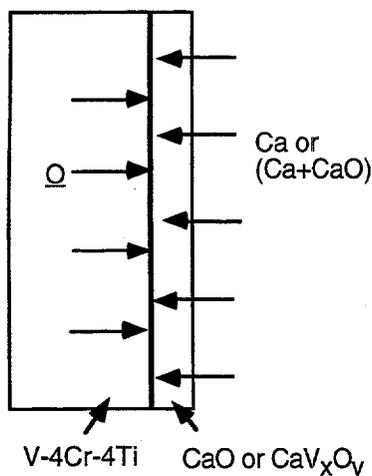


Figure 2.  
Schematic diagram of solid-state reaction steps  
at V-4Cr-4Ti/CaO interface:  $\text{Ca} + \underline{Q} = \text{CaO}$ :  
initial reaction

Sublimation of calcium in a relatively low vacuum of  $10^{-4}$ – $10^{-5}$  torr, in which oxygen was present as an impurity, enabled the formation of CaO clusters by oxidation of calcium vapor inside the chamber. After coating the V-4%Cr-4%Ti specimens at 800 or 850°C for electrical resistance measurements, the system was cooled to room temperature while purging with 99.999% argon. In one experiment, the calcium reservoir was raised to the top of the furnace (cool region) and the specimens remained at temperature for 3–5 h to determine if any additional oxidation occurred. No appreciable weight gain or loss was detected after CaO had been deposited. The weight gain for CaO coatings on V-4%Cr-4%Ti specimens at 230 min ( $\approx 4$  h) was determined over the range of 309–883°C and is given by

$$\log (\text{Wt. gain, g/cm}^2) = -0.983 - 2444/T (\text{K}), \quad (3)$$

which corresponds to coating thicknesses between  $\approx 0.02$  and  $2.4 \mu\text{m}$  at  $309\text{--}883^\circ\text{C}$  for a CaO density of  $3.346 \text{ gm/cm}^2$ .

To determine the electrical resistance of the coatings and also facilitate SEM/EDS analysis, the samples were coated with gold by sputter-deposition of an array of  $\approx 1\text{-mm}$ -diameter discs on the surface of the coatings (Fig. 3). The discs, when placed in contact with a gold foil, provided a good electrical connection over a large area of the specimen. Ohmic resistance was measured at  $25\text{--}500^\circ\text{C}$  in air (Fig. 4). Only the specimen charged with oxygen in 99.999% argon and coated with calcium by CVD exhibited insulator behavior. The specimens oxidized in air and in a 1% CO-CO<sub>2</sub> gas mixture and coated by CVD showed semiconductor behavior.

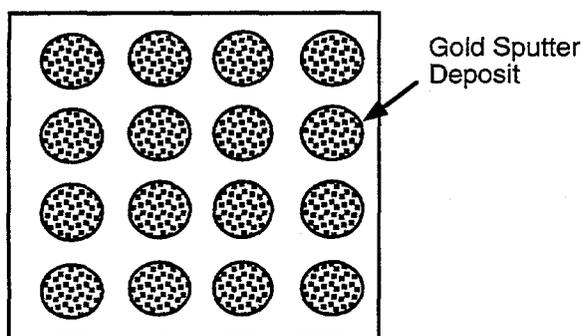


Figure 3.  
Schematic diagram of gold sputter coating on CaO coating for electrical resistivity measurements

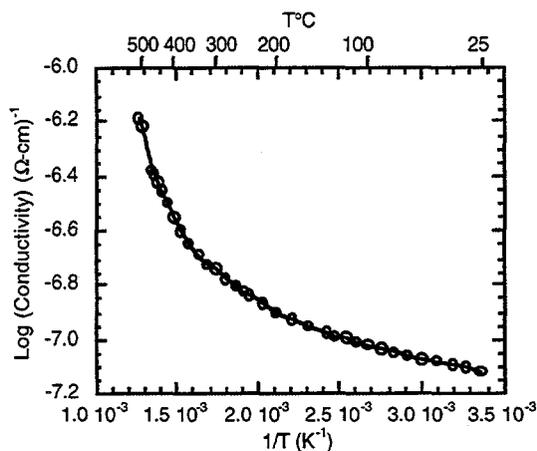


Figure 4.  
Log (conductivity) vs.  $1/T$  for the CaO coating in air

## CONCLUSIONS

CaO and calcium vanadate films were prepared on vanadium alloys and Types 304 and 316 SS by chemical vapor deposition (CVD) and high-temperature metallic-vapor deposition at  $800\text{--}850^\circ\text{C}$ . The films were examined by optical and scanning electron microscopy and by electron-energy-dispersive and X-ray diffraction analysis. We found that when the ratio of calcium to vanadium in the oxide coating was  $>0.9$ , the film was a good insulator, whereas when the ratio was  $<0.8$ , the coating layer exhibited semiconductor or metallic-conduction behavior. However, in some cases, when a CaO-coated sample was immersed in liquid lithium, semiconductor behavior was observed even though the calcium/vanadium ratio was  $>0.98$  for

a wide surface area. We attribute semiconductor behavior to local regions that contained a conductive calcium vanadate phase in the CaO coating.

The formation of either vanadate or titanate phases in thin (1–5  $\mu\text{m}$ ) coatings may not provide sufficient electrical resistance for magnetic fusion reactor (MFR) applications and could present potential problems regarding liquid–metal compatibility.

We believe that the oxygen charging and reactive CVD technique can be extended to other oxides, e.g., MgO, BeO,  $\text{MgAl}_2\text{O}_4$ ,  $\text{Y}_3\text{Al}_2\text{O}_{12}$ , etc., to determine whether they are suitable for insulator coatings in MFR applications.

#### SUGGESTED FUTURE WORK

Several other ternary oxide systems (e.g., spinel,  $\text{MgAl}_2\text{O}_4$ ; and/or garnet,  $\text{Y}_3\text{Al}_2\text{O}_{12}$ ) could be fabricated by the reactive CVD method and their insulator characteristics could be evaluated before and after exposure to liquid lithium.

CaO films on vanadium–base alloys could be fabricated by oxygen charging with nitrogen–argon gas mixtures to minimize the formation of calcium vanadates. These environments may suppress outward diffusion of vanadium during CaO film formation because of the presence VN or TiN phases. In-situ electrical resistivity should be measured to assess the potential of this approach.

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