ELSEVIER

Journal of Nuclear Materials 258–263 (1998) 488–494

journal of nuclear materials

Development and performance of aluminum nitride insulating coatings for application in a lithium environment

K. Natesan [*], C.B. Reed, D.L. Rink, R.C. Haglund

Argonne National Laboratory, Energy Technology Division, Building 212, 9700 South Cass Avenue, Argonne, IL 60439, USA

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 inner wall of cooling tubing 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 with liquid Li, and electrical characteristics of AlN as a coating material. 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. The 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 [1,2]. 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 an Li environment showed that aluminum nitride (AlN) will be stable in Li that contains a wide range of N concentrations [3,4]. Further, 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.

A review of available information on electrical resistivity values for several nitrides showed that AlN exhibits resistivities of $>10^5$ Ω m at temperatures below ≈600°C. Based on the resistivity value of AlN, a coating layer of <1 μm would be adequate from the insulating standpoint, provided that resistivity is not reduced during operation, i.e., by irradiation. Fig. 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

---

[*] Corresponding author. Tel.: +1 630 2525103; fax: +1 630 2523604; e-mail: ken_natesan@qmgate.anl.gov.

0022-3115/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII: S 0 0 2 2 - 3 1 1 5 (9 8) 0 0 3 7 0 - 5

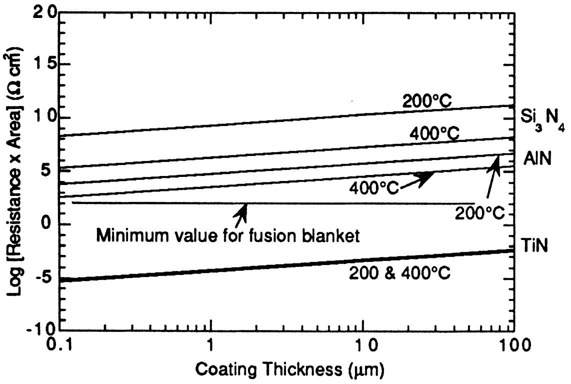

Fig. 1. Resistance of AlN, Si_3N_4, and TiN as a function of coating thickness; requirements for fusion blanket application are shown for reference.

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 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 obtained on the physical and mechanical characteristics and chemical compatibility of AlN coatings developed by PVD. This paper will discuss the information.

2. Experimental procedure

Coatings development. Aluminum nitride was sputtered reactively in the PVD process. 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 takes place at a relatively low temperature, generally not above ≈250°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 cm³/min and a chamber pressure of 20 mTorr. Subsequently, 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.

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 ≈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°C and/or 500°C to examine the compatibility of the insulator coatings. In one of the Li systems, 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

The AlN layers of V-alloy specimens coated by PVD were fairly compact and of uniform thickness in the ranges of 8–12 µm. XRD analysis showed hexagonal AlN phase with a (0 0 2) orientation [3]. No vanadium nitride (V_2N) was detected because the temperature of the substrate was <200°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 700–900°C prior to exposure in Li. XRD of these heat-treated specimens also showed hexagonal AlN phase with (0 0 2) orientation, but traces of the V_2N phase were noted because of a reaction between AlN and V at the coating/substrate interface.

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. 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. AlN-coated specimens were exposed to two Li environments, characterized by normal purity and containing higher N obtained by bubbling a N_2/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

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

Run no. [a]	Temp (°C)	Exposure time (h)	Objective	Specimens exposed	Wt. loss (mg mm^{-2})	Electrical behaviour [b]
2-8	300	600	Evaluation of AlN coatings with pretreatment at 900°C	AlN/V/900°C pretreat	0.0168	R
				AlN/Al on V/900°C pretreat	0.006	R
				TiN+AlN/V/900°C pretreat	0.0088	C
2-9	300	456	Evaluation of AlN coatings with pretreatment at 700°C for 284 h	AlN/V/700°C pretreat	0.016	R
				AlN/Al on V/700°C pretreat	0.046	Partially R
				TIN+AlN/V/700°C pretreat	0.012	C
2-10	300	5000	Long-term performance of performed AlN and Al_2O_3 coatings at 300°C in Li	AlN/V as-coated	0.0436	C
				AlN/Alum. V as-coated	0.0121	C
				AlN/V/900°C pretreat	0.0261	R
				AIN/Alum. V/900°C pretreat	0.0258	R
				Al_2O_3 coating on 304 SS	0.0179	C
3-5	300	480	Evaluation of AlN coatings with 900°C pretreatment	V/AlN with 900°C pretreat	0.009	R
				AlN bulk	0.004	R
3-6	300	456	Evaluation of AlN coatings with 700°C pretreatment	V/AlN with 700°C pretreat	0.0355	R
				Alum. V/AlN 700°C pretreat	0.027	Partially R
3-7 [c]	300	24,620	Evaluate transport of Al and/or N by addition of AlN powder to Li	V–5Cr–5Ti (no coating)	bare: 0 Ω	
				Alum. V alloy (no coating)	Al/V: 2–5 Ω	
				As-coated AlN on V alloy	High R on one side, flaking on other side	
3-8 [d]	500	120	Evaluation of in situ coating of AlN on V alloy and precoated samples at 500°C after Al and Li_3N addition to Li	V–5Cr–5Ti		C
				Alum. V alloy		C
				V/AlN with 900°C pretreat		R
				V/AlN (coated on one side) with 900°C Pretreat		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		C
				Alum. V. alloy		C
				V/AlN with 900°C pretreat		R
				V/AlN (coated on one side) with 900°C Pretreat (2 samples)		Coated side: R Uncoated side: C
				"Hot dip" Al on V alloy (FZK, Germany)		C

[a] Run numbers that start with 2 indicate normal-purity Li: those that start with 3 indicate N-enriched Li.

