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Fabrication and Performance of AlN Insulator Coatings for Application in Fusion Reactor Blankets*

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Abstract

The liquid-metal blanket concept for fusion reactors requires an electrically insulating coating on the first-wall structural material to minimize the magnetohydrodynamic pressure drop that occurs during the flow of liquid metal in a magnetic field. Based on the thermodynamics of interactions between the coating and the liquid lithium on one side and the structural V-base alloy on the other side, an AlN coating was selected as a candidate. Detailed investigations were conducted on the fabrication, metallurgical microstructure, compatibility in liquid Li, and electrical characteristics of AlN material obtained from several sources.

Lithium compatibility was studied in static systems by exposing AlN-coated specimens to liquid Li for several time periods. Electrical resistance was measured at room temperature on the specimens before and after exposure to liquid Li. The results obtained in this study indicate that AlN is a viable coating from the standpoint of chemical compatibility in Li, electrical insulation, and ease of fabrication; for these reasons, the coating should be examined further for fusion reactor applications.

Introduction

Lithium-containing liquid metals, e.g., pure Li or the eutectic Pb-0.7 wt.% Li alloy, are attractive breeder materials in fusion reactor blankets. The main challenge in the design of self-cooled blankets is to accommodate the strong influence of the magnetic field on the liquid-metal flow. If the flow direction is perpendicular to the field, a potential difference across the duct is induced in the liquid metal. This can cause a large electrical current flow if the potential difference is short-circuited by the duct walls. An electrical current flowing perpendicular to a magnetic field results in a mechanical force that leads to magnetohydrodynamic (MHD) pressure drop. It has been shown that even thin conducting walls would lead to a rather high pressure drop under the conditions of the ITER blanket. For example, pressure drop in a poloidal duct in an inboard blanket segment would reach a value of 8.6 MPa if there is a conducting liner of 0.1 mm thickness.[1] This unacceptably high pressure drop shows the need for electrically insulating coatings in contact with the flowing liquid metal. A lower limit for the pressure drop would be achieved with perfectly insulated walls. A perfectly insulating coating on the wall has been shown to decrease the pressure drop from 8.6 to 0.22 MPa.[1,2]

Even though a very low pressure drop can be achieved with a perfectly insulating coating, in practice such a coating will be difficult to obtain because any and all coating methods can only yield coatings with defects such as pinholes, cracks, minute flaws, etc. Further, a pressure drop of 1-2 MPa is acceptable for a liquid-metal blanket in a fusion reactor application. Malang and Bühler[1] calculated leakage currents through imperfections in the coatings and concluded that to obtain an acceptable pressure drop for the fusion blanket, the product of coating resistivity and the coating layer thickness should have a minimum value of 0.01 $\Omega \cdot m^2$.

Recently, tests were conducted at Argonne National Laboratory to evaluate the coating concept to reduce MHD pressure drop with an eutectic liquid metal of Na-78 wt.% K (NaK).[3] Aluminum oxide was coated on the inside of a stainless steel pipe 10.8 cm in dia x 2.9 mm in wall thickness. The length of the uniform magnetic field was ≈1.8 m, and the maximum magnetic field strength was 2.0 T. Test results showed that the pressure drop with an insulator coating was 25 times lower than that obtained on an uncoated tube under identical test conditions. The measured values for the insulated pipe were somewhat higher than that calculated for a perfectly insulated pipe; possible causes for this difference are discussed in Ref. 3.

Selection of AlN

The major requirements for a viable insulator coating are

- Chemical compatibility in liquid metal.
- Chemical compatibility with structural metal.
- Adequate electrical insulating characteristics.
- Stability under irradiation environment.
- Long-term stability, including self healing, under thermal cycling conditions.

Figure 1 depicts the thermodynamic stability of nitrides of several structural metals with respect to N concentration in an Li environment. Superimposed on this figure are lines corresponding to different concentrations of N in Li. It is evident that AlN will be stable in Li with a wide range of N concentrations, whereas Si_3N_4 will be stable up to ≈400°C in Li containing >300 ppm N. A coating of AlN should be chemically compatible in liquid Li, especially at temperatures below 400°C where the rate of dissociation of AlN will be low, even though the solubility values for Al and N are fairly high in liquid Li. The calculations show that Ti in a V alloy can also form a nitride in the same Li but that TiN is not viable as an electrical insulator. As a result, it is desirable to aluminize the surface regions of the first-wall alloy and to nitride the surface Al to form the insulating layer. Furthermore, Al is favored because a reservoir of Al can be built into the alloy surface by various techniques, and if the coating layer cracks or spalls, the Al-enriched surface could be renitrided by N dissolved in Li.

