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**DEVELOPMENT AND PERFORMANCE OF ALUMINUM NITRIDE  
INSULATING COATINGS FOR APPLICATION IN A  
LITHIUM ENVIRONMENT\***

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# DEVELOPMENT AND PERFORMANCE OF ALUMINUM NITRIDE INSULATING COATINGS FOR APPLICATION IN A LITHIUM ENVIRONMENT

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## Abstract

The blanket system is one of the most important components in a fusion reactor because it has a major impact on both the economics and safety of fusion energy. Based on the requirement that an electrically insulating coating on the first-wall structural material must minimize the magnetohydrodynamic pressure drop that occurs during the flow of liquid metal in a magnetic field, aluminum nitride (AlN) is considered a candidate coating material for the lithium self-cooled blanket concept. Detailed investigations were conducted on the fabrication, metallurgical microstructure, compatibility in liquid Li, and electrical characteristics of AlN as a coating material. A nanoindentation technique was used to evaluate the hardness of the coated samples in as-coated condition, after a hardening treatment, and after exposure to Li. Lithium compatibility studies were conducted in static systems by exposure of AlN-coated specimens for several time periods, at various temperatures, and in various lithium chemistries. Electrical resistance of the specimens was measured at room temperature before and after exposure to liquid Li. This paper discusses the results from ongoing activities on the development of AlN coatings.

## 1. Introduction

Lithium-containing liquid metals, e.g., pure Li or the eutectic Pb-17 at.% Li alloy, are attractive breeder materials in fusion reactor blankets. The main challenge in the design of self-cooled blankets is accommodating the strong influence of the magnetic field on the liquid metal flow. It has been shown that even thin conducting walls could lead to a significant pressure drop under fusion reactor blanket conditions. For example, the pressure drop in a poloidal duct in an inboard blanket segment could reach 8.6 MPa if a 0.1-mm-thick conducting liner is present [1]. This unacceptably high pressure drop shows the need for electrically insulating coatings that are in contact with the flowing liquid metal. A lower limit for the pressure drop could 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]. Malang and Bühler [1] calculated leakage currents through imperfections in coatings and concluded that to obtain an acceptable pressure drop for a fusion blanket, the product of that coating resistivity and the coating layer thickness should have a minimum value of  $0.01 \Omega \text{ m}^2$ . The major requirements for a viable insulator coating are chemical compatibility in liquid metal, chemical compatibility with structural metal, adequate electrical insulating characteristics, stability in an irradiation environment, and long-term stability (including self-healing), under thermal-cycling conditions.

An assessment of the thermodynamic stability of nitrides of several structural metals with respect to N concentration in a Li environment showed that aluminum nitride (AlN) will be stable in Li that contains a wide range of N concentrations [3,4]. For the stability of AlN in a Li environment, the N concentration in Li will be dictated by the Al concentration in the Li, because both N and Al are somewhat highly soluble in Li. Calculations that use the free energy value for the reaction



showed that the product of the activities of N and Al in Li required to maintain a stable AlN phase is very low, indicating that dissolution of the AlN will be small (even though the driving force for dissolution of either N or Al alone is large based on their solubility values in Li). Also, a coating of AlN should be chemically compatible in liquid Li. Furthermore, Al can be incorporated 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 AlN exhibits resistivities of  $>10^5 \Omega\cdot\text{m}$  at temperatures below  $\approx 600^\circ\text{C}$ . The requirement that the product of the electrical resistivity and the thickness of the coating should exceed a nominal value of  $0.01 \Omega\cdot\text{m}^2$  translates into a minimum resistivity value of  $10^4 \Omega\cdot\text{m}$  for a coating thickness of  $1 \mu\text{m}$ , or  $10^3 \Omega\cdot\text{m}$  for a coating thickness of  $10 \mu\text{m}$ . Based on the resistivity value of AlN, a coating layer of  $<1 \mu\text{m}$  would be adequate from the insulating standpoint, provided that resistivity is not reduced during operation, i.e., by irradiation. Figure 1 shows electrical resistances as a function of coating thickness and temperature for several nitride materials, along with the requirements for fusion reactor application.

Several approaches to the development of an AlN coating on the candidate structural material (both in bare and prealuminized conditions) were examined: physical vapor deposition (PVD) with and without bond coats; chemical vapor deposition (CVD); application of a low-temperature electrochemical method that involves sequential reactions; prealuminization of the surface of the alloy and converting it to a nitride in a high-N Li environment; in-situ formation of an AlN coating in Li with high thermodynamic activities for Al and N; and prealuminization of specimens of structural material and nitriding them with an  $\text{N}_2$  cover gas during Li exposure. An experimental procedure for aluminization of specimens was presented earlier [3-5]. At present, substantial information has been developed on the physical and mechanical characteristics and chemical compatibility of AlN coatings. This paper will discuss the information.

