



Compatibility of AlN with liquid lithium

T. Terai ^{a,*}, A. Suzuki ^{b,1}, T. Yoneoka ^a, T. Mitsuyama ^a

^a Department of Quantum Engineering and Systems Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^b Fusion Engineering Research Center, National Institute for Fusion Science, 322-6 Oroshi, Toki, Gifu 509-5292, Japan

Abstract

Development of ceramic coatings is one of the most important subjects in liquid blanket research and development. Compatibility of sintered AlN and AlN coatings with liquid lithium, a candidate breeding material, was investigated. Sintered AlN with or without the sintering aid of Y₂O₃ examined in lithium at 773 K for 1390 h showed a slight decrease in electrical resistivity because of a reduction in Al₂O₃ impurity, though AlN and Y₂O₃ components themselves were subject to no severe corrosion. On the other hand, AlN ceramic coatings on SUS430 with high resistivity (>10¹¹ Ω m) fabricated by the RF sputtering method disappeared in liquid lithium at 773 K in 56 h. This may be because cracks were formed due to the difference in thermal expansion between the coatings and the substrate or because the oxide formed between the two was removed by liquid lithium. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In fusion reactor designs, liquid blanket concepts are promising ones to realize DEMO fusion reactors of high power density, because they have advantages such as continuous replacement of breeders for reprocessing, no radiation damage of the breeder material, larger tritium breeding ratio, a simpler blanket structure and better heat transfer than solid blankets. On the other hand, they have several critical issues: (1) large magnetohydrodynamic pressure drop requires large pump power in self-cooled designs, (2) liquid breeders have high chemical reactivity, including low compatibility with structural materials and (3) tritium may leak to the environment due to permeation through structural materials. As a way to reduce the magnetohydrodynamic pressure drop, insulating ceramic coatings on the duct wall has been proposed. Coatings are also useful as a corrosion barrier protecting structural materials from liquid metal attack and as a tritium permeation barrier

decreasing tritium leakage through the blanket structural materials [1].

The material of the ceramic coatings is required to be sufficiently stable, in particular, in liquid lithium blanket systems, because liquid lithium is chemically reactive compared with the other liquid blanket candidates such as Li17–Pb83 and 2LiF–BeF₂. Therefore, the compatibility of candidate ceramics and their coatings with liquid lithium is an important subject of investigation. Limited candidate oxides for coatings have been proposed [2], such as Y₂O₃, CaO, MgO and BeO, which are thermodynamically more stable than Li₂O. Though CaO, MgO, BeO themselves have good compatibility [3], Y₂O₃ is reduced to produce Y₂O_{3-x} with an increase in electrical conductivity [4]. Limited nitrides are also stable in liquid lithium. Among them, AlN is stable in liquid lithium at a wide range of N concentration [5].

Since these coatings should be formed inside tubes, they should be fabricated by wet processes such as an in situ process in liquid lithium. Coating by the in situ process, however, has not been fully successful, because of the low temperatures required to fabricate amorphous coatings, which are not considered to be compatible with liquid lithium at low impurity concentration. On the other hand, a dry process such as physical vapor deposition (PVD) is a promising method to prepare ceramic coatings; e.g., AlN coatings

* Corresponding author. Tel.: +81-3 5841 7010; fax: +81-3 5841 7010.

E-mail addresses: tera@q.t.u-tokyo.ac.jp (T. Terai), asuzuki@nifs.ac.jp (A. Suzuki).

¹ Tel.: +81-572 58 2318; fax: +81-572 58 2676.

prepared by the PVD method are compatible with liquid lithium [6].

The main impurity in AlN coatings is considered to be oxygen, which may exist as Al_2O_3 . Since Al_2O_3 is severely corroded and dissolved or damaged in liquid lithium [4], it is necessary to reduce Al_2O_3 impurity in AlN coatings. In this study, the compatibility of sintered AlN, the impurity of which is captured by yttrium, and AlN coatings, of which the impurity is decreased by the preparation method (RF sputtering), with liquid lithium were examined.