[b] R = insulating; C = conducting.

[c] Chemical modification to Li = addition of 100 g high-purity AlN powder.

[d] Al, Li_3N addition: Al added to Li = 14.2 g; N added as Li_3N to Li = 25.55 g; N in Li in excess of AlN:825 ppm.

and that a hardening of the coating at elevated temperature may be necessary to improve adhesion. As a result, the AlN-coated specimens were given a thermal/chemical hardening treatment in which specimens were heated to 700–900°C in a controlled environment prior to exposure to the Li environment. 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. 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_2O_3 coating to Li for 5000 h at 300°C. Fig. 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_2O_3-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 ultra low-load indentation method that involved a nanoindenter was used to evaluate the hardness of several as-coated and Li-exposed specimens. Details on the test procedure and hardness calculations are presented elsewhere [4]. Several samples were analyzed by the nano-indentation 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.

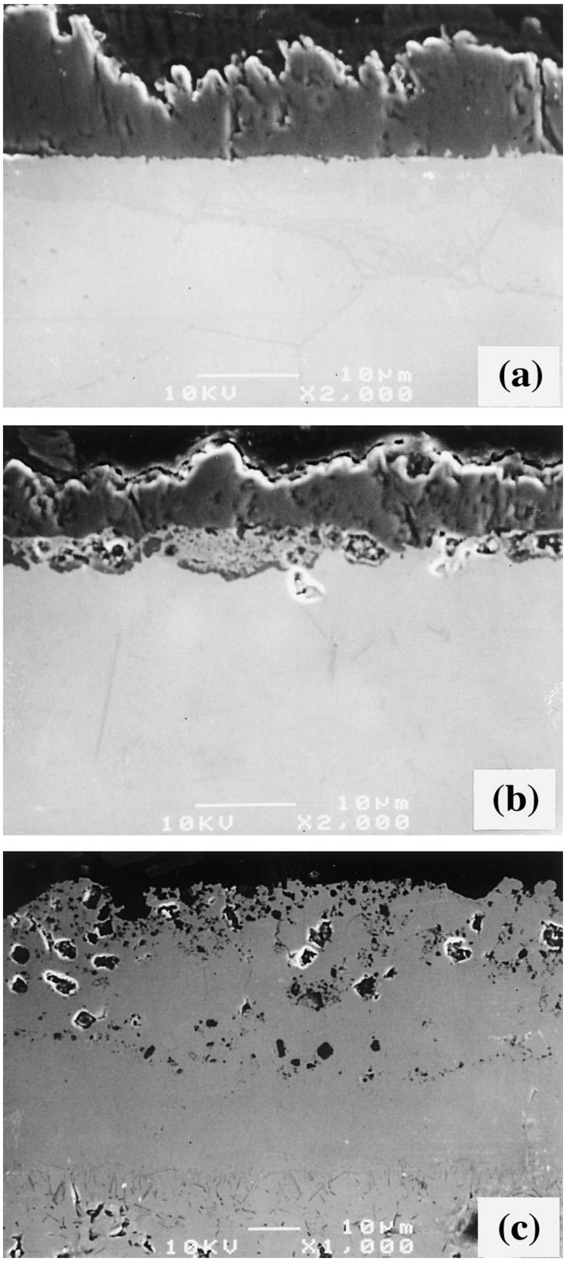

Fig. 2. SEM photomicrographs of cross sections of: (a) AlN-coating with 900°C hardening on V alloy; (b) AlN-coating with 900°C hardening on prealuminized V-alloy; (c) pack diffusion Al_2O_3 coating on Type 304 stainless steel, after 5000 h exposure to Li environment of normal purity at 300°C in Run 2-10.

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 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. 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. 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 result 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 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_3N. Additions of 14.2 g of Al and 25.5 g of Li_3N 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. Fig. 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

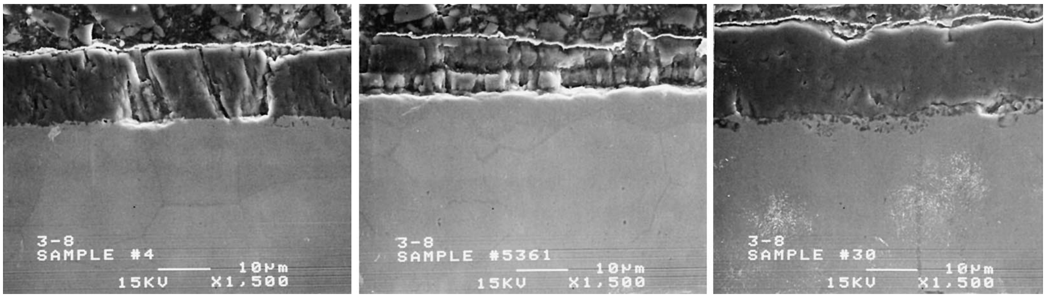

Fig. 3. SEM photomicrographs of cross sections of three different AlN-coated specimens after 120 h exposure in Run 3-8 at 500°C to Li environment with N and Al additions.

when in contact with Li. AlN can react with O in Li to form $LiAl_5O_8$, $LiAlO_2$, or Al_2O_3.

