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Research and development on ceramic coatings for fusion reactor liquid blankets

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Abstract

Fabrication and properties of three kinds of ceramic coatings for fusion reactor liquid blankets such as Cr_2O_3–SiO_2, Al_2O_3 and Y_2O_3 are reviewed, focusing on the activities in the University of Tokyo. A composite coating of SiO_2 particles in a Cr_2O_3 matrix was prepared on the surface of SUS316 by the chemically densified method. It has a very low tritium permeability and is quite effective as a tritium permeation barrier without the presence of the molten Li17–Pb83 alloy. An alumina (Al_2O_3) coating was prepared on the surface of SUS316 by the hot-dipping and oxidation method. It showed a very high corrosion-resistance to Li17–Pb83 and a very low tritium permeability. An yttria (Y_2O_3) coating was formed on the surface of SUS316 by the plasma-spraying method. The product has a poor compatibility with liquid lithium. However, since sintered Y_2O_3 is more resistant to degradation than plasma sprayed Y_2O_3, it may be possible to use Y_2O_3 as a ceramic coating for liquid blankets if crackfree coating is made on the surface of piping materials. © 1997 Elsevier Science B.V.

1. Introduction

In D-T fusion reactor systems, a blanket is a necessary component, where tritium is produced from lithium by the nuclear reaction with neutrons coming from the reactor core and recovered for fuel supply. In the component, heat is also generated by conversion of the kinetic energies of neutrons and γ-rays and radiation is shielded to prevent it from permeating outwards. Tritium breeders, in which tritium is generated, are categorized into two groups; solid breeders and liquid breeders. The former includes lithium-containing ceramics and the latter lithium-containing liquid metals and molten salts.

In fusion reactor designs, the liquid blanket concept is a promising one to realize a DEMO fusion reactor system of high power density, because it has advantages such as continuous replacement of breeders for reprocessing, no radiation damage for breeders, larger TBR, simpler blanket structure and better thermal transfer than solid blankets. On the other hand, it has several critical issues; (1) a large MHD pressure drop requires large pump power, in particular in self-cooling designs, (2) liquid breeders have a high chemical reactivity including low compatibility with structural materials and (3) a large amount of tritium may leak to the environment due to permeation through structural materials, particularly in Li17–Pb83 blanket concepts.

In order to solve these critical issues, a ceramic coating on the surface of structural materials is proposed. The coating should have a high electrical resistivity, high corrosion resistance, low tritium permeability and high thermomechanical integrity. Moreover, these properties should be maintained in the actual blanket conditions including a high radiation field, large production rate of hydrogen and helium atoms by transmutation, high temperature, large temperature gradient, thermal cycle, high magnetic and electric field and the presence of reductive liquid metals. Alumina (Al_2O_3), aluminum nitride (AlN), etc. have been already proposed as coating materials and some studies have been carried out on preparation, tritium permeability and compatibility with liquid metals [1–6].

The author's group has also been investigating the fabrication and properties of ceramic coatings in a collaboration with JAERI (Japan Atomic Energy Research Institute) and Tocalo in Japan. Up to the present, coatings of

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SiO_2–Cr_2O_3 [7], Al_2O_3 [8] and Y_2O_3 [9] have been prepared by several methods and examined for electrical resistivity, tritium permeability, compatibility with liquid lithium and Li17–Pb83, etc. In this paper, the author gives an overview of the research activities in the University of Tokyo.

2. SiO_2–Cr_2O_3 coating prepared by the chemically densified method as a tritium permeation barrier

The chemically densified coating (CDC) method was utilized to fabricate SiO_2–Cr_2O_3 composite coating, which has a thickness of 60 μm consisting of SiO_2 particles (30%) with a diameter of 10 μm and a Cr_2O_3 matrix (70%). Its structure is shown in Fig. 1(a). It has many good properties such as a high density, large hardness, small surface roughness, high electrical resistivity, high abration resistance, low frictional resistance, high thermal-shock resistance, high corrosion resistance and a strong adhesion to substrate [10,11].

The coating was prepared by the following procedure; (1) pre-treatment of a SUS316 specimen to remove grease from the surface, (2) coating with slurry including SiO_2 particles, (3) firing at 723 K, (4) dipping in CDC solution containing chromic acid, (5) firing at 723 K, (6) repeating the steps (4) and (5) 15 times and (7) polishing the surface.