## 2. Experimental Procedure

**Gas-Phase Nitridation.** Nitridation of V-5Cr-5Ti alloy specimens with and without pack-aluminized surfaces was conducted at 650 and  $800^\circ\text{C}$  in  $\text{NH}_3/\text{H}_2$  gas mixtures. The experiments were conducted in a thermogravimetric setup with an electrobalance that had a sensitivity of  $0.1 \mu\text{g}$  and a loading capacity of 2.5 g. Test coupons, measuring  $10 \times 10 \times 1$  to 2 mm, were suspended from the balance by a  $200\text{-}\mu\text{m}$ -diameter Pt wire and were placed in the constant-temperature section of a vertical three-zone furnace. Weight change of the specimens was monitored continuously and the specimens were examined in detail by several electron-optic and X-ray techniques.

**Coatings Deposited by PVD.** Aluminum nitride was sputtered reactively. That is, an aluminum target was sputtered in a partial pressure of high-purity N, with Ar as the primary sputtering gas. The process takes place at a relatively low temperature, generally not above  $\approx 250^\circ\text{C}$ . Specimens of bare and prealuminized V-5Cr-5Ti and an Al target were sputter-cleaned for 6 min with high-purity argon at a flow rate of  $45 \text{ cm}^3/\text{min}$  and a chamber pressure of 20 mtorr. Subsequently,  $\text{AlN}_x$  was sputter-deposited with a 1200-W RF power source for 10 h in an Ar/N gas mixture at a chamber pressure of 23 mtorr. The sputtered specimens were cooled in vacuum overnight, and the second side of the specimens was then coated in the same way.

**Coatings Deposited by the Chemical Route.** AlN coatings were also deposited by a chemical route with trimethyl aluminum (TMA) and  $\text{NH}_3$  as the precursor sources of Al and N, respectively.

The experimental procedure was as follows: the reaction chamber was flushed with Ar gas; 50 mL of dry toluene was added by syringe through the septum; then, 10 mL of TMA was added, also by syringe, taking care to avoid exposure of the pyrophoric TMA to the atmosphere. The solution was heated to 74°C while slowly purging the system with argon. Ammonia gas was then passed into the system at a rate of  $\approx 45$  mL/min for  $\approx 20$  min. The reaction of  $\text{NH}_3$  with TMA at temperatures above 60°C proceeds through adduct formation to give a cyclic trimer with a corresponding loss of methane according to the reactions



These reactions are exothermic, and temperature increases of 20-30°C were observed. Completion of the reaction corresponded to cessation of the exotherm. Evaporation of the toluene leaves the trimer as a crystalline white solid that melts to a clear, colorless liquid upon heating to 135°C. A coupon of V alloy was immersed in the liquid trimer for  $\approx 30$  s, raised out of the melt, and heated stepwise to drive off methane and convert the intermediate to AlN. Air was excluded during the heating process. Nitrogen was passed through the system, and the setup was held at 150°C for 20 min. During this period, the liquid trimer was converted to a solid, while methane was evolved. Methane evolution continued as the coated coupon was heated to 170°C for 25 min, then to 200°C for 30 min, and finally to 500°C for 24 h. The coatings were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

**Chemical Vapor Deposition.** Preliminary studies were conducted to evaluate deposition of AlN by CVD, an approach that has been shown capable of developing very thin electrical insulator coatings for semiconductor applications. The advantage of CVD is that the coating is applied from a gas-phase reaction rather than by line-of-sight application as in the PVD method, and, as a result, can be used to coat components with complex shapes. Because CVD requires fairly high temperatures (800-900°C), one must establish whether AlN can be deposited by CVD without degrading the properties of the substrate. To address this question, coupon specimens of V-5Cr-5Ti were coated by a combination of thermal and plasma-assisted processing at 600-800°C.

**Liquid Metal Exposures.** Two static liquid Li systems were designed and fabricated for studies on the compatibility of insulator coatings. The systems were filled with  $\approx 15$  L of high-purity (99.97 wt.%) Li. The concentration of trace impurities of Na, Ca, K, Fe, Si, and Cl in the Li was  $< 50$  ppm, and N concentration in the Li was 80 ppm. The temperatures of both systems were set at 300 and/or 500°C to examine the compatibility of the insulator coatings. In one of the Li systems,  $\text{N}_2$  was bubbled through a small tube immersed in the Li to increase the concentration of N in the Li.

Coupon specimens of AlN-coated samples were exposed in the liquid Li. Weight change was measured to establish the rate of corrosion of the coatings as a function of time and liquid metal temperature and chemistry. After exposure, the specimens were examined by SEM, energy dispersive X-ray (EDX) analysis, and XRD. The coated specimens were examined to evaluate coating integrity after exposure to liquid Li, microstructural changes in the coatings, coating/substrate interactions and bonding, and electrical insulation characteristics of the coatings.