2. Compatibility of sintered AlN with liquid lithium

2.1. Experimental

We have examined two kinds of sintered AlN specimens; sintered aluminum nitride (AlN) containing Y_2O_3 as the sintering aid ($15 \times 15 \times 1 \text{ mm}^3$; 0.75 g) and sintered AlN without Y_2O_3 ($15 \times 7 \times 1 \text{ mm}^3$; 0.35 g). Generally speaking, some amount of oxygen is included in nitride specimens, which tends to exist as Al_2O_3 in sintering-aid-free AlN specimens. On the other hand, AlN specimens with Y_2O_3 sintering aid were also examined. The Al_2O_3 concentration (0.7 at.%) in this specimens became much lower by the addition of Y_2O_3 (Y_2O_3 : 0.8 at.%) than that in the sintering-aid-free specimens (1.6 at.%). Therefore, less corrosion was expected in the case of specimens containing Y_2O_3 .

The corrosion experiment was carried out by a static method. The experimental apparatus is shown in Fig. 1.

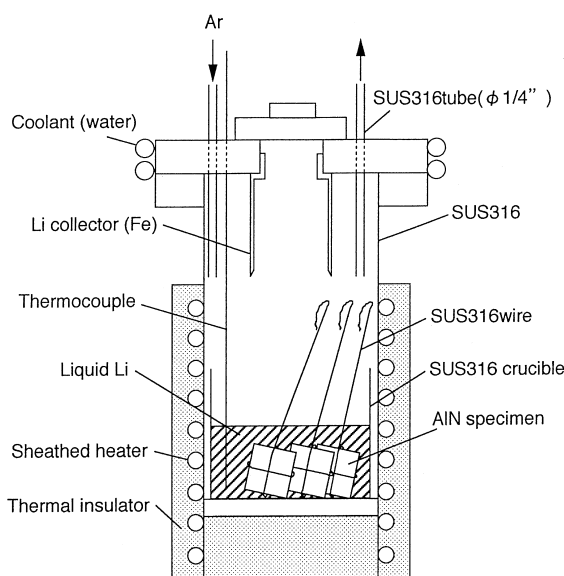


Fig. 1. Experimental apparatus for the compatibility test of sintered AlN with liquid lithium.

In a glove box with Ar gas, a crucible loaded with specimens and 20–30 g of lithium (99.9% in purity) was set in a heating container made of AISI type 316 stainless steel. At 773 K, a flow of Ar gas was introduced over the liquid. After the prescribed time, the corroded specimens were taken out from the crucible and the lithium metal adhering to them was cleaned off with water and ethyl alcohol.

The corroded specimens were analyzed as follows: (1) observation of the appearance, (2) weight change measurement, (3) X-ray diffraction (XRD) analysis and (4) electrical resistivity measurement by the two-probe method.

2.2. Sintered AlN without Y_2O_3

The AlN specimens were immersed in liquid lithium at 773 K for 1390 h. The shapes of the specimens did not change and the specimens did not become fragile, but their color changed from the original white to gray. The weights of the specimens decreased by 0.16%. The change of color was observed not only on the surface but also inside the specimens, because they were still gray after polishing the surface to reduce the thickness from 1.0 to 0.7 mm.

The weight change of the specimens was smaller than the amount of oxygen existing as solute in the AlN specimens. It is considered that part of the oxygen dissolved into the liquid, and that the Al metal left in the grains changed the color of the specimen from white to gray.

In the XRD patterns of the uncorroded specimens, two very weak peaks (shown as open circles in Fig. 2) were observed besides AlN peaks, but no Al_2O_3 peak was observed. Another very weak peak (shown as the open circle) besides the AlN peak was observed in the XRD patterns for the surfaces of the corroded specimens. For the corroded specimens, after polishing, however, all the very weak peaks were still observed, as

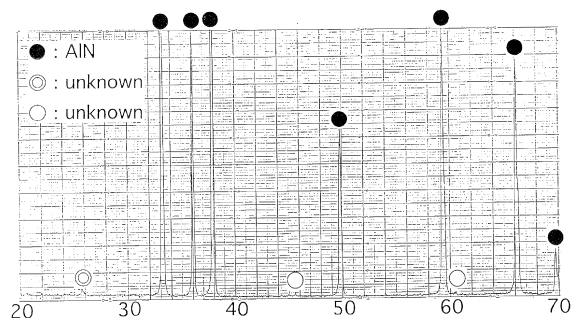


Fig. 2. XRD patterns of the polished surface of the sintered AlN without Y_2O_3 corroded by liquid lithium at 773 K for 1390 h.

shown in the Fig. 2. Assignment of these weak peaks is not clear at the moment.