A compatibility test of the coating with molten Li17–Pb83 was carried out [7]. A CDC-coated SUS316 specimen was immersed in a molten Li17–Pb83 alloy at 873 K for 49 h under a stream of Ar + 7% H_2. Fig. 1 shows the cross-section of the specimen observed by XMA after the test. In a position not in contact with the alloy, the CDC maintained a good feature, while in a position in contact with the alloy, the coating layer was severely attacked by the alloy. In the latter, in particular some parts of the Cr_2O_3 matrix and the SiO_2 particles were taken off from the surface, presumably due to the reduction of Cr_2O_3 by lithium in the alloy and the alloy invaded the substrate with internal corrosion. These results are reasonable from a thermodynamic point of view and CDC cannot be utilized in the presence of the molten alloy around 873 K.

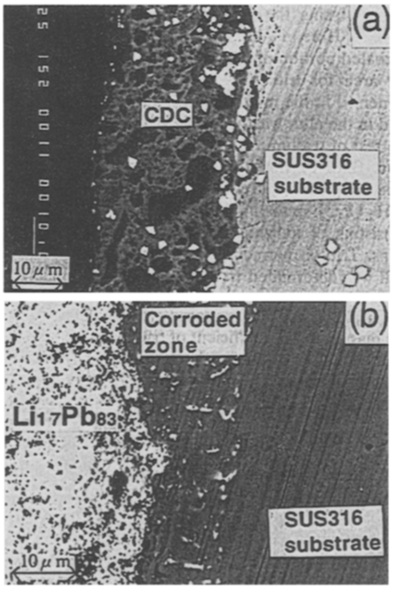

Fig. 1. XMA image on the cross section of the SiO_2–Cr_2O_3 coated SUS316 specimen after a compatibility test with Li17–Pb83 molten alloy; (a) SEM image of a position not in contact with Li17–Pb83 and (b) SEM image of a position in contact with Li17–Pb83.

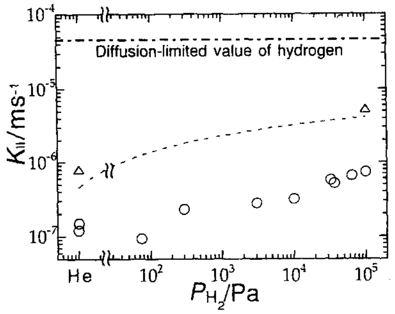

Fig. 2. Hydrogen pressure dependence of the mass-transfer coefficient at 873 K of tritium permeating through SUS 316 specimen (1 mm thick) with CDC on the front surface (△) and on the rear surface (○) and that (0.5 mm thick) without CDC (---) in the in-pile experiment.

Tritium permeability was measured in the in-pile experiment (named TREXMAN) [12,13]. Two types of CDC-coated SUS316 specimens were examined: One specimen was coated with CDC on the front surface facing the alloy and the other on the rear surface. Each of them was immersed in the molten alloy. A part of tritium generated in the alloy was released directly to purge gas and the rest of the tritium passed through the wall at the same time. Both portions of tritium released were carried separately by He purge gas including different pressures of H_2 ($P_{H_2} < 10^5$ Pa) to tritium monitoring systems consisting of ionization chambers and water bubbler traps. The mass-transfer coefficient of tritium from the molten alloy to the purge gas with permeating through the structural material (K_{II}) was obtained from the data on steady-state tritium concentrations in the both purge gas lines [14].

CDC showed a remarkably high reduction rate in the tritium permeation rate through the SUS316 specimen. Fig. 2 shows the values of mass-transfer coefficients of tritium permeating through the SUS316 specimens with CDC on the front surface or the rear surface and without CDC at 873 K. The mass-transfer coefficient of the specimen without coating slightly increases with H_2 partial pressure in the rear-side purge gas and at 10^5 Pa it has a value of 1/10 of the diffusion-limited value. This is due to a very