A review of available information on electrical resistivity values for several nitrides showed that nitrides such as AlN and Si_3N_4 exhibit resistivities of $>10^5$ $\Omega \cdot m$ at temperatures below ≈600°C. The requirement is that the product of the electrical resistivity of the insulator coating and the thickness of the coating should exceed a nominal value of 0.01 $\Omega \cdot m^2$ under operating conditions. This translates to a minimum

resistivity value of 10^4 $\Omega \cdot m$ for a coating thickness of 1 μm, or 10^3 $\Omega \cdot m$ for a coating thickness of 10 μm. Based on the resistivity values of the materials listed above, a coating layer of <1 μm of any of these materials would be adequate from the insulating standpoint, provided that resistivity is not reduced during operation, i.e., by irradiation. Figure 2 shows electrical resistances as a function of coating thickness and temperature for several nitride materials, along with the requirements for ITER application.

Experimental Procedure

Several possible approaches are being examined to develop an AlN coating on the candidate structural material (both in bare and prealuminized conditions) by a physical vapor deposition (PVD) process with and without bond coats; by a chemical vapor deposition process at temperatures between 600 and 900°C; by applying a low-temperature electrochemical method that involves sequential reactions; by prealuminizing the surface of the alloy and converting it to nitride in a high-nitrogen Li environment; by in-situ forming of an AlN coating in Li with high thermodynamic activities for Al and N; and by prealuminizing specimens of structural material and nitriding them with an N_2 cover gas during Li exposure. At present, substantial information has been developed on AlN coatings applied by PVD, and this paper will discuss the results of that evaluation.

Aluminizing Process. Surface aluminization of the V alloy is attempted by a pack-diffusion process, a well-established approach for covering stainless steels and Ni-base alloys with layers of an intermediate phase.[4] V-alloy coupons are contacted with a pack of powders and heated for 4-12 h at ≈900°C. The composition of such powders (e.g., 65 wt.% Al_2O_3, 33 wt.% Al, 2 wt.% NH_4Cl) provides the packing with metallic Al, alumina as filler material, and NH_4Cl as activator. The Al deposited on the substrate surface diffuses into the subsurface regions of the material, where it forms intermetallic phases such as aluminides of Al or V. Because the substrate materials are heated to near the annealing range for times sufficient to cause solution processes in the matrix, the materials need a final treatment to optimize the structure. The aluminide layers reach thicknesses of 0.02–0.04 mm, depending on the composition of the substrate materials.[5] The diffusion process produces layers with very good adhesion to the substrate. The high temperature of the formation process creates layers that develop compressive stresses at lower temperatures; thus, the layers do not contain cracks after preparation is complete.

Coating Processes. PVD was one of the methods used for the development of AlN coatings on both bare and prealuminized specimens of V-5Cr-5Ti alloy. The coatings were produced by Midwest Research Technologies (MRT) and by Basic Industrial Research Laboratory (BIRL). Coatings were also made by reaction sputtering in nitrogen atmosphere at Argonne and by ion-beam-assisted reactive evaporation at Cametoid Advanced Technologies, Inc. (CAT).

In the MRT approach, AlN was sputtered reactively, that is, an aluminum target was sputtered in a partial pressure of high-purity N_2, with Ar as the primary sputtering gas. The process proceeds at a relatively low temperature and generally does not exceed ≈250°C. Specimens of both bare and prealuminized V-5Cr-5Ti and the Al target were

sputter cleaned for 6 min with high-purity Ar flowing at a rate of 45 cm^3/min and a chamber pressure of 20 mtorr. Subsequently, the sputter deposition of AlN$_x$ was done with a 1200-W RF power source for 10 h in an Ar-N$_2$ gas mixture at a chamber pressure of 23 mtorr.

In the BIRL approach, AlN coatings were also deposited with reaction sputtering; some received an intermediate layer of TiN and an outer layer of AlN. An MRC 902M sputtering system was used, with control of the partial pressure of the reactive gas (N$_2$) and arc suppression of the Al sputtering target. The target was powered by a DC supply, which was run at 5 kW. The Ar sputtering gas was maintained at a constant pressure of 8 mtorr during sputtering. The partial pressure of N$_2$ was controlled with an optical gas controller and maintained constant at 1.6×10^{-4} torr during coating. The substrate was biased to 150 V, the coating deposition rate was 1300 Å/min, and the maximum temperature during the coating operation was <200°C.

