Fabrication of Intermetallic Coatings for Electrical and Corrosion Resistance on High-Temperature Alloys*

J.-H. Park
Energy Technology Division
Argonne National Laboratory, Argonne, IL 60439

W. D. Cho
Department of Metallurgical Engineering
University of Utah, Salt Lake City, UT 84112

October 1994

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Manuscript submitted for publication in TMS-AIME Conference on Coating Substrate Integrity of High-Temperature Components, TMS annual meeting, February 12-16, 1995, Las Vegas, NV

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

*This work has been supported by the U.S. Department of Energy, under Contract W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Several intermetallic films were fabricated to high-temperature alloys (V-alloys and 304 and 316 stainless steels) to provide electrical insulation and corrosion resistance. Alloy grain-growth behavior at 1000°C for the V-5Cr-5Ti was investigated to determine the stability of alloy substrate during coating formation by chemical vapor deposition (CVD) or metallic vapor processes at 800-850°C. Film layers were examined by optical and scanning electron microscopy and by electron-energy-dispersive and X-ray diffraction analysis and tested for electrical resistivity and corrosion resistance. The results elucidated the nature of the coatings, which provided both electrical insulation and high-temperature corrosion protection.
Introduction

Corrosion resistance of structural materials and magnetohydrodynamic (MHD) force and its influence on thermal hydraulics are major concerns in the design of liquid-metal cooling system for a first-wall/blanket in a magnetic fusion reactor (MFR).1,2 Vanadium and V-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in a fusion reactor.3 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 V-alloys in liquid-Li environments.4,5 Subsequent work addressed in-situ formation of CaO in a liquid-Li environment because the electrical resistivity of CaO is 10,000 times higher than that of AlN, and CaO has a high thermodynamic stability in liquid Li among the available insulator candidates (i.e., CaO, Y_2O_3, BeO, MgO, MgAl_2O_4, Y_3Al_2O_12, etc.).5-7 The electrically insulating coatings should be capable of forming on various shapes such as the inside of tubes or irregular shapes during operational conditions to prevent adverse currents that are 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, viz., deuterium and tritium.

Approaches for insulator coating development

Several experimental steps were employed to develop insulator coatings on vanadium based alloys: namely, (a) screening of selected electrical insulators in liquid Li based on thermodynamic stability, electrical resistivity, coefficients of thermal expansion (CTE), and diffusion coefficients of cations and anions within the coating layer; (b) liquid-Li compatibility tests for candidate electrical
Solid-state interactions: bonding of AlN and metal/alloy substrates

Solid-state interactions between AlN and several metals and alloys (viz., V, V-5%Cr-5%Ti, Ti, and Type 316 stainless steel) were investigated. Sintered discs of Y$_2$O$_3$-enriched AlN (12.7 x 50 x 9 mm) were obtained from the Ceramic Section in Argonne National Laboratory. ICP-spectrochemical analysis of the AlN samples indicated the following composition (in wt.%): As <0.05, Ba = 0.005, Be <0.001, Ca = 0.54, Co <0.002, Cr <0.002, Cu = 0.006, Fe = 0.015, Y = 3.77, Y$_2$O$_3$ = 4.79, Mg = 0.004, Mn < 0.001, Ni = 0.002, Pb < 0.02, Sb < 0.05, Sn <0.02, Sr <0.001, Ti = 0.022, V <0.002, Zn <0.002, Zr < 0.002, and Te <0.05. The discs were cut into pieces of ~12.7 x 12.7 x 2.7 mm and ground flat on Struers™ 4000 silicon carbide paper. The discs were then ultrasonically cleaned in isopropyl alcohol. An disc of each metal or alloy was placed between two AlN discs and the entire stack was placed in a furnace. A compressive force was applied to the stack by using a 120°-three-spring-loaded- alumina rod on the top of the stack. A detailed description of the apparatus is reported elsewhere. The AlN/alloy stack was annealed in a furnace at 900°C for 129 h in flowing 3%H$_2$–N$_2$. After cooling, the specimen stack was examined for indications of strong bonding between AlN/alloy substrates. Interfaces between the alloys and AlN were examined by SEM/EDS to determine diffusion profiles of various elements. Results for the diffusion couples are as follows.
**V/AlN:** V diffused into AlN, but a bond was not formed and VN was not detected. The absence of a good bond and no interdiffusion of N are not conducive to the development of an adherent coating by a high-temperature process. In this case, a low-temperature physical vapor deposition (PVD) technique could be tried, but if the temperature of operation increases or the service time is very long, the base metal (V) could be degraded by formation of vacancies at the metal/AlN interface, grain-boundaries, and dislocations. Eventually, vacancies would coagulate to form voids within the V substrate, which could lead to debonding of the coating.

