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Properties of AlN coatings produced by RF sputtering method

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Abstract

The development of insulating coatings is one of the most important subjects in fusion reactor liquid lithium blankets. AlN, Y_2O_3 and Er_2O_3 are thought to be good candidate materials for ceramic coatings because of their high electrical resistivity and high compatibility with liquid lithium. In this study, AlN coatings were fabricated by the RF sputtering method, and their properties were investigated. The coatings were similar to the composition rate by XPS analysis, and crystal grains grow as (1 0 0) face when the fabrication temperature became higher. Although deterioration of electrical resistivity was shown in all coatings, the coatings still have high resistivity. After annealing, the crystallinity of the coatings increased. After exposure in liquid lithium, almost all of the coatings were lost and only small fragments remained.

1. Introduction

A liquid blanket system is attractive for a DEMO (demonstration) fusion reactor, because liquid tritium breeding material can be continuously reprocessed, its thermal transfer is higher than the solid breeders, and it has no radiation damage and a large TBR (tritium breeding ratio). Liquid lithium is considered to be one of the best candidate breeding materials for a self-cooled liquid blanket system. In this system, a sufficient TBR can be obtained without neutron multipliers, such as Be, due to the high lithium density in the blanket. Thus, the liquid lithium blanket concept offers an economic system with a simple structure. One of the critical issues for a self-cooled liquid lithium blanket concept is the magneto-hydrodynamics (MHD) pressure drop. The pressure drop, induced by electric current between the coolant and the pipe wall, will require intolerably large pumping power for the metallic coolant. To solve this problem, an electrically insulate ceramic coating is needed on the inner surface of pipe walls [1–3]. These coatings should have high electrical resistivity, high corrosion resistance, high thermo mechanical integrity and low nucleus reactiveness. Aluminum nitride (AlN) [4–14], yttrium oxide (Y_2O_3) [7,12] and erbium oxide (Er_2O_3) [12] have been proposed as good candidate materials based on compatibility with liquid lithium.

In previous work, several kinds of methods were used to fabricate coatings. Vapor deposition is one of the most major methods that have been used to fabricate MHD coatings. RF sputtering method is another major method to fabricate ceramic coatings. It has the ability to coat high melting temperature materials and can fabricate more adhesive and crystalline coatings than vapor deposition. From tests of bulk AlN, it was determined that the coating should have high crystallinity and low oxygen impurity to be compatible with liquid lithium [13]. The goal of this study was to fabricate high crystalline and low impurity AlN coatings, using RF sputtering.

2. Fabrication and properties of coatings

2.1. Fabrication apparatus

The target was bulk material of AlN whose purity was 99.9% and diameter was φ60 × 5 mm. Substrates

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which were 10 mm × 10 mm × 0.5–1.0 mm size of SUS 430 or V–4Cr–4Ti (called NIFS-HEAT-II) were cleaned in an ultrasonic bath. The substrates were put into a vacuum chamber and the chamber was evacuated. After the chamber exhausted sufficiently, environmental gas which is 99.995% of purity N_2 was introduced into the chamber at 0.17–0.80 Pa. In sputtering method, sputtering gas is usually Ar, but in fabrication of AlN coatings, lacking of N of the coatings occur. This problem can be avoided by using of N_2 gas [14]. Substrates were heated up to 423–673 K. While fabricating coatings, substrates were heated and controlled to 573, 673 K or not heated. In the no-heating process, surfaces of the substrates were heated to 423 K in the N_2 plasma. Radio frequency electric power was introduced to generate plasma for 100–400 W. Distance between the target and the substrates were fixed at 40 mm.

2.2. Coatings properties

All the coatings had interference fringes, and the coating thickness was 0.3–7.0 μm. The coating thickness increased as the sputtering gas pressure increased, and it also increased with the input electrical power. Observed by SEM-EDS, the coatings appeared to be smooth and uniform. By X-ray photoelectron spectroscopy, the coatings have almost no impurities except oxygen. The ratio of Al and N is about 1:1, and there is about 3–10 at.% of oxygen in the coatings. After fabrication, the coatings were observed by X-ray diffraction with Cu-Kα (Fig. 1). Specimens were fabricated on V–4Cr–4Ti substrates, with a gas pressure of 0.7 Pa and input power of 200 W. Crystallinity of the coatings was affected by the fabrication temperature. Several peaks can be seen in the pattern of the coatings fabricated at 423 K, however, almost no other peak except the peak at 33° (1 0 0) can be seen in the pattern of the coatings fabricated at 673 K. This suggests that crystal grains grow in several directions at low substrate temperature, and when the temperature becomes high, most grains grow to (1 0 0).

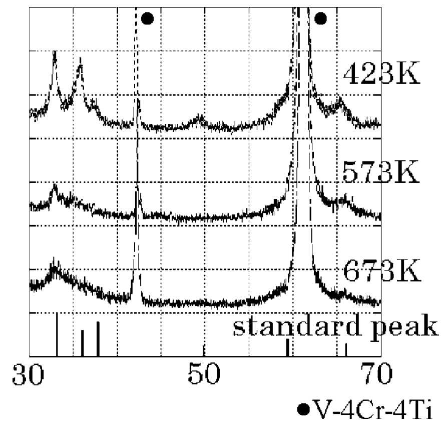

Fig. 1. Difference of XRD pattern of the coatings fabricated at different temperature.