### 3. Results and Discussion

**Gas Phase Nitrided Specimens.** The nitridation process followed a parabolic rate expression for both bare and prealuminized alloys. The parabolic rate constants for nitridation of bare V-5Cr-5Ti alloy were  $9.1 \times 10^{-6}$  and  $6.9 \times 10^{-7}$   $\text{mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$  at 800 and 600°C, respectively. A detailed examination of the surfaces and cross sections of nitrided specimens showed V-rich nitrides. The

results indicated that N enrichment via gas-phase nitridation is possible but that an exclusive binary nitride layer of V was not observed. The rate constant for nitridation of prealuminized V-5Cr-5Ti alloy was  $2.2 \times 10^{-8} \text{ mg}^{-2} \text{ cm}^{-4} \text{ s}^{-1}$ , which is lower than the rate constant for nitridation of the bare alloy; however, the surface and subsurface regions consisted predominantly of V-rich nitride and not AlN.

Calculation of the thermodynamic stability of several oxides indicates that the O partial pressures should be  $<10^{-40}$  atm at  $650^\circ\text{C}$  to prevent formation of the  $\text{V}_9\text{O}$  phase. The pressures needed to prevent formation of oxides of Ti and Al are lower by a few orders of magnitude. Such low O partial pressures will be difficult to achieve in experiments that involve flowing gas, even if the gases are purified by hot getting. Another consideration for the formation of a "pure" binary nitride such as AlN is that the required partial pressures of N in the exposure environment are extremely low. The calculations showed that, to obtain the AlN phase by gas-phase nitridation, the ratio  $\text{NH}_3/\text{H}_2^{3/2}$  must be  $<10^{-18}$  and  $10^{-12}$  at  $800$  and  $400^\circ\text{C}$ , respectively. Such low values cannot be maintained experimentally because even a  $\text{H}_2/\text{NH}_3$  mixture that contains 1 vppm  $\text{NH}_3$  can only result in a value of  $\approx 10^{-6}$  for the ratio. Based on the experimental data developed with gas-phase reactions and on the analysis of data, it is concluded that gas-phase nitridation is not a viable method for developing electrically insulating AlN coatings.

**PVD-AlN-Coated Specimens.** The AlN layers of V-alloy specimens coated by PVD were fairly compact and of uniform thickness in the ranges of  $8\text{-}12 \mu\text{m}$ . XRD analysis showed hexagonal AlN phase with a (002) orientation [3]. No vanadium nitride ( $\text{V}_2\text{N}$ ) was detected because the temperature of the substrate was  $<200^\circ\text{C}$  during the coating process. Even though the coatings were fairly adherent, early exposure of these coated specimens to Li resulted in complete disappearance of the coating layer by either spallation or dissolution. As a result, the coated specimens were subjected to a thermal-hardening treatment at  $700\text{-}900^\circ\text{C}$  prior to exposure in Li. XRD of these heat-treated specimens also showed hexagonal AlN phase with (002) orientation, but traces of the  $\text{V}_2\text{N}$  phase were noted because of a reaction between AlN and V at the coating/substrate interface.

**CVD-AlN-Coated Specimens.** Very few samples were coated by CVD because the primary purpose of the effort was to evaluate the feasibility of the approach rather than to make dense, thick coatings. In general, the coatings prepared by CVD were fairly thin and exhibited significant cracking. XRD analysis of the coated specimen showed some weak lines of AlN, but the specimen was not examined further. Because the coatings exhibited significant cracking, electrical resistivity of these coated samples was not measured, nor were the samples used in Li exposure experiments. The preliminary results for the CVD approach showed that the probability of producing good coatings is quite high, but significant additional work is needed to experiment with the coating parameters and to develop dense, adherent coatings.

**Coatings Deposited by the Chemical Route.** Even though the chemical route followed the general procedure described earlier, several runs were conducted to examine the effect of various coating parameters on coating integrity. In some experiments, coupons were immersed in just enough liquid cyclic trimer precursor to cover the coupon surface, and the entire mass was then heated to convert the precursor to a solid. The coatings produced by this procedure were thick but they were heavily cracked and adhered weakly to the substrate. In another experiment, a coupon was immersed briefly in the molten precursor, removed, and heated to convert the film of precursor to a coating of AlN. Formation of AlN was confirmed and, in most cases, the coatings were optically transparent. Although severe cracking was observed in thick coatings, the thin coatings appeared to be crack-free. In an attempt to determine the cause of the cracking, two coating runs were prematurely arrested after a brief low-temperature ( $200^\circ\text{C}$ ) annealing that should

have driven off most of the methane byproduct. The coatings cracked at this stage, proving that the cracking occurs fairly early in the pyrolysis. The cause of cracking may be due to shrinking of the coatings as the composition changes toward AlN, or it may be due to methane evolution within the thicker coatings. XRD patterns of the coated coupons showed peaks that correspond to the substrate alloy and several weak peaks that match the X-ray pattern of hexagonal AlN. The chemical approach requires significant additional effort to obtain crack-free, fairly thick (10-20  $\mu\text{m}$ ) AlN coatings.