In the Argonne approach, AlN coatings were made by reaction sputtering in a low-pressure N$_2$ atmosphere at 350, 400, and 450°C. The specimens were heated by passing an electric current through the substrates. The thickness of the coating after 1 h of deposition was in the range of 0.8-1.4 μm; after 4 h of deposition, it was ≈5.2 μm. The coating covered the entire surface of the V-alloy specimen, and the layer was fairly hard. Coatings developed at 350 and 450°C tended to crack, but those developed at 400°C were fairly adherent, mechanically harder, and scratch-resistant.

In the CAT approach, deposition of single-layer and graded AlN coatings on a V substrate was done by ion-beam-assisted reactive evaporation. Al is evaporated and deposited either by resistive heating or by an electron beam source while the growing film is bombarded with accelerated N ions produced in an ion gun. A basic advantage of this technique is controllability of the flux (arrival rate) and energy of the ion species, independent of the rate of deposition of Al. In contrast, in plasma-based processes, the voltage, current, chamber pressure, and deposition rate are all interdependent.

Liquid Metal Exposures. Two static liquid-Li systems were designed and fabricated for studies on compatibility of insulator coatings. The systems were filled with ≈15 L of high-purity (99.97 wt.%) Li. Concentrations of trace impurities of Na, Ca, K, Fe, Si, and Cl in Li was <50 ppm, and N concentration in the Li was 80 ppm. The temperatures of both systems were set at 300°C to examine the compatibility of insulator coatings, in support of the proposed MHD test, with an insulated test section to be conducted at a maximum temperature of 300°C. In one of the Li systems, N$_2$ gas was bubbled through a small tube immersed in Li to increase N concentration.

Coupon specimens of AlN-coated samples from several sources (discussed above) were exposed in the liquid Li. Weight change was measured to establish the corrosion rates for the coatings as a function of time and liquid metal chemistry. After exposures, the specimens were examined by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer and by X-ray diffraction. The coated specimens were examined to evaluate coating integrity after liquid-metal exposure, microstructural changes in coatings, coating/substrate interactions, and electrical insulation characteristics of the coatings.

Results and Discussion

Characteristics of Coated Specimens. Figure 3 shows SEM photomicrographs of AlN-coated V-alloy specimens in the as-deposited condition. The AlN layers were fairly compact and of uniform thickness in the range 8-12 μm. X-ray diffraction analysis showed hexagonal AlN phase with an (002) orientation for the coating. No vanadium nitride was detected because the substrate was at <200°C during the coating process. Even though the coatings were fairly adherent, early exposures of these coated specimens in Li resulted in complete disappearance of the coating layer by either spallation or dissolution. As a result, the coated specimens were given a thermal-hardening treatment at 700-900°C prior to exposure in Li. Hexagonal AlN phase with (002) orientation was maintained after the hardening treatment, but traces of the V_2N phase were noted because of a reaction between AlN and V at the coating/substrate interface. Detailed analysis of the CAT-developed coatings have been reported elsewhere[6] and no additional analysis was performed. The coated specimens, analyzed by CAT with the Rutherford backscattering (RBS), indicated that the N/Al ratio in the coatings ranged from 1.04 to 1.32.

Electrical Insulating Behavior of Coatings. Electrical resistances of several of the coated specimens were measured at Argonne. Coating resistance must be characterized at different locations on each sample to examine the electrical integrity of the coating and to identify the types and location(s) of defects. For this purpose, pure gold was sputter-deposited (in a vacuum chamber) on the coated specimens in a grid form by masking the sample to control the area of gold deposit. Coating resistances were measured at room temperature at several gold-coated locations. Because the gold-deposited areas are known, the measured resistances at different locations can be used to calculate the product of resistivity and thickness, which should be in excess of 0.01 $\Omega \cdot m^2$ or 100 $\Omega \cdot cm^2$. The measured resistance values at most locations of the coated specimens were several orders of magnitude higher than are needed for ITER application.