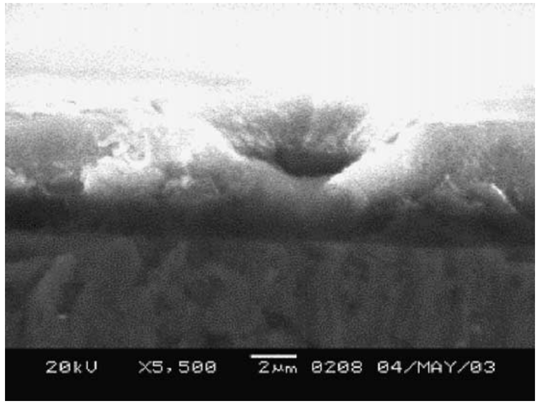

Fig. 2. SEM photomicrograph of cross section of AlN coatings.

For electrical resistivity measurements, the two-electrode method was used. Resistivity was measured at room temperature in air. In the measurements, three kinds of electrodes were used, copper tape, silver paste and a sputtered platinum layer. Electrical resistivity was $\sim 10^{13}$–10^{14} μm using copper tape, $\sim 10^{10}$–10^{12} μm using silver paste, and $\sim 10^{3}$–10^{7} μm using sputtered platinum. This difference is due to short circuits by pits or cracks on the surface of the coatings. Fig. 2 shows the coating surface. A typical crack on the surface is about 2 μm in diameter. About 5–10 of these cracks were observed in 10×100 μm^2 by SEM. Therefore, the cracks were about 0.6–1.0×10^{-2} of the coatings.

2.3. Li exposure test procedure

After fabrication, some of the coated specimens were exposed to Li. Specimens were suspended with SUS316 wire. In an Ar gas glove box, the specimens were put into a Mo crucible, contains 15 g of lithium, and the Mo crucible was put into a sealed vessel. The vessel was taken out of the glove box and was pressurized with Ar gas and heated to 673 and 973 K in 50 h. After the exposure time, Ar gas flow was stopped and the vessel cooled naturally to room temperature. After cooling, the specimens were remove in the glove box. The specimens were cleaned in water to remove residual Li on the surface.

3. Behavior under fusion reactor environment

3.1. Property changes after annealing

The coatings were annealed at 673 and 973 K in 1 atm Ar. No change was observed by SEM-EDS. Using

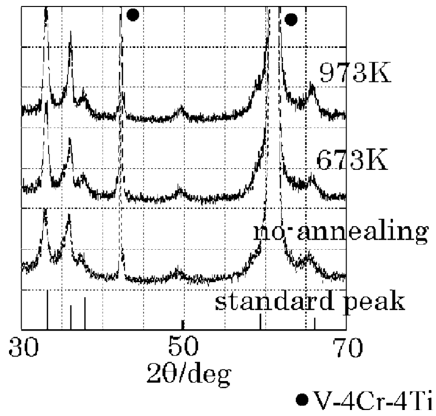

Fig. 3. Difference of XRD pattern of the coatings fabricated at 423 K.

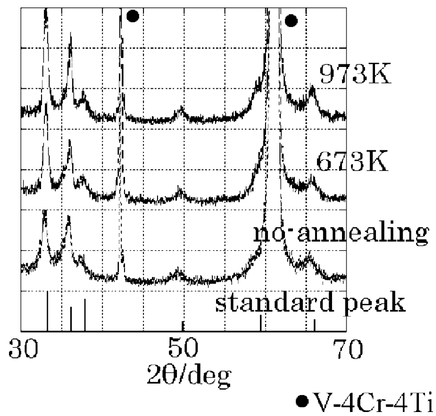

Fig. 4. Difference of XRD pattern of the coatings fabricated at 673 K.

XRD, the specimens have different crystallinity with peaks shifted to a higher angle, which is close to the standard peak of AlN [15] (Fig. 3). The peaks also became sharp as and their intensity increased. This suggests that the crystallinity was increased by annealing.

The ratio of intensity of the peak at 36° (0 0 2) to 33° is 60% from the standard AlN pattern. The ratio of the un-annealed specimen is higher than 60%. Although the intensity of the peak at 36° became higher by annealing, the ratio of 36° to 33° became close to 60%. Ratio of intensity of the peak at 38° to 33° is 80% from the standard AlN peaks, however, the intensity of the peak at 38° is much lower than 80%. It is suggested that most grains grow to (1 0 0) or (0 0 2) and a few grow in other directions. After annealing, the crystal structures becomes close to bulk materials.

Fig. 4 shows the XRD pattern of the coatings fabricated at 673 K. The intensity of the peak at 33° increased with annealing. This peak is the only one observed. It is suggested that the coatings have formed a (1 0 0) orientation during temperature fabrication, and this orientation increases with annealing.

3.2. Compatibility test with liquid lithium

Liquid lithium exposures were made at 573, 673 and 773 K for 75 h. After the exposures, almost all coatings were lost, and only small fragments remained after 573 K exposure. It is believed that oxygen in the coatings exists as Al_2O_3, which dissolved in liquid lithium. This may have attacked the substrate–coating interface and pealed off the coatings. Reducing the oxygen impurity is needed for developing liquid lithium compatible AlN coatings.

4. Conclusion

AlN coatings were fabricated by RF sputtering. The coatings had 3–10 at.% of oxygen as impurity, and ratio of Al to N 1:1. All the coatings had some amount of crystallinity observed by XRD, and the orientation depended on fabrication temperature. Crystal grains grow as (1 0 0) faces when the fabrication temperature was high. Crystallinity of the coatings increased with annealing. Coatings sintered in liquid lithium were mostly lost.

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