**Ti/AlN:** Ti did not bond with AlN but a thin layer formed at the Ti/AlN interface. This is indicative of a TixNy phase and some diffusion of N into Ti was evident. Bonding of AlN/TixNy exhibited sintering-like behavior; however, TixNy was detached from Ti in some areas, which indicates outward diffusion Ti during formation of TixNy. These processes are shown in Fig. 1.

**V-5Cr-5Ti/AlN:** Neither V, Ti, or the V alloy bonded with AlN. Minimal information was obtained from this couple because no bonding occurred. Coarsening of grains in V-5Cr-5Ti at the alloy/AlN interface was observed, which may have been accelerated by applied pressure.

**Type 316 stainless steel/AlN:** Reaction occurred between a thin oxide scale (Cr$_2$O$_3$) on the Type 316 stainless steel and AlN to form Al-Cr-O. AlN particles were found on the surface of the steel, which suggests that a strong bond could be produced in this couple. Dissolved oxygen in the steel transferred to the surface and reacted with AlN to form Al-O-N at the interface. The predicted products from this diffusion couple are AlN/Al-O-N/Al-Cr-O/SS after long-term exposure. Strong bonding formation between Type 316 stainless steel/AlN interface was observed. This couple is applicable to the development of insulator coatings.
because the ohmic resistance of Al-O-N phase was higher than expected. In a same vein, we may pursue the interaction of oxygen-charged V-5Cr-5Ti alloys with AlN to produce a V-5Cr-5Ti-(O)/Al-O-N/AlN couple, which may also reveal enhanced ohmic resistance. Preparation of oxygen-charged in V-5Cr-5Ti was described previously.8

**Diffusion approach for in-situ formation of insulator coatings in liquid Li**

Ionic diffusion (cation, anion or both) within the coating has to be considered during formation as well as long-term exposure of insulator coatings in liquid-Li environments.

*Outward cation or anion diffusion from alloys or ceramic substrates:* In this case, a metal ion (cation) or anion leaves the substrate and migrates to the scale/liquid-metal interface and a vacancy may be produced at a grain-boundary, dislocation, or other active defect area within the substrate (Fig. 2). The consequences of predominately outward diffusing species at the metal/coating interface are vacancy formation and coalescence (void formation) near the interface, and reduction in the bond strength between coating/substrate. However, if the chemical potential gradient at the coating/substrate is relatively small at elevated temperatures, void formation may not occur. In general, outward cation or anion diffusion from alloys or ceramic substrates should be avoided.

*Inward diffusion via insulator layer:* If anions of O, N, (or C) within the coating layer diffuse inward toward the alloy, insulator layer growth occurs at the alloy/coating interface. However, diffusion of cations from metal atoms in the liquid environment must also be considered.
Grain-growth behavior of V-5%Cr-5%Ti

In coatings produced by high-temperature processes such as CVD or thermally grown layers, grain growth and changes in morphology of the alloy influence coating properties. Even though the CTE of the substrate and coating layer are similar in magnitude, adherent coatings may not form because of inadequate stabilization of alloy substrate. This is more prevalent in the case of brittle ceramic or intermetallic coatings on metallic substrates because of diffusion-related phenomena in the metal (e.g., grain growth) rather than in the ceramic at high processing temperatures. For high-temperature alloys, viable coatings require alloy stabilization before coating application, otherwise, the coating layers tend to spall during high-temperature operation because of grain growth or other morphological changes. In the case of Fe-Cr steels, a small amount of Y (~0.3 wt.%) in the alloy inhibits grain growth.