**Electrical Insulating Behavior of As-Coated Coatings.** The electrical resistance of several of the AlN-coated specimens was measured by sputter-deposition (in a vacuum chamber) of pure Au in a grid form by masking the sample to control the area of Au deposition. Coating resistance was measured at room temperature at several Au-coated locations. Because the Au-deposited areas are known, the measured resistance at various locations can be used to calculate the product of resistivity and thickness, which should be  $>0.01 \Omega\cdot\text{m}^2$  or  $100 \Omega\cdot\text{cm}^2$ . Because only the PVD technique yielded adherent, crack-free AlN coatings, the electrical resistance of several of these coated specimens was measured. The measured values of electrical resistance at several locations on bare and prealuminized specimens in as-coated condition and after a hardening treatment were orders of magnitude higher than needed for blanket application [4,5].

**Lithium Compatibility of Coatings.** Lithium compatibility tests were conducted primarily with specimens that were coated with AlN by PVD. The coatings developed by other techniques were neither crack-free nor of adequate mechanical integrity for exposure to Li. AlN-coated specimens were exposed to two Li environments, characterized by normal purity and containing higher N obtained by bubbling a  $\text{N}_2/\text{Ar}$  gas mixture into Li. Table 1 lists the tests that were performed and details on the objectives of the various exposure runs, exposure times and temperatures, specimens exposed, and results obtained from some of the experiments performed in Li.

Early exposures of AlN-coated specimens to Li showed that the specimens in as-coated condition exhibited poor bonding between the coating and substrate and that a hardening of the coating at elevated temperature may be necessary to improve adhesion. As a result, we attempted a thermal/chemical hardening treatment in which the AlN-coated specimens were heated to 700-900°C in a controlled environment prior to exposure to the Li environment. Such an approach seemed to harden the coating, as evidenced by substantial improvement in the scratch resistance of the coating surface. Several AlN-coated specimens of V-5Cr-5Ti alloy that were subjected to the 900°C hardening treatment were prepared and exposed to Li for 600 h at 300°C in Run 2-8. As shown in Table 1, all of the specimens performed well in Li and the coatings exhibited high resistance values. In contrast, the resistance of a sample with a bond coating of TiN was significantly low after Li exposure. After Li exposure, EDX analysis revealed that the coating surface exhibited a reaction product that contained only Al and O. XRD analysis of the three specimens showed hexagonal AlN as the predominant phase in all three specimens; no Li, Al, O, and/or N compounds were observed. Because these Li-exposed specimens were cleaned in alcohol and water prior to analysis, all of the Li-containing compounds would have dissolved in water and none would be expected in the analysis.

To examine whether similar insulating characteristics can be maintained in Li by coatings that were subjected to hardening at a lower temperature, several specimens were prepared with a thermal/chemical treatment at 700°C (instead of 900°C) for 284 h. The specimens were subsequently exposed to Li for 456 h at 300°C in Run 2-9. The AlN-coated specimen of the V alloy exhibited good insulating characteristics; the coating on a prealuminized V alloy showed high resistance on only one side of the specimen while the other side exhibited flaking and cracking of the coating. The specimen with a bond coating of TiN exhibited almost no resistance, as indicated

by the complete loss of coating during Li exposure. The lower hardening temperature seemed to reduce the reaction between the coating and the Li environment, as evidenced by the thinner layer of the reaction product and also by the lack of continuous coverage of the coating.

A long-term endurance test was conducted in Run 2-10 by exposing specimens of V alloy with and without prealuminization, AlN coated samples of V alloy with and without prealuminization, and a prealuminized Type 304 stainless steel pipe sample with a pack-diffusion Al<sub>2</sub>O<sub>3</sub> coating to Li for 5000 h at 300°C. Figure 2 shows SEM photomicrographs of specimens after a 5000-h exposure to Li. The AlN-coated specimens exhibited high resistance after exposure to Li, and the Al<sub>2</sub>O<sub>3</sub>-coated stainless steel specimen lost the coating in Li.

In Run 3-5, several AlN-coated specimens were exposed to Li at 300°C for 480 h. As before, coating with thermal/chemical treatment exhibited insulating characteristics. Run 3-6 is analogous to Run 2-9 in that the AlN-coated specimens were pretreated at 700°C prior to Li exposure. The results showed that the coating on the V alloy had adequate resistance, whereas the coated prealuminized V alloy exhibited high resistance on only one side of the specimen.

**Hardness of AlN Coatings.** An ultralow-load indentation method that involved a nanoindenter was used to evaluate the hardness of several as-coated and Li-exposed specimens. The instrument is a mechanically highly sensitive microprobe capable of sensing both load and displacement continuously as indents are made in a sample. Details on the test procedure and hardness calculations are presented elsewhere [4]. Several samples were analyzed by the nanoindentation technique, and for each indent, unloading curves were generated after total displacements of 40, 80, and 150 nm. The results showed that substrate hardness of samples without prealuminization is 14-17 GPa; values for the prealuminized samples are 7-8.5 GPa which correspond to an Al-rich zone of the V alloy. The hardness of the AlN coating after 900°C treatment but without Li exposure showed higher values (28-31 GPa) for the specimen that was not prealuminized than the values (20-24 GPa) for the specimens that were prealuminized.