The electrical resistivity of the bulk of the uncorroded specimen was determined by a Cole–Cole plot in impedance measurement at room temperature to be larger than the measurable limit of about $10^{12} \Omega \text{ m}$, but it decreased to $\sim 1 \times 10^9 \Omega \text{ m}$ for the corroded specimens before and after polishing. The reason for this decrease is believed to be aluminum deposits left in the specimens.

2.3. Sintered AlN containing Y_2O_3

The AlN specimens were immersed in liquid lithium at 773 K for 1500 h. The shapes of the specimens did not change and the specimens did not become fragile, but their original color of white changed to gray and the tone of the color was not uniform. The color change was observed only on the surface and not inside the specimen, because the color was still white after polishing the surface to reduce the thickness from 1.0 to 0.8 mm, as shown in Fig. 3.

Besides the AlN peaks, $\text{Al}_2\text{Y}_4\text{O}_9$ peaks were observed in the XRD patterns of the uncorroded specimens. As shown in Fig. 4, LiYO_2 and $\text{LiAl}_2(\text{OH})_7 \cdot x\text{H}_2\text{O}$ peaks were observed in the XRD pattern on the surfaces of the corroded specimens. For the corroded specimens after polishing, however, almost the same XRD pattern as in the case of the uncorroded specimens was observed. The hydroxide $\text{LiAl}_2(\text{OH})_7 \cdot x\text{H}_2\text{O}$ was probably formed when the specimens were immersed in water in order to remove the lithium covering them. It is considered that, on the grain boundaries of the specimens, Y_2O_3 reacts with lithium to produce LiYO_2 , which is observed in the XRD patterns.

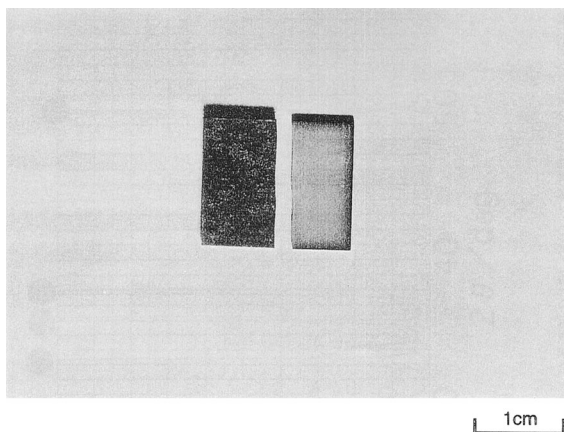


Fig. 3. Sintered AlN containing Y_2O_3 corroded by liquid lithium at 773 K for 1500 h; (left) before polishing, (right) after polishing.

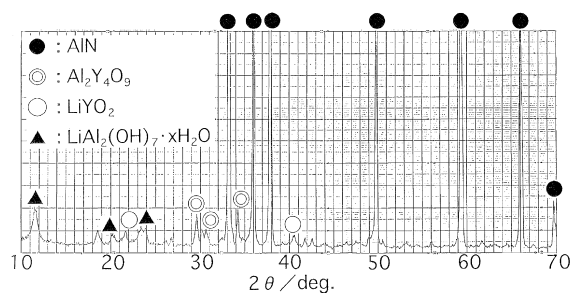


Fig. 4. XRD patterns of sintered AlN containing Y_2O_3 corroded by liquid lithium at 773 K for 1500 h.

The electrical resistivity of the uncorroded specimens was larger than the measurable limit of about $10^{12} \Omega \text{ m}$ at room temperature, and it decreased to $3.6 \times 10^8 \Omega \text{ m}$ in the case of the corroded specimens before polishing. After polishing, however, it became larger than the measurable limit again. This indicates that the decrease of resistivity was limited only to the gray-colored region, which is less than 0.2 mm in depth from the surface, and that the current was conducted only near the surface and not in the bulk in the case of the corroded specimens before polishing.

