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Fabrication of Ceramic Coatings on NIFS-HEAT by Arc-source Plasma-assisted Deposition Method for Fusion Blanket Application

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Abstract

Al_2O_3 coatings and AlN coatings were fabricated by filtered arc-source plasma assisted deposition method on a low activation vanadium alloy 'NIFS-HEAT-2' for self-cooled liquid blanket application. The AlN coating had a low electrical resistivity due to relatively large amount of Al deposited in the coatings than that of N. Al_2O_3 bulk specimens and the Al_2O_3 coating were sintered in Li20-Sn80 and Flibe. They showed a high compatibility in the Li20-Sn80 at 823 K for 1 day. In the Flibe at 823 K for 2 days, on the contrast, slight mass decreases of the bulk specimens were observed and the coatings disappeared.

Keywords:

MHD coating, PVD, Li-Sn, Flibe, corrosion, compatibility, arc-source plasma

1. Introduction

Self-cooled liquid blanket is a promising concept to realize a DEMO fusion reactor of high power density and less radioactive wastes. However, the concept has a several important issues remaining to be investigated: (1) liquid breeders have high chemical reactivity including low compatibility with tubing materials, (2) a large amount of tritium may leak to the environment due to permeation through tubing, and (3) magneto-hydrodynamics (MHD) effect causes a large pressure drop in a coolant. Ceramic coating on an inner surface of the tubing material has been proposed to reduce the corrosion of the tubing, the tritium permeation, and the MHD pressure drop by electrical insulation between the tubing and the coolant [1]. To develop the ceramic coating, it is important to investigate, first of all, the abilities of bulk ceramic candidates under the fusion blanket environments and then coating methods to maintain the abilities of the candidates.

Several liquid breeding materials have been proposed such as lithium (Li), lithium-lead (Li-Pb), lithium-tin (Li-Sn), and Flibe (a mixture of lithium fluoride and beryllium fluoride). There are a number of investigations on the coatings for Li blanket [2] and for Li-Pb one [3], however, little efforts were made for developing on the coatings for Flibe and Li-Sn. As candidate coating materials for the liquid Li blanket, CaO [4], AlN [5] and Y_2O_3 [6] have been proposed due to a high compatibility with liquid Li shown by the sintering tests. As a coating method for the Li blanket, in-situ coating method has been developed for CaO [4], and AlN coating was fabricated by plasma sputtering deposition method [7] to show its insulating ability in liquid Li [8]. On the other hand, Al_2O_3 has a high compatibility with liquid Li-Pb [9] and its coatings have

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been developed [10] to reduce tritium permeation through the tubing [11].

A coating material candidate for Li-Sn and Flibe had not been proposed. However, Al_2O_3 can be considered not only as a candidate for Li-Pb, but also as one for Li-Sn and Flibe, because this material has high thermodynamic stability and sophisticated utilities. As for a coating method, an arc-source plasma-assisted deposition method is considered to be appropriate to fabricate coatings for the fusion blankets, because high-crystalline and high-density coating can be produced at high deposition rate to a large surface area [12].

In this paper, Al_2O_3 bulk specimen was sintered in liquid Li-Sn and Flibe to investigate their compatibility, and Al_2O_3 coating and AlN coating were fabricated by filtered arc-source plasma deposition method to investigate their ability for each blanket applications. As a substrate for the coating, Japanese reference vanadium alloy 'NIFS-HEAT-2' [13] made by National Institute for Fusion Science in Japan is selected, because vanadium alloy is a promising candidate material for liquid blanket system.

2. Compatibility of Al_2O_3 with Li-Sn and Flibe

The self-cooled Li-Sn blanket strongly require an insulator coating to avoid MHD pressure drop as well as Li or Li-Pb blanket. Al_2O_3 was dissolved into liquid Li at high temperatures [14], because Li_2O is thermodynamically much more stable than Al_2O_3. However, Al_2O_3 is stable in liquid Li-Pb, which contains 17 atom-% of Li. This is because Li dissolved in Pb is stabilized to reduce chemical activity to about 4 orders in magnitude [15]. In the case of Li-Sn blanket 20 % Li was proposed as a candidate composition [16]. In these cases, Li is also stabilized. However, this could not guarantee Al_2O_3 is also compatible with Li-Sn as well as Li-Pb, because Li concentration proposed is higher than that in Li-Pb and Sn is more reactive than Pb. Therefore, experimental verification is strongly required.