The V-5%Cr-5%Ti specimens were wrapped in Ta foil, sealed quartz capsules in vacuo to avoid Si or O contamination, and annealed for 0.3 – 61.3 h at 1000°C during annealing. Figures 3 and 4 show the grain morphology and change in grain diameter of V-5%Cr-5%Ti as a function of time, respectively. At 1000°C, grain growth decreases rapidly after ≈2.5 h; the grain size of a specimen annealed for 24 h is almost the same as the one annealed for 2.5 h. The grain size, Δd was 7 μm for an initial average grain size of 7 μm. Grain-growth behavior at 1000°C in terms of log Δd versus log time can be represented by

\[
\log \Delta d = 0.58 + \log t^{0.53},
\]

(1)
where the \( \approx 0.5 \) exponent of time is indicative of a diffusion mechanism. Based on these results, we expect that grain growth will not have a significant effect on high-temperature coating by processes such as CVD, pack cementation, or PVD.

**Formation of intermetallic coatings on high-temperature alloys**

Various intermetallic and insulator layers were developed by different methods, namely, CVD, high-temperature PVD, ion-beam-assisted deposition (IBAD), and exposure of specimens to liquid Li containing dissolved metallic solutes (Al, Be, Mg, Si, Ca, Pt, Y, and Cr) to form coatings by chemical reaction with constituents in various metals and alloys (Ti, V-5Cr-5Ti, V-Ti, Types of 304 and 316 stainless steel, Fe-25Cr with 0.3 Y or 6 Al). Most of the solutes in Li were chosen on the basis of thermodynamic stability of their metal oxides or nitrides in Li, as well as on results of compatibility screening tests for ceramic materials in Li.

**Chemical vapor deposition**

*Aluminide and AlN coatings:* Aluminide coatings that form on structural alloys during exposure to liquid Li that contained dissolved Al suggest a means for producing stable electrical insulator layers, such as AlN, by subsequent nitration of the intermetallic layer in the liquid-metal environment\(^7\). The formation of several aluminides (\( V_xAl_y \)) that contain >40–50 at.% Al on V-base alloys can be predicted from the V-Al phase diagram shown in Fig. 5.\(^{10,11} \) These phase relations make up the underlying basis for the formation of aluminide coatings on V and its alloys. Aluminide coatings were produced on the alloys by CVD method at 800-850\(^\circ\)C using trimethyl aluminum, \( (CH_3)_3Al \), as a source of Al to be diffused/reacted on the sample surfaces. In this study, atmospheric pressure
CVD was used because of its utility for engineering applications. Figure 6 shows a schematic diagram of the CVD apparatus. The (CH$_3$)$_3$Al vapor was asperated by a 3% H$_2$-Ar carrier gas and carried to the high-temperature zone via a Ta tube where the vapor decomposed and reacted with the specimens. The reaction for the formation of aluminides is

$$V + 3\text{Al} = \text{Al}_3\text{V}, \quad (4)$$

and the $\Delta G^\circ$ range for the reaction is -4 to -5 kcal/mole (Fig. 7).

This process was followed by mixing of NH$_3$ into the gas stream to convert the aluminide to an AlN coating according to the reaction

$$\text{Al}_3\text{V} + N \rightarrow 3\text{AlN} + \text{V}, \quad (5)$$

where N represents nitrogen activity in the gas phase or dissolved in liquid Li. The free-energy of formation of AlN is -45.94 kcal/mole; therefore, the $\Delta G^\circ$ for the reaction in Eq. (5) is -40.94 kcal/mole at 700K. This reaction will occur spontaneously and the rate-determining step will be ionic diffusion through the nitride layer. Residual V formed during the reaction will either redistribute within Al$_3$V or AlN will become enriched in V, depending on the direction of V diffusion and the thermodynamic stability of V$_2$N near the Al$_3$V/AlN interface. Because of the high thermodynamic stability of TiN, the formation of this phase on aluminided V-5%Cr-5%Ti is also a possibility.$^a$

---

$^a$ When we exposed the prealuminide V-5Cr-5Ti to liquid Li containing 100-200 ppm N, TiN grew outward between the aluminide grains.
Figure 7 (a) is an SEM photomicrograph of an intermetallic of vanadium aluminide coating on a V-5Cr-5Ti substrate. The chemical composition of the coating surface by electron-energy-dispersive spectroscopy (EDS) is as follows:

- **Al** 61.34 at.% (45.72 wt.%)
- **V** 33.57 at.% (47.23 wt.%)
- **Cr** 2.72 at.% (3.91 wt.%)
- **Ti** 2.37 at.% (3.13 wt.%).