For specimens exposed to Li in Run 2-8, the difference between the hardness of the coating and that of the substrate in the specimen without prealuminization is small (2-3 GPa) and may be responsible for the improved adhesion of the coating to the substrate. In the prealuminized specimen exposed in the same Li, the difference between the hardness of the coating and that of the substrate is 14-16 GPa. In the case of specimens exposed in Run 2-9, the pretreatment temperature was 700°C and the hardness of the coating, even after Li exposure, is high for the specimen without prealuminization than that of the specimen that was prealuminized. This seems to indicate that the absolute values of the hardness for the coating, rather than the difference in hardness between coating and substrate, may play a role in adhesion and spallation.

**Electrical Resistance of Li-Exposed AlN Coatings.** After examination of the physical and chemical characteristics of the coatings and the coating integrity of as-coated and hardened specimens after exposure to Li environments was completed. We measured the electrical resistance of the Li-exposed, initially coated specimens and compared the measured values with the minimum values required for application in fusion reactors. For this purpose, several specimens were selected for resistance measurements. Specimens included those that were initially bare and prealuminized, those with coatings from differing sources, with differing hardening treatment, and several exposure times in Li environments. After the specimens were masked and Au-plated, resistances were measured at room temperature. Measured resistance values from several specimens, at differing locations within the same specimen exceeded the minimum value for the resistance required for application in a fusion reactor blanket [4,5].

**In-Situ Development of AlN Coatings in Li.** Even though AlN coatings developed by PVD

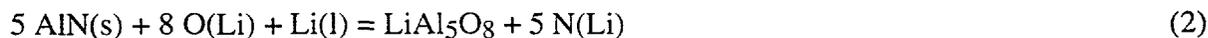
had potential as electrically insulating coatings, the ultimate objective is to develop the coating in situ in Li by controlling the activity of N and/or Al. To examine this approach, we attempted to increase the N and Al activity in Li by adding 100 g of fine AlN powder at 300°C and by heating the Li to 500°C for 24 h to equilibrate the Li with dissolved Al and N. In Run 3-7, specimens of V alloy with and without prealuminization and AlN coatings in as-coated condition were exposed to Li for 24 and 620 h to examine whether N and/or Al were transferred to the alloy surface or whether the coating reacted with Li. The results showed no significant transfer of either N or Al from Li to the alloy, as evidenced by resistance measurements and SEM analysis of the specimens. The specimen coatings were insulating on one side of the specimen but tended to flake off from the other side of the specimens. Based on these results, we concluded that the dissociation of AlN in Li may be a slow process, even at 500°C, and that an alternate method is needed to increase the activity of N and Al.

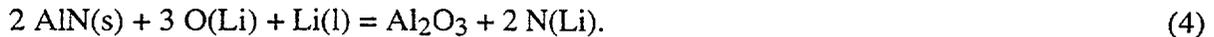
Because Al and N are highly soluble in liquid Li, an increase in the activity of these elements in Li was obtained by addition of solid Al and Li<sub>3</sub>N. Additions of 14.2 g of Al and 25.5 g Li<sub>3</sub>N yielded Al and N concentrations of 4057 and 2929 wppm, respectively. Even if all of the Al reacted to form AlN, N concentration in Li in excess of AlN was 825 ppm. Subsequent to these additions, the Li was maintained at 500°C for 120 h to equilibrate the system. Specimens of V alloy with and without prealuminization and several specimens of thermally/chemically treated AlN coatings on a V alloy substrate were exposed to Li for 120 h at 500°C in Run 3-8. Two major observations were noted from a detailed analysis of the exposed specimens from this run. The first was that no transfer of either N or Al was observed from Li toward the bare and prealuminized V alloy specimens. The second observation was that the thermally treated coatings of AlN performed well and exhibited high resistivity values. Furthermore, no surface reactions were noted between the coating and the Li or the impurities in Li, even though the temperature was as high as 500°C. Figure 3 shows SEM photomicrographs of several AlN-coated specimens tested in Run 3-8.

Subsequently, the Li temperature in the vessel was lowered to 300°C and additional specimens of V alloy with and without prealuminization, several thermally/chemically treated AlN-coated specimens, and a "hot-dip" Al-coated V alloy specimen were exposed to Li for 120 h in Run 3-9. For the same concentration of N and Al in Li, the thermodynamic activities of these elements in Li will be much higher at 300°C than at 500°C. Analysis of exposed specimens still showed no transfer of N or Al to the V alloy specimens. All of the AlN-coated specimens performed well in terms of physical characteristics and all of them exhibited high electrical resistivity. The hot-dip specimen, which initially had a poorly adhered Al layer, exhibited complete loss of Al from the surface after exposure to Li.

