FABRICATION OF ALUMINUM NITRIDE AND ITS STABILITY IN LIQUID ALKALI METALS*

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OBJECTIVE

The objectives of this task are to (a) evaluate several fabrication procedures for development of aluminum nitride (AlN) coatings on the candidate first–wall structural material V-5wt.%Cr-5wt.%Ti, (b) evaluate the stability of coatings in contact with the structural alloy and liquid Li at temperatures of 200 to 400°C, (c) measure the electrical resistivity of the coated films after exposure to liquid Li, (d) evaluate the effects of coating defects on electrical resistivity, and (e) establish in-situ repair procedures to maintain adequate electrical insulating properties for the coatings.

SUMMARY

AlN has been selected as a prime candidate to electrically insulate the V–alloy first wall in the self-cooled concept for ITER application. Several methods are being evaluated for fabrication of AlN coatings with adequate thickness and the desirable physical, electrical, chemical, and mechanical properties. Coatings developed thus far are being evaluated by exposure to liquid Li at temperatures of 300 to 400°C.

BACKGROUND

Extensive thermodynamic calculations have been made to evaluate potential candidates that are (a) chemically compatible in liquid Li and (b) possess adequate insulating characteristics for use as a coating on the first–wall and blanket structural material. A review of available information on the electrical resistivity values for several oxides, nitrides, and oxynitrides showed that a number of oxides (e.g., CaO, MgO, SiO_2, Al_2O_3, $MgAl_2O_4$) and nitrides (e.g., AlN, Si_3N_4) have resistivities $>10^5$ Ω-m at temperatures below ≈600°C. The requirement is that the product of insulator coating electrical resistivity times thickness should exceed a nominal value of 0.1 $\Omega\ m^2$ under operating conditions. This translates to a minimum resistivity value of 10^5 Ω-m for a coating thickness of 1 µm, or a resistivity of 10^4 Ω-m for a coating thickness of 10 µm. Based on resistivity values of the materials listed above, a coating layer <1 µm in thickness of any of these materials would be adequate from the insulating standpoint, provided the resistivity is not reduced during operation, i.e., by irradiation. The primary candidate for application in Li is AlN, which, based on thermodynamic stability calculations, will be stable in Li with a wide range of N concentrations [1].

EXPERIMENTAL PROGRAM

Several possible approaches are being examined to develop an AlN coating on the structural material. Some of these are (a) prealuminize the surface of the material by a (pack) diffusion process and subsequently convert it to nitride in an external gas atmosphere, (b) a physical vapor deposition process with and without bond coats, (c) a chemical vapor deposition process at temperatures of 600 to 900°C, (d) a low-temperature method involving sequential reactions, (e) prealuminize the surface of the alloy and convert it to nitride in a high-N Li environment, (f) preexpose the material to liquid Al and convert it to nitride in Li, (g) in-situ formation of coating in Li with high thermodynamic activities for Al and N, and (h) prealuminize specimens of structural material and nitride it by using N_2 cover gas during Li exposure.

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RESULTS

Fabrication of Coatings. The pack process is a well-established approach for covering stainless steels and Ni–base alloys with layers of an intermediate phase [2]. The substrate materials are contacted and heated for 4-12 h at ≈900°C with a pack of powders. 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 amount of Al can be reduced by partial replacement with Ni. The Al deposited on the substrate surface diffuses into the subsurface regions of the material, where it forms intermetallic phases as aluminides of Fe or Ni. Because the substrate materials are heated to temperatures close to the annealing range for times sufficient to cause solution processes in the matrix, the materials need a final treatment in order to optimize the structure. The aluminide layers reach thicknesses of 0.025–0.20 mm, depending on the composition of the substrate materials. Aluminum concentrations as high as 60 wt.% have been obtained at depths of 5-10 µm in the V alloy and decreasing to 30 wt.% at depths of 15-30 µm [3]. The diffusion processes lead to layers of 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.

During this period, aluminum nitride coatings were made by reaction sputtering in low–pressure N_2 atmosphere at a temperature of 400°C. The coating thicknesses after 4 h of deposition were ≈5.2 µm. The coating covered the entire surface of the V–alloy specimen and the layer was found to be of very high resistance, indicating adequate insulating properties. The coated specimens were also given a thermal/chemical treatment at elevated temperature to harden the coating without affecting its insulating characteristics. Aluminum nitride coatings on the V alloy were also prepared by a commercial physical deposition technique. Specimens with ≈10-µm-thick coatings of pure AlN were prepared; they exhibited high resistances similar to those of bulk AlN samples sintered from powder.

Testing of Coatings in Liquid Metals. AlN-coated samples of V-5Cr-5Ti and bulk samples of AlN were exposed at 300°C to a static lithium environment for 120-430 h. Lithium purity was maintained at the levels normally present in commercially available lithium. Another set of specimens were exposed for 430 h to a static lithium environment in which the nitrogen concentration was increased by bubbling 1 vol.% N_2-Argon mixture for 24 h at 300°C. After exposure, lithium from the exposed specimens was dissolved in alcohol and then in water, and the specimens were examined for their insulating characteristics and coating integrity. Figure 1 shows scanning electron micrographs of aluminized V-5Cr-5Ti alloy specimens with sputter-deposited AlN coating after exposure to low- and high-nitrogen lithium environments at 300°C for 430 h. These specimens exhibit multiple layers, the outermost of which is pure AlN. The intermediate layer consists of Al, V, and N. The layer adjacent to the substrate alloy consists predominantly of Al and V and corresponds to that developed during the prealuminizing treatment. Figure 2 shows a scanning electron micrograph of V-5Cr-5Ti alloy specimen with a physical-vapor-deposited layer of AlN after exposure at 300°C to a high-nitrogen lithium environment for 430 h. The thickness of the coating layer initially was ≈12 µm, and after exposure the coating seems to be intact. Resistances of these coated specimens after lithium exposure were high (measurement was not possible with a simple voltmeter) and comparable to those observed in bulk AlN samples. Detailed analysis of these specimens are in progress. Further, long-term exposures of specimens coated by different techniques are in progress in a lithium environment. In addition, coatings with and without deliberately made defects will be exposed to lithium environments.

