§2. Compatibility of Al_2O_3 Coatings with Liquid Breeding Material

Suzuki, A., Muroga, T.,
Yoneoka, T., Tanaka, S., Nishimura, H., Terai, T.
(Quantum Eng. and Systems Sci., Univ. of Tokyo),
Koch, F., Maier, H. (Max-Planck-Institute für Plasmaphysik, EURATOM Association)

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) magnetohydrodynamics (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. 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 and for Li-Pb one, however, little efforts were made for developing on the coatings for Flibe and Li-Sn. A coating material candidate for Li-Sn and Flibe had not been proposed. However, Al_2O_3 can be considered as one for Li-Sn and Flibe, because this material has high thermodynamic stability and sophisticated utilities. In this report, Al_2O_3 bulk specimen was sintered in liquid Li-Sn and Flibe to investigate their compatibility to investigate their ability for each blanket applications.

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 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. 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,

$$Al_2O_3 + 6HF \;\text{-->}\; 3H_2O + 2AlF_3 \qquad [1],$$

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-crystal of Al_2O_3 were sintered in liquid Flibe dissolved in SUS-316 crucible installed in the sample container. 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. X-ray diffraction (XRD) analysis of the poly-crystal sample by CuK$\alpha$with XRD shows Al_2O_3, $BeAl_2O_4$, and BeO perks. 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

$$Al_2O_3 + BeF_2 \;\text{-->}\; BeO + AlF_3 \qquad [2],$$

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. Therefore, it is considered that Al_2O_3 may still have a possibility to be a candidate coating material for the Flibe blanket.