Lithium Compatibility of Coatings. Several AlN-coated V-alloy specimens from different sources were exposed to liquid Li at 300°C, after which detailed microstructural analyses of all specimens, and X-ray diffraction analysis of selected specimens, were performed. Further, electrical resistance was measured on several of the Li-exposed AlN-coated specimens. Figure 4 shows an SEM photomicrograph in cross section, and EDX depth profiles for Al, N, V, Cr, and Ti, of an MRT-supplied, AlN-coated V-5Cr-5Ti alloy specimen after 430 h exposure at 300°C to an Li environment in which argon-nitrogen gas was bubbled for 24 h. It is evident that the coating was intact and appears dense and fairly adherent to the substrate alloy. EDX analysis shows that the coating consists predominantly of Al and N, with almost no contamination from either the impurities in Li or the substrate constituents. Figure 5 shows an SEM photomicrograph in cross section, and EDX depth profiles for Al, N, V, Cr, and Ti, of an Argonne-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430 h exposure at 300°C to an Li environment of normal purity. Figure 6 shows data for a similar specimen exposed to an Li environment in which argon-nitrogen gas was bubbled for 24 h. The coatings are somewhat thinner in these specimens than those obtained from MRT, but integrity of the coating, adhesion to the substrate, and morphology of the coating are very good. Because these specimens

were prealuminized, a thin layer of (Al, V) nitride seems to form as an intermediate layer during the coating process, primarily because the specimens were heated to 350-450°C during coating in the Argonne approach.

A comparison of the data for specimens exposed in Li with normal N content (Fig. 5) and in Li with N_2 bubbling (Fig. 6) shows that the coating morphologies and coating compositions are virtually identical, indicating that nitrogen concentration in Li may not have a significant effect on coating performance, especially at 300°C. The AlN-coated specimens, obtained from CAT, were also exposed to Li environments at 300°C, but the coatings completely disappeared into the Li in 120 h of exposure, as evidenced by the high electrical conductivity of the specimens after exposure.

Figure 7 shows SEM photomicrographs of cross sections of 900°C-hardened AlN-coated specimens after 600 h exposure to an Li environment of normal purity. The substrates in samples #9 (Fig. 7a) and #13 (Fig. 7b) were initially in bare and prealuminized condition, respectively. The AlN coating deposited by MRT had thicknesses of 10-12 μm. After Li exposure, the coating surface exhibited a reaction product that contained only Al and O, based on EDX analysis. The photomicrograph in Fig. 7c is of a 900°C-hardened AlN-coated specimen developed by BIRL and exposed to Li along with samples #9 and #13 mentioned above. Thicknesses of BIRL-developed coatings were 4-6 μm, and specimen #56-1 also developed an Al- and O-rich reaction product after Li exposure. X-ray diffraction analysis showed that the dominant phase in all three specimens was hexagonal AlN; no Li, Al, O and/or N compounds were observed.

Several Li-exposed AlN-coated specimens were masked and gold plated (as before) and resistances were measured at room temperature. Figure 8 shows measured resistance values for several specimens and at different locations within the same specimen. Also shown in the figure is the minimum value for resistance required for ITER application. The results show that the experimental approaches used in the present program can deliver coatings with adequate electrical resistance for application in Li-cooled fusion reactor blankets. Additional experiments and analysis of the coating procedures and coating/Li interactions are underway to examine the long-term performance of these coatings in Li and under thermal cycling conditions.

Summary

The requirements of liquid metals such as Li and NaK for application in the ITER have been discussed in detail. The assessment included corrosion performance of first-wall candidate materials and of electrical insulating coatings in the liquid metals from the standpoint of chemical compatibility, especially mass transfer of metallic and nonmetallic elements in the temperature range of interest in the ITER. The structural material and the coating selected for the study were V-5Cr-5Ti alloy and aluminum nitride, respectively. Detailed investigations were conducted on fabrication, metallurgical microstructure, compatibility in liquid Li, and electrical characteristics of AlN material obtained from several sources. Coating fabrication methods included physical vapor deposition, reaction sputtering, ion-beam-assisted deposition, chemical vapor deposition, and a chemical route. Microstructural characterization of the coated samples was conducted by scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction. Lithium compatibility studies were conducted in static

systems by exposure of AlN-coated specimens to over several time periods. Electrical resistance measurements were made at room temperature on the specimens before and after exposure to liquid lithium. The results obtained in this study indicate that AlN is a viable coating from the standpoint of chemical compatibility in lithium, electrical insulation characteristics, and ease of fabrication, and that the coating should be examined further for fusion reactor application.