A significant difference is seen in the microstructures of the coatings of specimens that were exposed to normal-purity Li and those exposed in Li that contained deliberate additions of Al and N. In the former, the surface regions of the coatings reacted with Li or impurities in Li, to produce a layer that was rich in O, Al, and probably Li. In the case of specimens exposed to Li that contained added N and Al, no such layer was observed.

To examine the thermodynamic stability of AlN in Li and the possible reactions between the AlN coating and O in Li, calculations were made to evaluate, in terms of O and N in Li, the regions in which AlN will be stable when in contact with Li. AlN can react with O in Li via three possible reactions:





Based on knowledge of the free energy of formation of AlN and various oxides, calculations were made to establish the minimum N concentration in Li that is required for AlN to be stable at several O concentrations in Li. Figure 4 shows plots of N concentration as a function of temperature for reactions 2-4 at O levels of 1, 10, 100, and 1000 wppm in Li. Also shown in the figure is a curve for the O level in Li that corresponds to a cold-trap temperature of 200°C. In these plots, for a given concentration of O in Li, AlN will be stable in the region above the curve and the oxide phase will be stable in the region below the curve. The curves also indicate that for a given temperature and at a given concentration of O in Li, there exists a definite concentration of N in Li below which the oxidation of AlN will occur. For example, based on reactions 2, 3, and 4 at 300°C and 100 ppm O in Li, the minimum N concentration needed to maintain stable AlN is 5000, 4000, and 0.1 wppm, respectively. In normal-purity (without a cold trap) Li, the O and N concentrations are generally  $\approx 100$  wppm each.

Under these conditions, the AlN coating will not react to form  $\text{Al}_2\text{O}_3$  but will react to form either  $\text{LiAl}_5\text{O}_8$  or  $\text{LiAlO}_2$ . This confirms the SEM and EDX analysis of the reaction phases observed in the present experiments. The calculations also indicate that at the higher temperature of 500°C and a concentration of O in Li of 100 wppm, the N concentrations in Li needed to maintain AlN as a stable phase are 900, 200, and 0.08 ppm, based on reactions 2, 3, and 4, respectively. The data also show that at 500°C and for an O concentration in Li cold-trapped at 200°C, the N concentrations are 180, 30, and 0.02 wppm, based on reactions (2), (3), and (4), respectively. These calculations clearly demonstrate the importance of controlling and maintaining low O levels in Li for the nitride coating to perform adequately. Furthermore, such control of O in Li is essential for the in-situ development of AlN coatings by transfer of Al and N from Li to the V alloy surface. The calculations also indicate the importance of experiments in a flowing system, in which the impurity levels can be effectively controlled by a cold trap, in contrast to experiments in either small capsules or in static vessels, as in the present experiments.

#### 4. Summary

Detailed investigations were conducted on the fabrication, metallurgical microstructure, compatibility with liquid Li, and electrical characteristics of AlN as a coating material. Several conclusions can be drawn from the study.

Coatings of AlN on a V alloy substrate can be successfully prepared by PVD. Processes that use CVD and chemical routes have potential, but substantial additional effort is needed to obtain reliable, crack-free coatings. Gas-phase nitridation has limitations unless the O content of the exposure environment is substantially reduced.

Coatings developed by PVD need a thermal/chemical hardening treatment to improve the adhesion characteristics and probably reduce the porosity of the coatings. Coating characteristics may be improved if the substrate temperature is increased during the coating process.

Experiments conducted with PVD-developed AlN coatings showed adequate chemical compatibility in normal-purity Li. They also retained their insulating properties after exposure to Li. However, the coating surfaces reacted with Li to form ternary oxides of Li, Al, and O. The growth rates of these oxides have not been established.

An endurance test of 5000 h exposure in normal-purity Li showed the AlN coating to be adherent and have high resistance after Li exposure.

Within the range of the present study, the effect of increased N content in the Li environment on the coating performance was minimal.

Hardness measurements made by nanoindentation seem to indicate that the absolute values of the hardness of the coating, rather than the difference in hardness between the coating and the substrate, may play a role in adhesion and spallation.

Significant additional effort must be expended to study the in-situ measurement of coating resistance; the concentration of impurities such as O in the coating and thermal-cycling effects are considered important.

The study of in-situ development of AlN coatings in Li must be extended. It has been established that, for a given exposure temperature and concentration of O in Li, there exists a minimum concentration of N in Li below which the AlN will react to form binary or ternary oxides with Li and Al. This minimum N concentration decreases with increasing temperature.