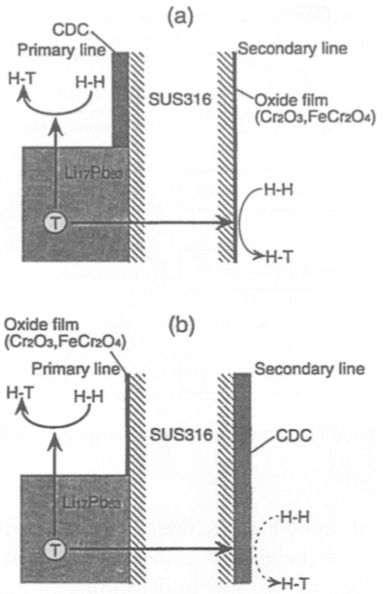

Fig. 3. Role of CDCs (a) on the front surface and (b) on the rear surface as a tritium permeation barrier.

thin oxide layer consisting of Cr_2O_3 and $FeCr_2O_4$ formed on the rear surface [15]. The specimen with CDC on the front surface showed a similar value of tritium mass-transfer coefficient as the specimen without CDC, which is explained by the degradation of the coating due to lithium attack. On the other hand, the specimen with CDC on the rear surface showed lower values by one order of magnitude than that with CDC on the front surface. This means that CDC can act as a good tritium permeation barrier on the rear surface. These situations are illustrated in Fig. 3.

It can be seen that the coating decreases hydrogen permeability by more than 2 orders of magnitude from the diffusion-limited value, depending on the partial pressure of H_2 in the rear-side purge gas and it is concluded that the coating is quite effective as a tritium permeation barrier in the absence of a molten Li17–Pb83 alloy.

3. Fabrication process and properties of Al_2O_3 coating prepared by the hot-dipping and high-temperature oxidation method

The fabrication process was investigated to obtain an Al_2O_3 coating on the surface of SUS316 specimen with high resistivity, good compatibility with Li17–Pb83 and low tritium permeability [8]. After investigation by changing some parameters such as temperature, time, atmosphere for hot-dipping, heat treatment and oxidation, the following procedure was finally determined for the preparation:

(1) Removal of natural oxide film by polishing a SUS316 specimen with sand paper.

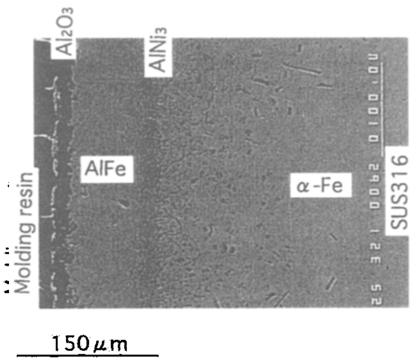

Fig. 4. Compositional image of Al_2O_3 coated SUS316 specimen.

(2) Dipping the specimen in molten aluminum at 1063 K for 3 min in Ar atmosphere for an aluminum coating on the surface.

(3) Heat treatment at 923 K for 12 h and 1223 K for 6 h to alloy aluminum with the base metal.

(4) Removal of a brown surface oxide layer formed in process (3) by polishing with sand paper.

(5) Oxidation of the surface at 1223 K for 120 h in the atmosphere of Ar + 5% H_2 + 2% H_2O.

The coating finally fabricated had a multilayered structure consisting of an Al_2O_3 layer with a thickness of several μm and alloyed layers of the base metal and aluminum, as shown in Fig. 4. In the processes mentioned

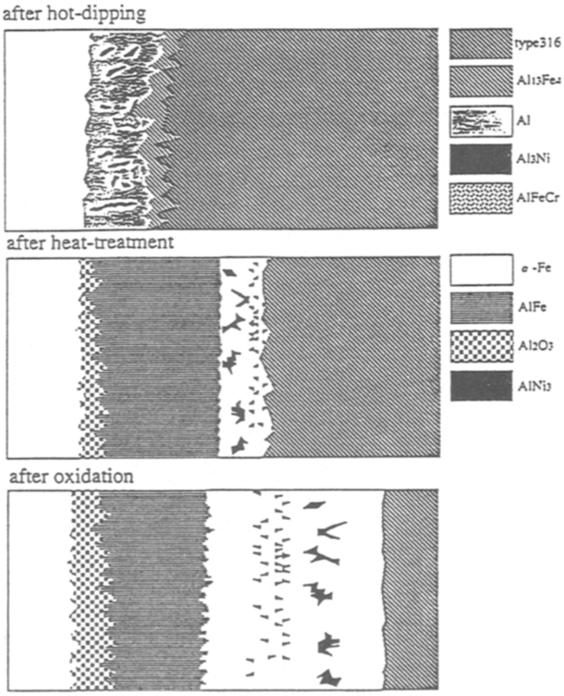

Fig. 5. Schematic drawing of each process in the formation of Al_2O_3 coating.