Acknowledgments

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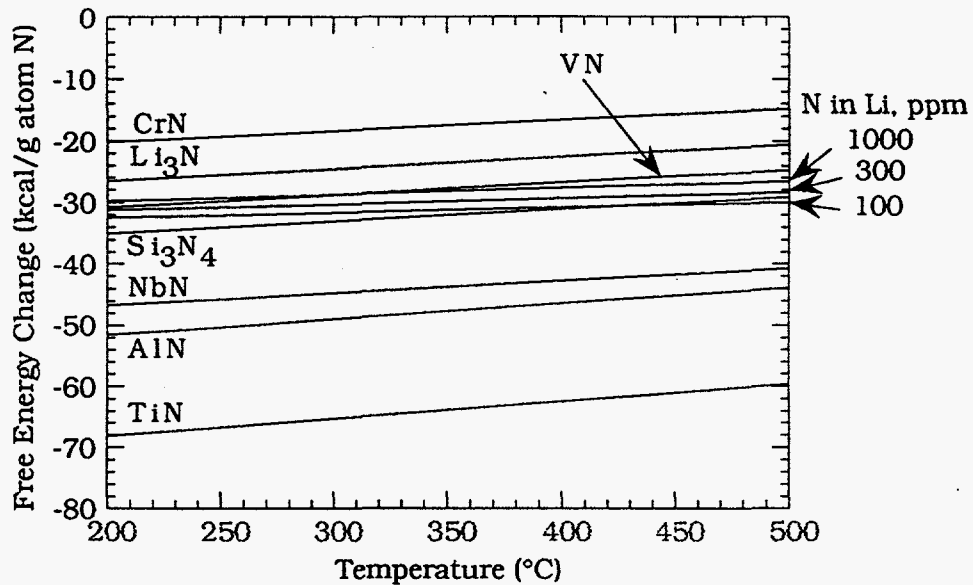
Figure 1. Thermodynamic stability of nitrides of several structural metals in an Li environment.
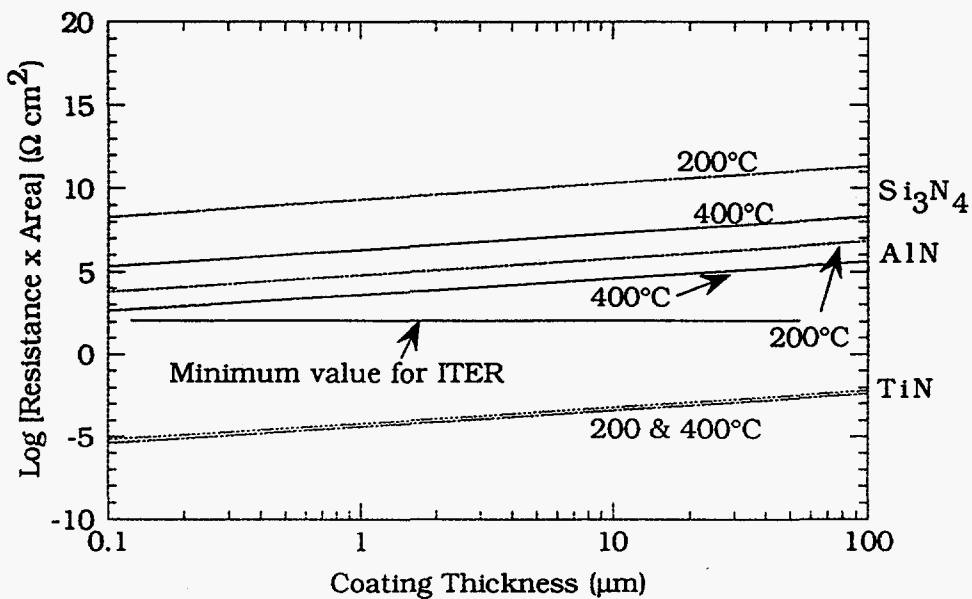