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Table 1. Experiments performed in Li of normal purity and in N-enriched Li

Run No. <sup>a</sup>	Temp. (°C)	Exposure time (h)	Objective	Specimens exposed	Wt. loss (mg mm <sup>-2</sup> ) and Electrical behavior <sup>b</sup>
2-8	300	600	Evaluation of AlN coatings with pretreatment at 900°C	AlN/V/900°C pretreat AlN/Al on V/900°C pretreat	0.0168 R 0.006 R
2-9	300	456	Evaluation of AlN coatings with pretreatment at 700°C for 284 h	TiN+AlN/V/900°C pretreat AlN/V/700°C pretreat AlN/Al on V/700°C pretreat TiN+AlN/V/700°C pretreat	0.0088 C 0.016 R 0.046 partially R 0.012 C
2-10	300	5000	Long-term performance of preformed AlN and Al <sub>2</sub> O <sub>3</sub> coatings at 300°C in Li	AlN/V as-coated AlN/Alum. V as-coated AlN/V/900°C pretreat AlN/Alum. V/900°C pretreat Al <sub>2</sub> O <sub>3</sub> coating on 304 SS	0.0436 C 0.0121 C 0.0261 R 0.0258 R 0.0179 C
3-5	300	480	Evaluation of AlN coatings with 900°C pretreatment	V/AlN with 900°C pretreat AlN bulk	0.009 R 0.004 R
3-6	300	456	Evaluation of AlN coatings with 700°C pretreatment	V/AlN with 700°C pretreat Alum. V/AlN 700°C pretreat	0.0355 R 0.027 partially R
3-7 <sup>c</sup>	300	24, 620	Evaluate transport of Al and/or N by addition of AlN powder to Li	V -5Cr-5Ti (no coating) Alum. V alloy (no coating) As-coated AlN on V alloy	bare: 0 Ω Al/V: 2-5 Ω High R on one side, flaking on other side
3-8 <sup>d</sup>	500	120	Evaluation of in-situ coating of AlN on V alloy and precoated samples at 500°C after Al and Li <sub>3</sub> N addition to Li	V -5Cr-5Ti Alum. V alloy V/AlN with 900°C pretreat V/AlN (coated on one side) with 900°C pretreat	C C R coated side: R uncoated side: C
3-9	300	120	Evaluation of in-situ coating of AlN on V alloy and precoated samples at 300°C	V -5Cr-5Ti Alum. V alloy V/AlN with 900°C pretreat V/AlN (coated on one side) with 900°C pretreat (2 samples) "Hot dip" Al on V alloy (KfK, Germany)	C C R coated side: R uncoated side: C C

<sup>a</sup>Run numbers that start with 2 indicate normal-purity Li; those that start with 3 indicate N-enriched Li.

<sup>b</sup>R = insulating; C = conducting.

<sup>c</sup>Chemical modification to Li = addition of 100 g high-purity AlN powder.

<sup>d</sup>Al, Li<sub>3</sub>N addition: Al added to Li = 14.2 g; N added as Li<sub>3</sub>N to Li = 25.55 g; N in Li in excess of AlN: 825 ppm.

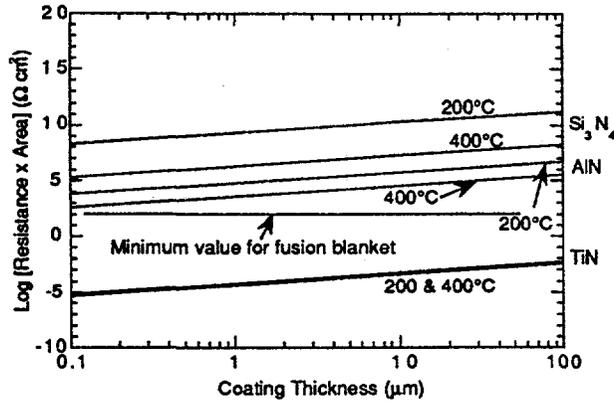


Figure 1. Resistance of AlN, Si<sub>3</sub>N<sub>4</sub>, and TiN as a function of coating thickness; requirements for fusion blanket application are shown for reference

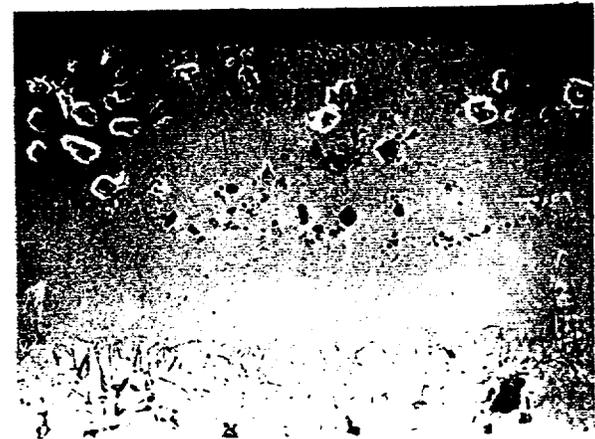


Figure 2. SEM photomicrographs of cross sections of (a) AlN-coating with 900°C hardening on V alloy, (b) AlN-coating with 900°C hardening on prealuminized V alloy, and (c) pack diffusion Al<sub>2</sub>O<sub>3</sub> coating on Type 304 stainless steel, after 5000 h exposure to Li environment of normal purity at 300°C in Run 2-10