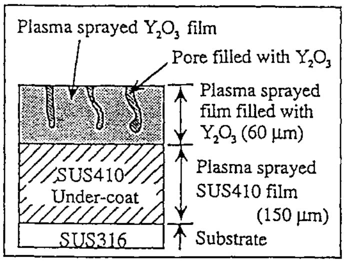

Fig. 6. Schematic view of a specimen with plasma-sprayed Y_2O_3 coating.

above, some structural changes occurred in the specimen. The schematic drawing of the structural changes identified by SEM, XMA and XRD is shown in Fig. 5.

The Al_2O_3 coating thus prepared was fairly dense, adhesive to the substrate and had a very large electrical resistivity. The Al_2O_3 coated specimen showed a very large corrosion-resistance to Li17–Pb83 and a very small tritium permeability at 873 K. From these results, it is concluded that the Al_2O_3 coating can act as a barrier to corrosion, electric current and tritium permeation in the presence of molten Li17–Pb83.

4. Fabrication and compatibility of plasma-sprayed Y_2O_3 coating with liquid lithium

An yttria (Y_2O_3) coating was successfully obtained on the surface of SUS316 by the plasma-spraying method. Actually it consisted of a plasma sprayed Y_2O_3 layer of about 50–60 μm in thickness and a plasma sprayed ferritic stainless steel (SUS410) layer of 150–170 μm in thickness on an austenitic stainless steel (SUS316) substrate shown in Fig. 6. The SUS410 intermediate layer was utilized to relax internal stress due to the difference in the thermal expansion coefficients between the other two phases. Specimens were prepared according to Fig. 7 [16].

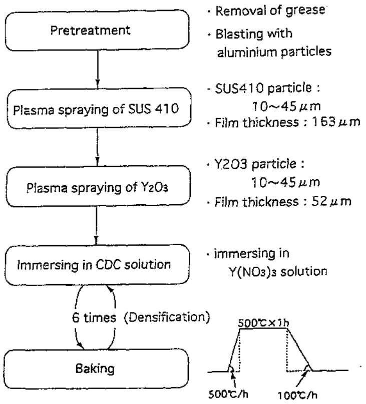

Fig. 7. Diagram for preparation of plasma-sprayed Y_2O_3 coating.

Two tests for compatibility with liquid lithium were carried out at 773 K for 150 h; with and without electric field applied. In both cases, the electrical resistivity of the specimens was monitored continuously or at intervals. Resistivity became too low to detect just 30 min after the specimen was heated. After all the experimental procedure was finished, the specimen was taken out and dipped in water for 15 min. In water, numerous gas bubbles were evolved for more than several hours from cracks of the coating by the reaction of water with lithium having penetrated into the coating. After 12 h, many black fragments of several hundred micrometers in size had been taken away from the coating into water. Almost the same results were obtained also in the experiment with no electric field applied. In these two experiments, almost all part of the coating layer were taken away from the surface of the specimens after the experimental procedure. Fig. 8 shows an example of scanning electron micrographs of the cross-section of the specimens, indicating this fact clearly.

On the other hand, in the case of the compatibility test of Y_2O_3 sintered specimens for 1419 h at 773 K with liquid lithium, no significant configuration change such as fragmentation of the specimens and crack formation in the specimens were observed after the experimental procedure; only a little increase in thickness (less than 1%) was observed. The color of the specimens changed from the

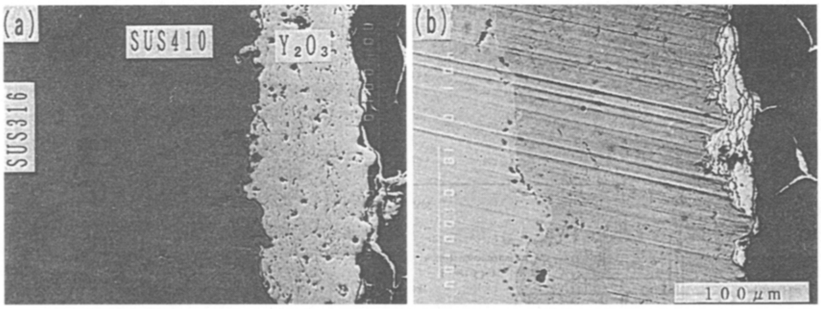

Fig. 8. Scanning electron micrographs of the cross-sectional view for the plasma spray-coated specimens after the compatibility test; (a) uncontacting region and (b) contacting region with lithium.