Figure 2. Electrical resistance data for several nitride coatings as a function of coating thickness and temperature.
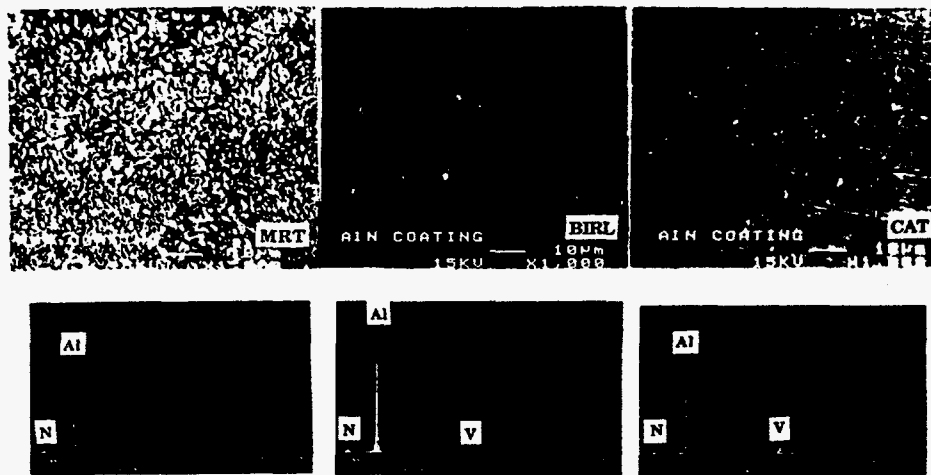
Figure 3. SEM photomicrographs and EDX analysis of MRT-, BIRL-, and CAT-deposited AlN coating on V-alloy specimens in as-deposited condition.
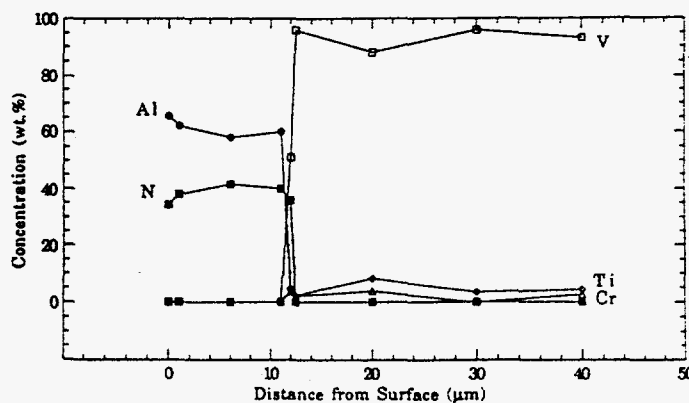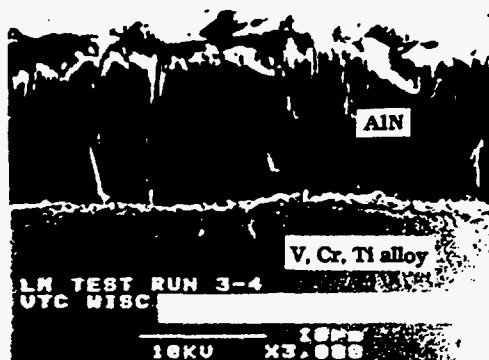