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. Fig. 4 shows plots of N concentration as a function of temperature for reactions leading to $LiAl_5O_8$, $LiAlO_2$, or Al_2O_3 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 the stability of $LiAl_5O_8$, $LiAlO_2$, or Al_2O_3 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 Al_2O_3 but will react to form either $LiAl_5O_8$ or $LiAlO_2$. 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 the stability of $LiAl_5O_8$, or $LiAlO_2$, and Al_2O_3, 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. 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

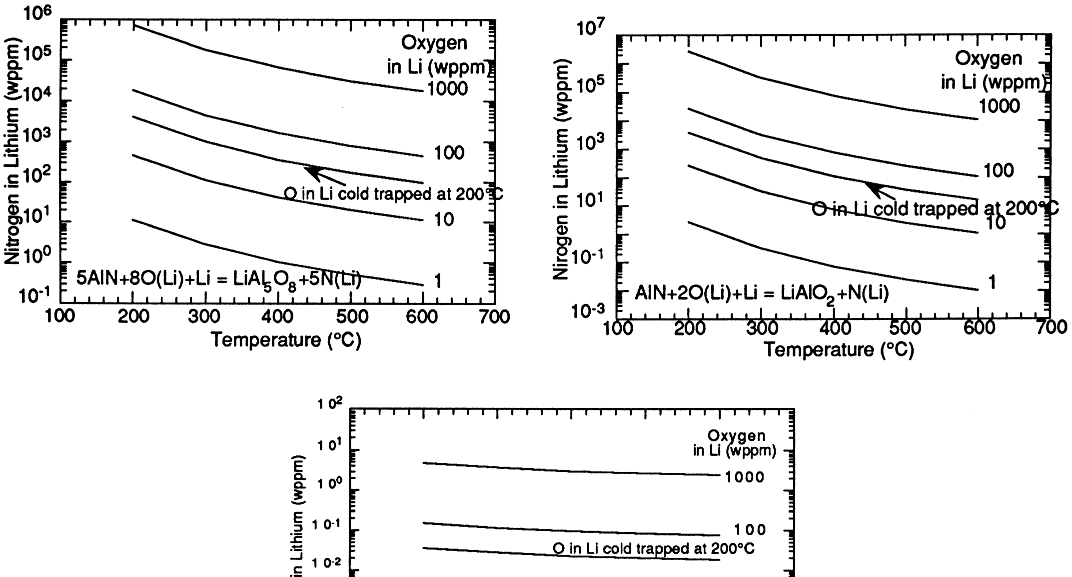

Fig. 4. Regions of stability of AlN, $LiAl_5O_8$, $LiAlO_2$, Al_2O_3 phases as a function of temperature and O and N concentrations in Li.

the study. Coatings of AlN on a V-alloy substrate can be successfully prepared by PVD. These coatings needed a thermal/chemical hardening treatment to improve the adhesion characteristics and probably reduce the porosity of the coatings. These 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 Li of normal purity showed the AlN coating to be adherent and have high resistance after Li exposure. Within the range of the present study, the effect of the increased N content in the Li environment on the coating performance was minimal. Hardness measurements made by nano-indentation 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 a play a role in adhesion and spallation.

Significant additional effort must be expended to study the in situ measurement of coating resistance; the concentrations 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.

Acknowledgements

The authors thank J. Kammer of Midwest Technologies for assistance in developing and/or supplying coated specimens. At Argonne National Laboratory, B. Tani and M. Lanagan assisted with X-ray diffraction analysis of specimens. This work has been supported by the US Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38.

References

[1] S. Malang, L. Bühler, MHD pressure drop in ducts with imperfectly insulating coatings, Argonne National Laboratory Report ANL/FPP/TM-269 (1994).
[2] S. Malang, H.U. Borgstedt, E.H. Farnum, K. Natesan, I.V. Vitkovksi, Fusion Eng. Design 27 (1995) 570.
[3] K. Natesan, Development of aluminium nitride insulator coatings for fusion reactor applications, Argonne National Laboratory ANL/FPP/TM-278 (1995).
[4] K. Natesan, D.L. Rink, Physical and mechanical characteristics and chemical compatibility of aluminium nitride insulator coatings for fusion reactor applications, Argonne National Laboratory Report ANL/FPP/TM-290 (1996).
[5] K. Natesan, J. Nucl. Mater. 233–237 (1996) 1403.