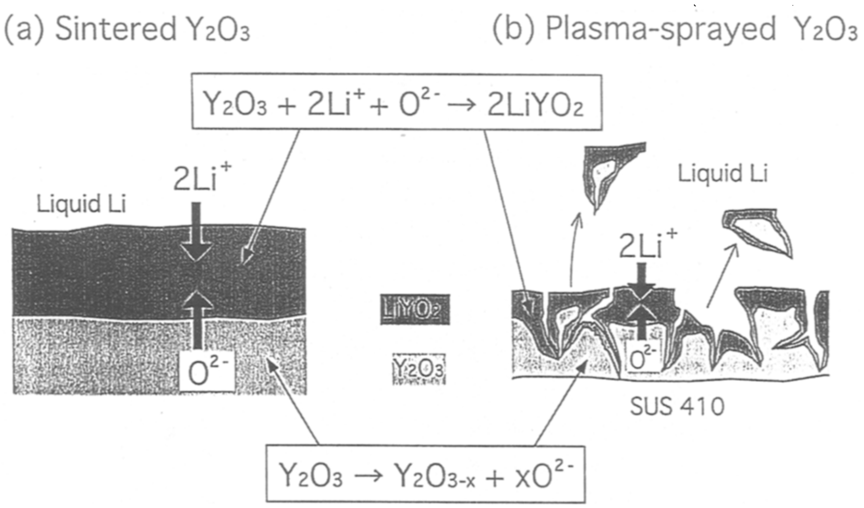

Fig. 9. Schematic drawing for the mechanism of lithium corrosion to Y_2O_3.

initial color (white) to black or gray during the experiment. On the surface of the specimen, $LiYO_2$ was formed and grew with time. Although the electrical resistivity decreased to the order of 10^7 Ω m from the initial value of undetectable level (larger than 10^{11} Ω m) for 1419 h, the final value satisfies the design criterion for ITER (international thermonuclear experimental reactor) (> 0.1 Ω $m^2/1$ μm) [1].

As mentioned above, sintered specimens were corroded only on the surface by lithium, while plasma splayed coating specimen were more severely attacked by lithium and, as a result, most part of the coating was taken away in water. What is the mechanism giving these different results between the two?

There were many pores and cracks observed in the plasma-sprayed specimens, while there were few pores and cracks in the sintered specimens. It is plausible that lithium penetrated into the coating through small cracks and pores and then reacted with Y_2O, or Y_2O_{3-x} to form $LiYO_2$. This phase is speculated to have a different density from Y_2O_3 and to be more brittle than Y_2O_3 [17], which resulted in fragmentation of the coating. Some mechanisms supposed to occur in the compatibility test are illustrated in Fig. 9. In the inner part, oxygen ions move outward resulting in the reduction of Y_2O_3 to Y_2O_{3-x}. On the surface of the specimen, on the other hand, lithium ions penetrate into Y_2O_3 with the formation of $LiYO_2$. From this model, the following conclusion can be drawn; if Y_2O_3 can made into a coating layer with high density on the surface of piping materials, it can act as an insulating layer. Unfortunately, the plasma sprayed coating specimens tested in this study did not have a good enough quality. Further investigation on the fabrication of Y_2O_3 coating is strongly required.

5. Conclusion

In this study, the following conclusions were drawn.

(1) A chemically densified coating (CDC) consisting of SiO_2 particles and a Cr_2O_3 matrix was formed on the surface of SUS316. It is quite effective in reducing tritium permeability in the absence of a molten Li17–Pb83 alloy.

(2) An alumina (Al_2O_3) coating was prepared on the surface of SUS316 by the hot-dipping and oxidation method. It showed a very large corrosion-resistance to Li17–Pb83 and a very small tritium permeability.

(3) Yttria was coated on the surface of SUS316 by the plasma-spraying method. The product has poor compatibility with liquid lithium. However, since sintered Y_2O_3 is more resistant to degradation than plasma sprayed Y_2O_3, it may be possible to use Y_2O_3 as a ceramic coating material for liquid blankets if it is made into a dense coating on the surface of piping materials.

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