A single crystal of Al_2O_3 with 10 mm in diameter and 1 mm in thickness supplied from Ohyo Koken Kogyo Co. and poly-crystal of Al_2O_3 (15 mm × 15 mm × 2.5 mm) with 99.6 % in purity (grade SSA-S) made by Nikkato Corp. are sintered in about 20 cc of liquid Li-Sn (containing 20 atom % of Li) dissolved in a Mo crucible under Ar atmosphere in a glove box. Li-Sn was made by solid Li (99 % in purity) being sintered in dissolved Sn (99.5 % in purity) in the Mo crucible at about 773 K under Ar atmosphere. The composition of Li to Sn was confirmed by measurement of its melting point. Compatibility test was performed in the Mo crucible set in a sample container, as shown in Fig. 1, heated up to 823 K for 1 day. After the sintering test, Al_2O_3 samples were picked up from dissolved Li-Sn in the glove box and sintered in nitric acid for about 4 days to remove Li-Sn remaining on the surface of the samples.

The single crystal and poly-crystal of Al_2O_3 after the sintering test did not change their thickness and weight. The single crystal did not change its appearance while the poly-crystal changed its original color of white to partly gray. This is considered to be due to very small amount of Li-Sn remaining inside small pores on the surface of the poly-crystal. Thus, compatibility of Al_2O_3 bulk specimens with Li20-Sn80 was fairly high.

As for the Flibe blanket, MHD pressure drop is much smaller than liquid metal blanket and requirement on MHD coating is small. However, there is a requirement on coating for protecting tubing material from corrosion, because hydrogen fluoride (HF) as an impurity in Flibe sometimes corrode metal samples [17]. In case of Flibe, the ceramic coatings are considered to be candidates as the corrosion-protect coating, because at high temperatures, chemical reaction of possible corrosion by HF,

$$Al_2O_3 + 6HF \rightarrow 3H_2O + 2AlF_3 \qquad (1)$$

may be highly reduced by existence of small amount of H_2O impurity in Flibe.

The other set of the single crystal and the poly-

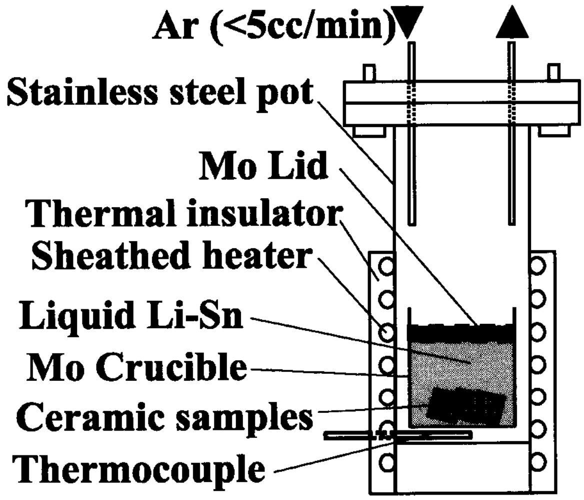

Fig. 1 Apparatus for sintering experiment.

crystal of Al_2O_3 were sintered in liquid Flibe dissolved in SUS-316 crucible installed in the sample container in almost the same apparatus as Fig. 1. Flibe was made by heating up a 2 : 1 mixture of reagent grade powder of LiF (99.9 % in purity) and BeF_2 (99.5 % in purity) supplied from Furuuchi Chemical Corp. in the Ni crucible under Ar atmosphere in a globe box. After the sintering test at 823 K for 2 days under Ar atmosphere, Al_2O_3 samples were picked up from dissolved Flibe in the glove box and sintered in a dissolved mixture of LiCl and KCl to remove Flibe remaining on the surface of the samples. The mixture of LiCl and KCl remaining on the sample was removed by water.

The weight decrease of the single crystal and the poly-crystal of Al_2O_3 were 6.6 mg/cm^2 and 1.7 mg/cm^2 respectively. The thickness decreases are calculated to be more than 5 micrometer, which means rather thick Al_2O_3 coating is required for the corrosion-protect.