Based on these compositions and the V-Al binary phase diagram (Fig. 1), the composition of the intermetallic phase at the surface lies between \( \text{Al}_3\text{V} \) and \( \text{Al}_9\text{V}_5 \). When we consider the free-energy of formation of Al-V intermetallic phases (Fig. 7), the \( \text{Al}_3\text{V} \) phase should form because of its greater stability, but at high temperatures (850°C, 1123K) a mixture of \( \text{Al}_3\text{V} \) and \( \text{Al}_9\text{V}_5 \) could arise due to the similar magnitude in free energies of formation. However, if the Al concentration is not high enough (e.g., >40 at.%), V-Al intermetallic phases will not form at the surface and Al will only diffuse into the bcc sublattice of V according to the phase diagram (Fig. 5). Based on our previous work,\(^{12}\) \( \text{Al}_3\text{V} \) was prevalent on various V-Cr-Ti alloys.

Figure 8 (a) shows an SEM photomicrograph and EDS spectra of an aluminide surface on V-5%Cr-5%Ti at 850°C, and (b) shows similar information for an AlN surface formed at 800°C. The Ta tube that carried the gas into the high-temperature zone was also analyzed. Figures 9 (a) and (b) show the Ta-Al intermetallic and AlN coatings on the inner surface of the tube. CVD in which \( \text{AlCl}_3/\text{NH}_3 \) is the source of Al may not be applicable for many materials because of Cl-induced corrosion. Figure 10 is an SEM photomicrograph of a CVD coating on
V-5%Cr-5%Ti at 850°C where AlCl₃ was used. When vanadium chloride compounds form during the coating process, they tend to spall and prevent the formation of an adherent AlN layer at the surface.

**Al₂O₃ coatings on stainless steels in air**

Low rates of elemental diffusion and electron transport in Al₂O₃ are desirable properties for high-temperature corrosion resistant coatings. However, benefits from these properties for high-temperature coating applications have rather limited because crack-free Al₂O₃ coatings are extremely difficult to fabricate. In this study, we have had some success in forming Al₂O₃ coating layers on Types 304 and 316 stainless steel. Coatings were produced by growing an intermetallic aluminide layer (FeAl) on the steels in liquid Li containing 4-5 wt.% dissolved Al, followed by oxidation of the aluminide layer in air at 1000°C. Figure 11 shows a circular and longitudinal cross sections of a 1/2-in. diameter Type 304 stainless steels tube in which the aluminide coating layer on the inside surface was oxidized in air for 72 h at 1000°C. To determine the minimum required Al content of the steel to form an Al₂O₃ coating layer, samples of aluminided steel tube were sectioned and polished and an Al depth profile was measured by EDS (detection limit of ≈1 at.%). After oxidation, an Al spectrum from EDS analysis indicated a continuous Al₂O₃ coating layer had formed. Figure 12 shows Al₂O₃ coating layers formed on the inside of other Type 304 stainless steel tubes. According to our previous experience, most Al₂O₃ coating layers formed on Fe-Cr-Al alloys contained numerous cracks, mainly due to mismatch of the CTE (=8 x 10⁻⁶/K for Al₂O₃ and ≈17 x 10⁻⁶/K for stainless steel). We believe that Li (130 ppm) in the aluminide layer that formed in liquid Li containing Al plays a role in
accommodating thermal stresses during Al₂O₃ growth and cooling because of fast diffusion of Li⁺ ion owing to its small size.

**High-temperature metallic Mg vapor deposition of MgO coating**

MgO is another potential candidate for an insulator coating for use in a liquid-Li blanket of an MFR. An MgO coating could applied by to various components by vapor deposition because metallic Mg has a high vapor pressure at elevated temperatures. This coating method was investigated with the apparatus similar to that shown in Fig. 6. Mg vapor was generated in a high-temperature Knudsen cell located at the bottom of the stainless steel chamber, which provided a homogeneous source of Mg vapor. Mg was contained in a tungsten or Type 304 stainless steel boat and covered with a plate containing a small hole (≈1.5 mm diameter pin-hole). Sublimation of Mg in a relatively low vacuum of 10⁻³ to 10⁻⁴ torr, in which O₂ was present as an impurity, enabled the formation of MgO clusters by oxidation of Mg vapor inside the chamber. After coating the V-5Cr-5Ti specimens at 800°C, the system was cooled to room temperature by purging with Ar (99.999%). The ohmic resistance of the coatings was measured at room temperature and the coatings were evaluated by SEM/EDS. Figure 13 (a) shows a typical MgO coating on V-5Cr-5Ti, and its EDS spectrum is shown in Fig. 13 (b). The measured two-point contact resistance at room temperature is >10¹² Ω. This coating technique could be extended to other oxides, e.g., CaO, BeO, MgAl₂O₄, Y₃Al₂O₁₂, etc.