REFERENCES

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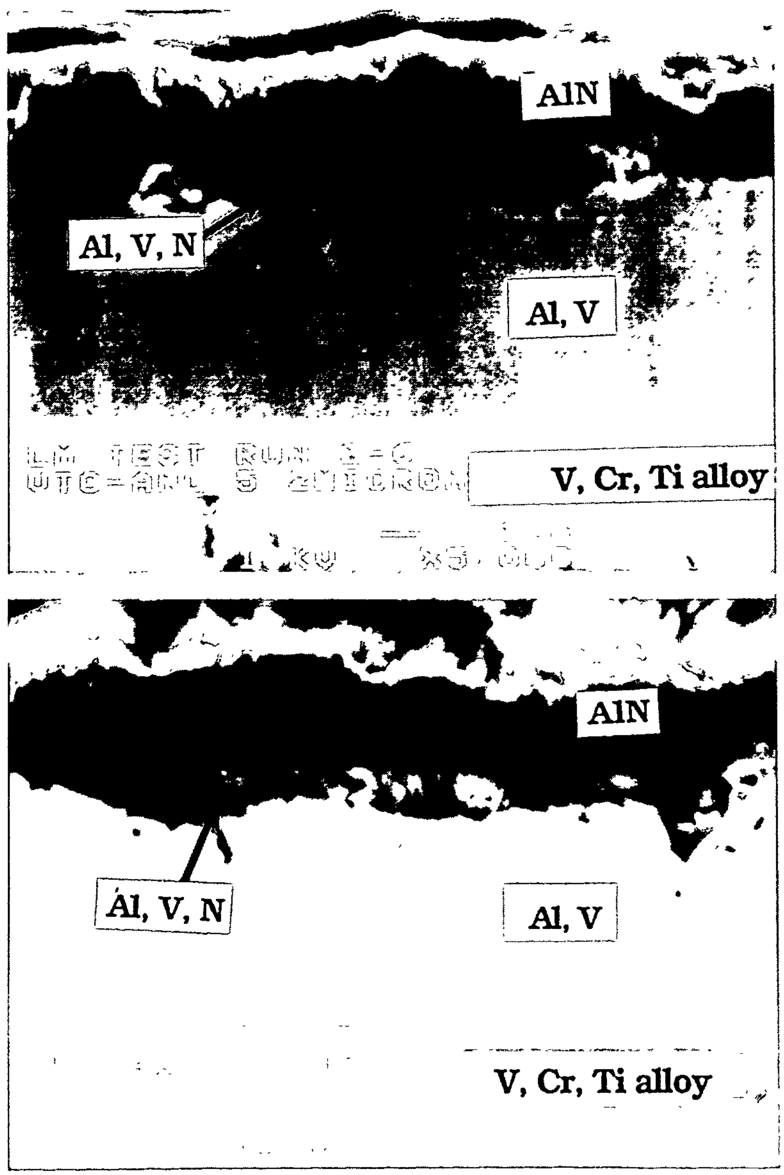

Figure 1. Scanning electron micrographs of aluminized V-5Cr-5Ti alloy specimen with sputter-deposit coating of AlN after exposure at 300°C for 430 h in lithium environment containing (top) low nitrogen and (bottom) high nitrogen.

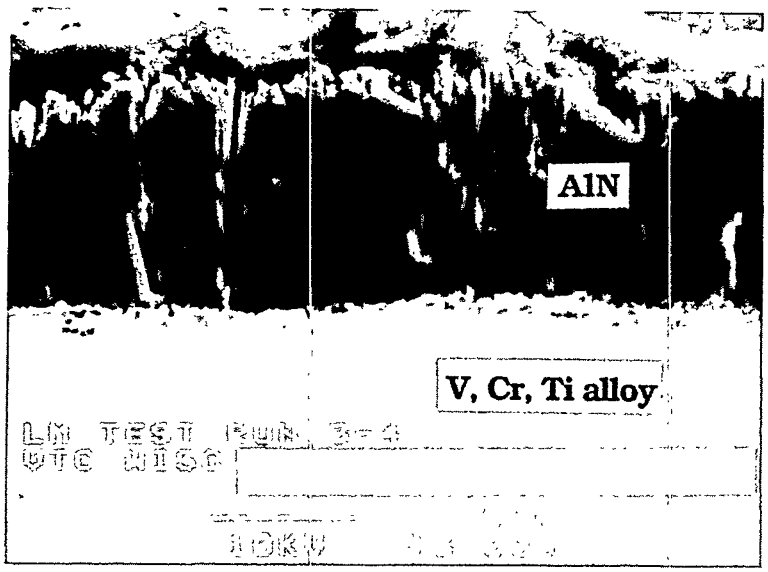

Figure 2. Scanning electron micrograph of V-5Cr-5Ti alloy specimen with physical-vapor-deposited coating of AlN after exposure at 300°C for 430 h in lithium environment containing high nitrogen.