The single crystal of Al_2O_3 changed its appearance into partly white and the poly-crystal change its original color of white to partly gray. These indicate chemical change may be occurred on the surface of the specimen. Figure 2 shows an X-ray diffraction (XRD) analysis of the poly-crystal sample by CuK_α with XRD peaks of Al_2O_3, $BeAl_2O_4$, and BeO. The BeO observed on the surface of the specimen is considered to be originated from O near the surface of the Al_2O_3 and Be in the mixed salt of BeF_2 and LiF. This indicates chemical reaction of possible corrosion on the surface is considered to be

$$Al_2O_3 + BeF_2 \rightarrow BeO + AlF_3 \qquad (2)$$

where BeO remains on the surface of the specimen and AlF_3 dissolved into liquid Flibe due to a large solubility of AlF_3 into Flibe. However, the weight decreases of the Al_2O_3 samples are much smaller than those of structural material candidates, such as vanadium alloy [17]. Therefore, it is considered that Al_2O_3 may still have a possibility to be a candidate coating material for the Flibe blanket.

3. Fabrication and Property of Al_2O_3 Coating

Arc-source plasma assisted deposition method is an attractive method to fabricate coatings for fusion blankets. In this method, however, the concurrent deposition of metallic macro-particle has to be avoided. The arc spot on metal cathode surface subjected to very high local power density melts and ejects macro-particles with a diameter of micrometers in magnitude. And the particles sometimes cause a significant degradation of the properties of the coating. The filtered arc-source plasma vapor deposition device at Max-Planck- Institute fur Plasmaphysik in EURATOM association, separates plasma stream from the macro-particle by toroidal separator, where the plasma is magnetically guided through a toroidal segment to the substrate and the macro-particles are caught on the walls of toroid, as shown in Fig. 3.

With this device, Al_2O_3 coatings for Li-Pb, Li-Sn, and Flibe blanket application were deposited on a plane plate substrate (25 mm × 25 mm and 1 mm in thickness)

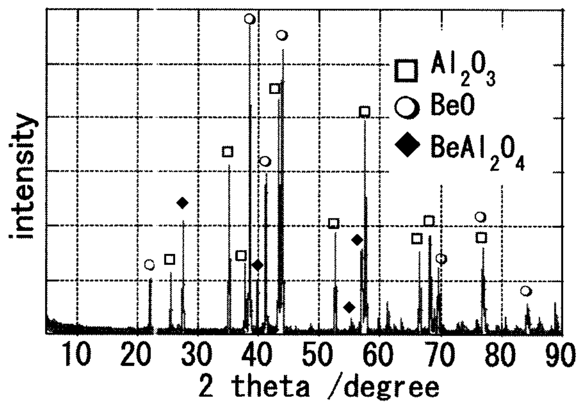

Fig. 2 XRD pattern of poly-crystal Al_2O_3 after the sintering test in Flibe.

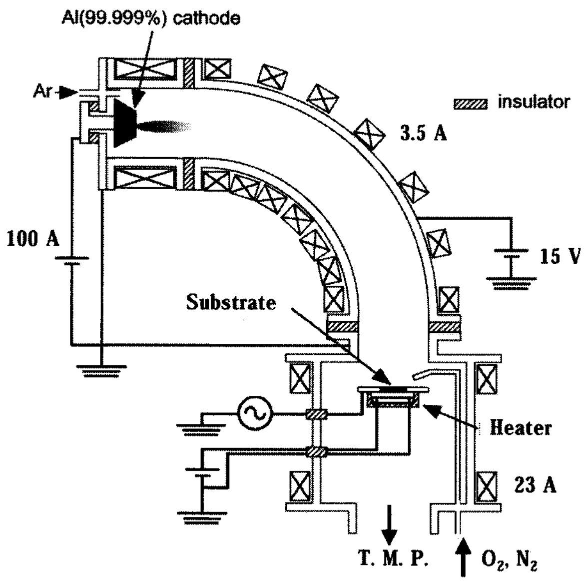

Fig. 3 Apparatus for filtered arc-source plasma-assisted vapor deposition device.

of the vanadium alloy 'NIFS-HEAT-2'. From the cathode made of 99.999 % pure Al metal, Al ions were sputtered out by the arc. The arc current was approximately 100 A. Al ions were confined to form plasma with the electron density of 10^{10} – 10^{11} cm^{-3} by magnetic fields made by a focusing coil and torus coils and main coils. To form and add O ions into the plasma, O_2 gas was introduced from a capillary near the substrate to pressure of about 5×10^{-2} Pa during the deposition. The plasma containing aluminum ions and oxygen ions is introduced to the substrate, which was heated up to about 850 K to promote relaxation of a deposited Al_2O_3 coating. After 20 minutes of deposition, the Al_2O_3 coatings with the thickness of about 1 micrometer was obtained. Characteristics of the Al_2O_3 coating deposited with this device were investigated in ref. [18] in details.