**Conclusions**
High-temperature couples between AlN and V-alloys, Ti, and Types 304 and 316 stainless steel showed different interface bonding behavior. Basically, V-alloy/AlN couples did not bond. In the case of Ti/AlN, TiN formed at the interface, but the bonding strength was too low and separation occurred at the Ti/TiN interface. Strong bonds were obtained between AlN and the stainless steels, but mismatch in the thermal expansion coefficients caused fracture in the relatively thick AlN layer above the alloy/AlN interface.

Intermetallic films were prepared on V-alloys and Types 304 and 316 stainless steel by chemical vapor deposition, high-temperature metallic vapor deposition, and liquid metal processing in the temperature range of 800-850°C. The films were examined by optical and scanning electron microscopy and by electron-energy-dispersive and X-ray diffraction analysis. Aluminide films containing >45 wt.% Al and AlN were produced on V-alloys by CVD. The aluminide films on Types 304 and 316 stainless steel were converted to Al2O3 by oxidation in air at high-temperature. The results elucidated the nature of the coatings, which provided both electrical insulation and high-temperature corrosion protection.

Acknowledgments

The authors appreciate discussions with Dr. T. F. Kassner. This work was, in part, supported by the Division of Educational Programs at Argonne National Laboratory during a summer research appointment of W. D. Cho. B. Tani of the Argonne Analytical Chemistry Laboratory provided the X-ray diffraction results. G. Dragel and R. W. Clark assisted in the experimental work.

References


Schematic of solid-state reaction steps at Ti/AlN interface:

1) $\text{AlN} + \text{Ti} = \text{Ti}_x\text{N}_y + \text{AlN}_{1-\delta}$: initial reaction; $(x$ and $y \approx 1$, $\delta \ll 1)$

2) $\text{AlN/AlN}_{1-\delta}/\text{Ti}_x\text{N}_y/\text{Ti} \rightarrow \text{Ti}_x\text{N}_y$: layer grows by N diffusion from AlN to Ti

3) $\text{AlN/AlN}_{1-\delta}/\text{Ti}_x\text{N}_y/\text{Ti}$: Ti and N interdiffusion and growth occurs in $\text{Ti}_x\text{N}_y$ layer; TiN/Ti interface bond weakens due to outward diffusion of Ti

Figure 2. Coating layer formation by different diffusion profiles
Figure 3. SEM photomicrographs of V-5%Cr-5%Ti specimens after annealing for several times at 1000°C in grain-growth experiments.

Figure 4. Increase in grain size ($\Delta d$, $\mu$m) from as-received value (7 $\mu$m) for V-5%Cr-5%Ti specimens as a function to time at 1000°C.
Figure 5. Al-V binary phase diagram

Figure 6. Schematic of CVD apparatus
Figure 7. Gibbs free-energy of formation for various intermetallic compounds in Al-Vi system as a function of temperature.

Figure 8. SEM/EDS photomicrographs of (a) aluminide coating on the V-5Cr-5Ti, and (b) Al/AlN coating.
Figure 9. SEM photomicrograph of (a) aluminide coating, and (b) Al/AlN coating on inside surface of Ta tubes.

Figure 10. AlN coating produced by CVD with AlCl₃/NH₃ showing heavy spallation (light area: V-Cl compound) and V-Al-N coating (dark area).
Figure 11. Al₂O₃ coating by air oxidation of 1/2-in. diameter aluminided Type 304 stainless steel tube at 1000°C
(a), (b), (c)

Figure 12. Al₂O₃ coating by air oxidation of aluminided Type 304 stainless steel tube at 1000°C; (a) cross section of tube, (b) longitudinal cross section of tube, (c) polished region near outside surface of tube to investigate grain-boundary penetration of oxygen, (d) view of extended scale of (b), (e) view of extended scale for (c), and (f) details of (e) by back scattered electron image
Figure 13. (a) MgO coating on V-5Cr-5Ti and EDS of (b)

(a) Mg:MgO on V-5%Cr-5%Ti (PVD) T = 800°C

(b) EDS of (a)