Figure 4. SEM photomicrograph in cross section and EDX depth profiles for Al, N, V, Cr, and Ti for MRT-supplied, AlN-coated V-5Cr-5Ti alloy specimen after 430 h exposure at 300°C to Li environment in which argon-nitrogen gas was bubbled for 24 h.
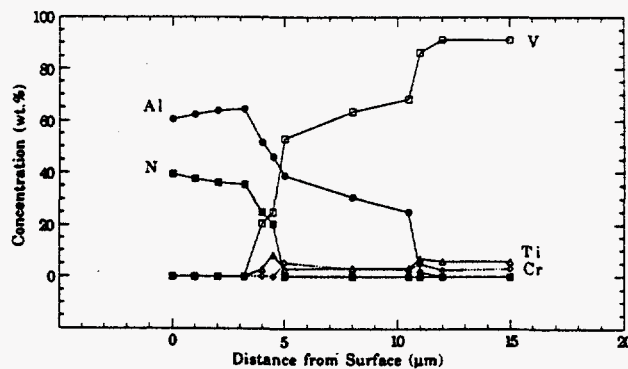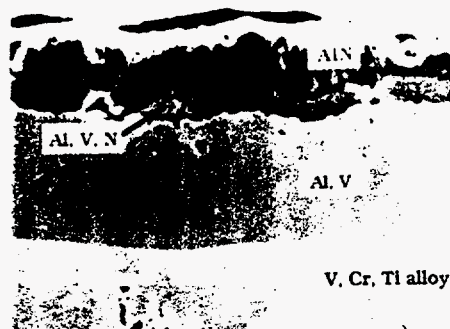
Figure 5. SEM photomicrograph in cross section and EDX depth profiles for Al, N, V, Cr, and Ti for Argonne-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430 h exposure at 300°C to Li environment of normal purity.
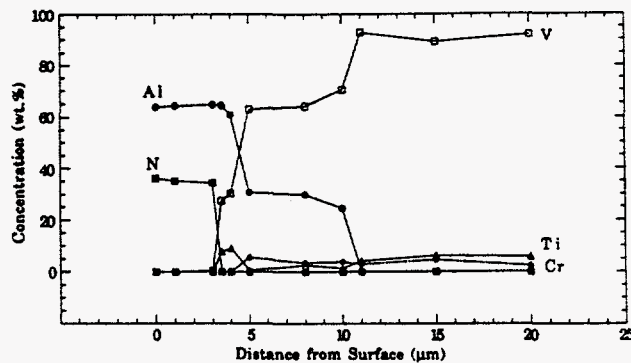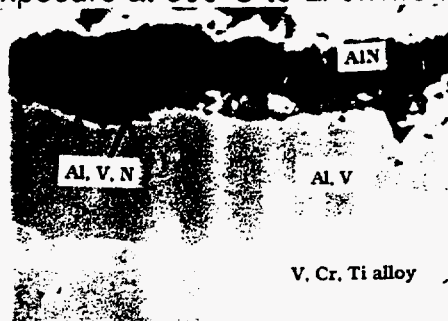

Figure 6. SEM photomicrograph in cross section and EDX depth profiles for Al, N, V, Cr, and Ti for ANL-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430 h exposure at 300°C to Li environment in which argon-nitrogen gas was bubbled for 24 h.
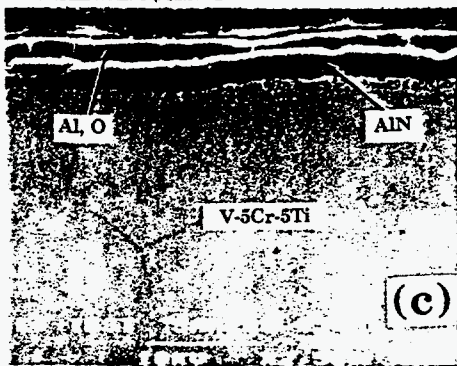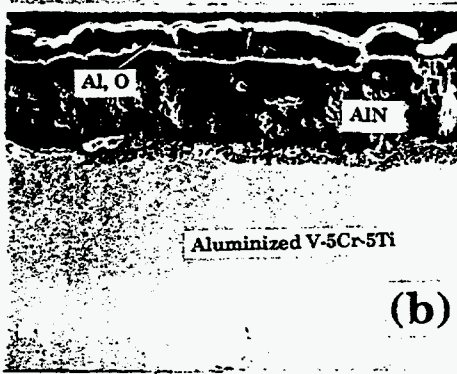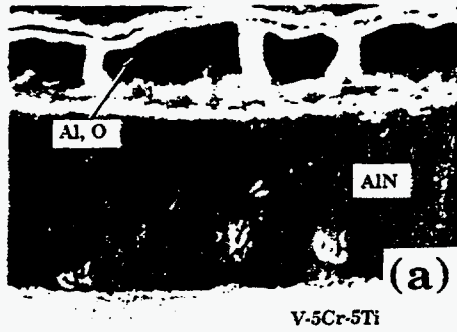
Figure 7. SEM photomicrographs of cross sections of 900°C–hardened AlN–coated specimens after 600 h exposure to Li environment of normal purity.

Key to Specimen Treatment

#36: V-5Cr-5Ti alloy, AlN coated
#10: Alloy, AlN coated, hardened for 110 h at 900°C
9: Alloy, AlN coated, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
#16: Alloy, prealuminized, AlN coated, hardened for 110 h at 900°C
#13: Alloy, prealuminized, AlN coated, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
#33: Alloy, AlN coated, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C
#12: Alloy, prealuminized, AlN coated, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C
#56-1: Alloy, AlN coated by 2nd vendor, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
#56-2: Alloy, AlN coated by 2nd vendor, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C

Figure 8.   Electrical resistance data for several AlN–coated specimens in as–coated and hardened conditions and before and after Li exposure.