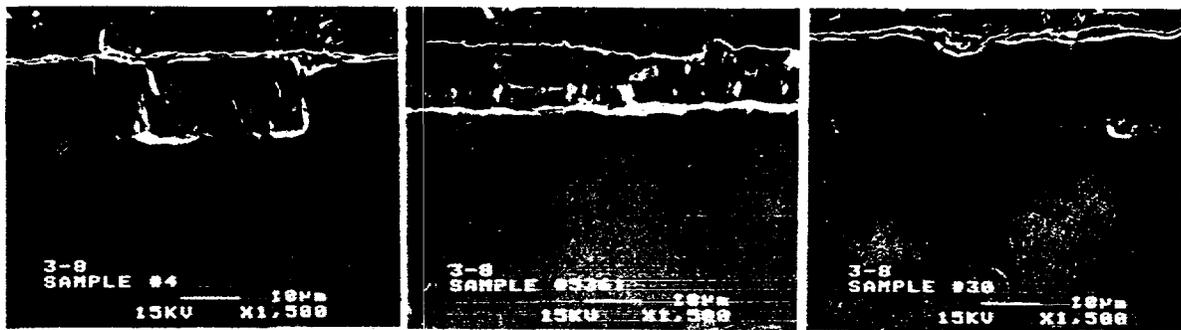


Figure 3. SEM photomicrographs of cross sections of AlN-coated specimens after 120 h exposure in Run 3-8 at 500°C to Li environment with N and Al additions

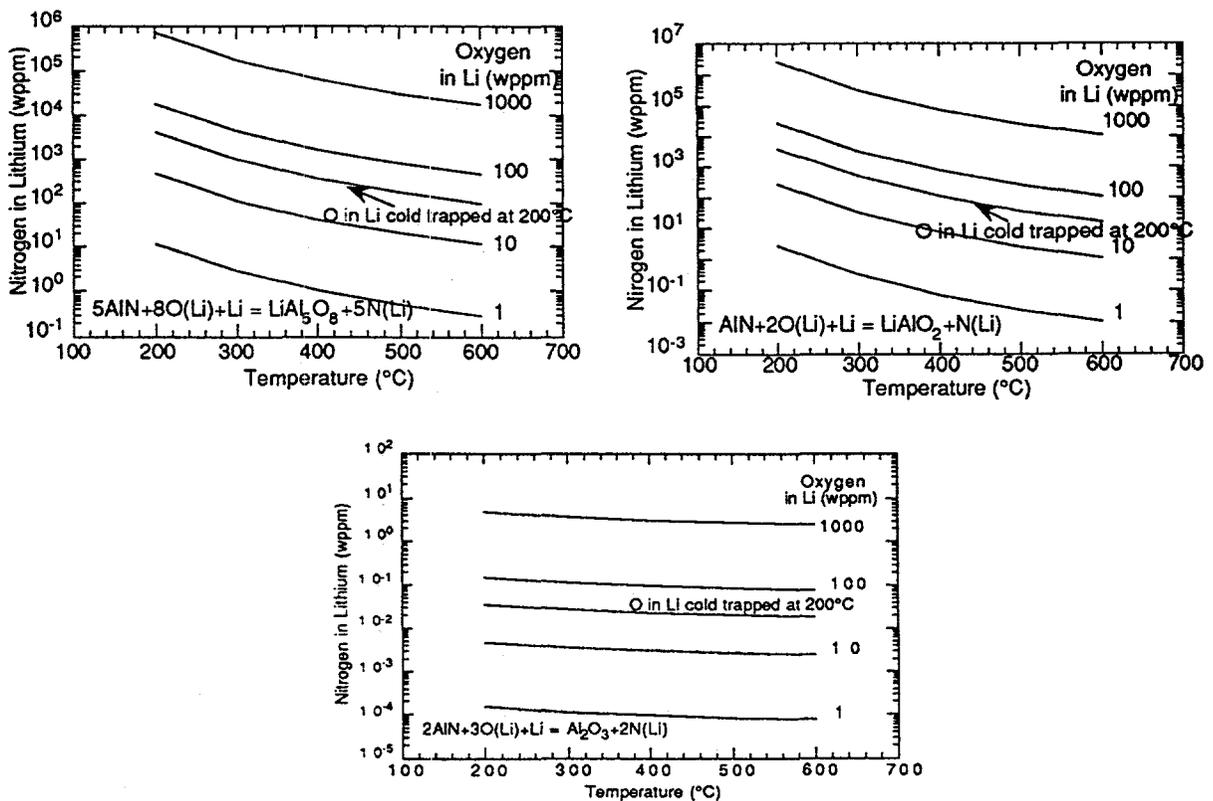


Figure 4. Regions of stability of AlN,  $LiAl_5O_8$ ,  $LiAlO_2$ ,  $Al_2O_3$  phases as a function of temperature and O and N concentrations in Li