The property of the Al_2O_3 coating for the liquid blankets was tested by sintering in liquid Li-Sn and Flibe. After a compatibility test with Li-Sn at 823 K for 1 day, performed at almost the same apparatus as Fig. 1, an Al_2O_3 coating remained its high electrical resistivity (> 10^6 Ωm) as before the test. On the other hand, whole coating was disappeared after the sintering test in Flibe at 823 K for 2 days. This is because the thickness of the coating was too small to withstand the dissolution observed by the sintering test of bulk materials. Thus, the compatibility of the Al_2O_3 coating is considered to be similar to that of the bulk Al_2O_3.

4. Fabrication and Property of AlN Coating

With the filtered arc-source plasma vapor deposition device, AlN coatings for Li blanket application were deposited on the 'NIFS-HEAT-2'. Instead of O_2, N_2 gas was introduced from a capillary near the substrate or near the arc to form N ions efficiently. The N_2 pressure in the chamber was controlled from 2–10 × 10^{-2} Pa during the deposition. The substrate temperature was controlled from room temperature to 873 K. In order to increase nitrogen content in the coating, the chemical reactivity on the surface of the substrate was physically induced by the acceleration of the ionic species using 100 V of RF bias voltage in some depositions.

The deposition rate was decreased from 0.8 nm/s to 0.4 nm/s by increasing the substrate temperature from the room temperature to 873 K. Addition of RF bias voltage to the substrate effectively increased the deposition rate up to 1.2 nm/s in case of the substrate temperature being 873 K. Fig. 4 shows SEM image of a cross section of NIFS-HEAT-2 coated by AlN with 100 V of RF bias voltage and 873 K of substrate temperature. In Fig. 4, because of the plastic deformation of the NIFS-HEAT-2 during the cross cutting, an edge of the coatings was bent to broken when cutting the coated sample. This shows the coating was compact and adhesive to the substrate.

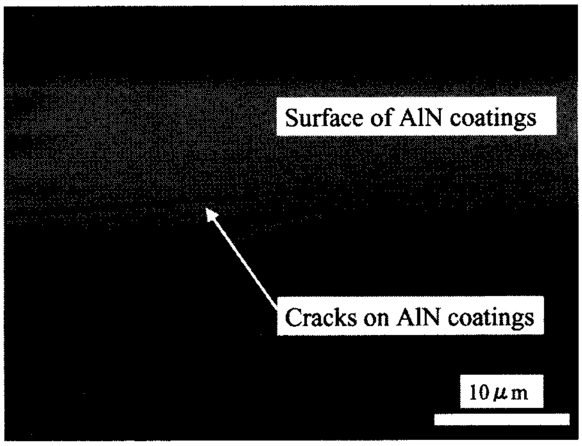

Fig. 4 Surface and cross section of AlN coatings.

One of an important property of the AlN coating as a MHD coating for the Li blanket is the electrical insulating ability (> 10^{12} Ωm). However, the electrical resistivity of the coating with 1.2 nm/s of deposition rate was only 0.05 to 1.3 Ωm depending on the location of the coating. This is far below than the required value of 10^4 Ωm for application to liquid Li blanket [2]. By the Rutherford back scattering (RBS) analysis, the concentration of N atoms in the coating was 20 – 50 % depending on the substrate temperature and the addition of bias voltage. This indicates relatively smaller amount of N ions in the plasma leads to an Al-rich coating, because N_2 has a higher binding energy than O_2. Further investigations on the arc-source plasma to increase N ions are required to develop the coatings for Li blanket application.

5. Conclusion

Al_2O_3 coatings and AlN coatings were made by the filtered arc-source plasma assisted deposition method. Al_2O_3 bulk specimens and the Al_2O_3 coating have a high compatibility with Li20-Sn80. With Flibe, however, Al_2O_3 coating shows a poor compatibility. AlN coating has a low electric insulating ability because of the depletion of N. Thus, it is obvious that the present technique can be applied to the Li-Sn blanket, however, more investigations are necessary for application to Li or Flibe blanket.

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