Thus, the sintered AlN containing Y_2O_3 was corroded only near the surface, and the inside of the specimen was not corroded at all in our experiment for 1500 h. The corrosion behavior near the surface is considered to be the same in the case of AlN without Y_2O_3 . The Al metal deposits left in the AlN grain may change the color and the electrical resistivity. On the other hand, the inside of the specimen was not corroded because most of the oxygen exists as $\text{Al}_2\text{Y}_4\text{O}_9$, which is thermodynamically more stable in lithium than Al_2O_3 . Probably this causes less removal of oxygen from the specimen.

3. Compatibility of AlN coatings with liquid lithium

The compatibility test of AlN coatings with liquid lithium was carried out. AlN coatings with less oxide impurity were prepared on SUS430 substrates by the RF sputtering method [7]. In order to improve the bonding between the coatings and the substrate, some AlN-coated specimens were heated at 1073 K for 100 h. The electric resistivity of the AlN coatings (about $9 \mu\text{m}$ thick) before and after heat treatment was larger than the measurable limit of about $10^{11} \Omega \text{ m}$.

The corrosion experiment was carried out in the system shown in Fig. 5. In a glove box with Ar gas, 0.5 g of lithium was set on the AlN-coated specimen with an SUS430 lid to avoid lithium vaporization, and the specimen was put in the heating container. At 773 K, a

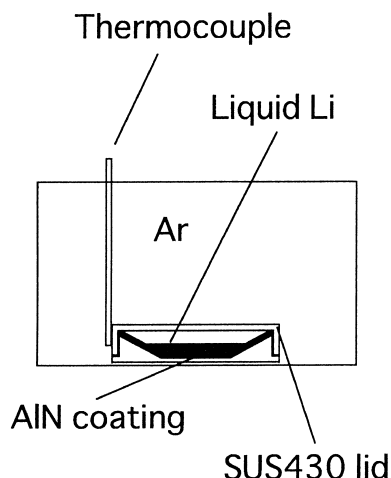


Fig. 5. Experimental apparatus for the compatibility test of AlN coatings with liquid lithium.

flow of Ar gas was introduced over the specimen. After 50 h, the specimen was taken out and immersed in water for 3 h to remove the lid and for another one hour to remove the lithium on the coatings.

After the corrosion experiment, the AlN coatings with and without the heat treatment changed in color from light yellow to metallic gloss with some white parts. Only SUS430 peaks were observed in the XRD patterns of these specimens. The electrical resistivity of these specimens was almost nothing. These means that almost all the AlN coating disappeared in the corrosion experiment, leaving only the substrate.

Thus, sintered AlN was subject to no severe corrosion, while AlN coatings prepared by RF sputtering method were severely corroded regardless of the heat treatment before the corrosion experiment. There are two ideas explaining our experimental results. The first is that the difference in thermal expansion coefficients between the substrate and the coatings causes cracks and breaks in the coatings. Crack formation in coatings by thermal expansion was also observed in Ref. [6]. The average thermal expansion coefficient of SUS430 from room temperature to 773 K is $11.7 \times 10^{-6} \text{ K}^{-1}$ [8], while that of AlN is $4.6 \times 10^{-6} \text{ K}^{-1}$ [9]. It is believed that the many small cracks generated in the AlN coatings by thermal cycles in the experiments permit liquid lithium to invade along the cracks; this destroys the whole

coating in the process of removal of lithium with water. The second is that an oxide layer on the surface of the SUS430 substrate is easily corroded by liquid lithium, thus separating the AlN layer from the substrate.

In order to avoid the separation of AlN coatings, it is believed that the surface of the substrate should be made clean by removing the oxide layer by sputtering before the formation of the coatings. It is also believed that a material having a thermal expansion coefficient close to AlN should be selected for use as the substrate or as an intermediate layer between the substrate and the AlN coatings.

4. Conclusion

The compatibility of sintered AlN and AlN coatings with liquid lithium was investigated. Sintered AlN with or without the sintering aid of Y_2O_3 examined in lithium at 773 K for 1390 h showed a slight decrease in electrical resistivity because of the reduction of Al_2O_3 impurity, though AlN and Y_2O_3 components themselves were subject to no severe corrosion. On the other hand, AlN ceramic coatings on SUS430 with high resistivity ($>10^{11} \text{ } \Omega \text{ m}$) fabricated by the RF sputtering method disappeared in liquid lithium at 773 K in 50 h. This may be because cracks were formed due to the difference in thermal expansion between the coatings and the substrate or because an oxide formed between the coating and substrate removed by liquid lithium.

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