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Characterization of Y_2O_3 coating for liquid blanket

Masaru Nakamichi [a,*], Hiroshi Kawamura [a], Takayuki Terai [b], Satoru Tanaka [b]

[a] *Oarai Research Establishment, Japan Atomic Energy Research Institute, 3607 Narita-cho, Oarai-machi, Higashi Ibaraki-gun, Ibaraki-ken, 311-13, Japan*

[b] *University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113, Japan*

Abstract

Ceramic coating on the surface of structural material is being considered for an electrical insulator to reduce the magneto-hydro-dynamic (MHD) pressure drop. Ceramic coating such as Y_2O_3 is a promising electrical insulator due to its high electrical resistance and good compatibility with liquid lithium. The purpose of this study are to develop a ceramic coating method and to obtain a material database of the coating. 410SS was coated with about 160 μm by the vacuum plasma spraying method using particles of 10–45 μm on 316SS substrate as an undercoating between the substrate and atmospheric plasma sprayed Y_2O_3 coating for improvement of thermal shock resistance of the Y_2O_3 coating. In this study, measurement of electrical resistance, verification tests of open pore and compatibility tests as detailed characterization were performed. © 1997 Elsevier Science B.V.

1. Introduction

In a liquid blanket of fusion reactors, development of insulating ceramic coatings is considered to be a critical subject. Ceramic coating materials such as Y_2O_3 [1–4], $MgO \cdot Al_2O_3$ [5], Al_2O_3 [6], AlN [6], CaO [7], TiN and TiC [8] have been studied in fabrication and properties up to the present. Y_2O_3 is a candidate material for insulating coating because it has high electrical resistance [9] and high radiation resistance. In this study, Y_2O_3 coating was fabricated by the plasma spraying method and its properties were investigated.

In the case of ceramic coating fabricated on the surface of austenitic stainless steel (316SS) by the plasma spraying method, it has been observed that crack formation occurs in the coating and a peeling of the coating due to the difference in thermal expansion between the coating and the substrate. In order to prevent them, an undercoating of ferritic stainless steel (410SS) was fabricated by the plasma spraying method under the Y_2O_3 coating, because 410SS has a thermal expansion coefficient close to the ceramic coating [1]. Plasma-sprayed coating has also a lot of pores. They were successfully filled by the chemically densification method, where the coated specimen was immersed in a $Y(NO_3)_3$ solution and fired at 500°C [1]. Among the conditions investigated, the specimen with a 50 μm thick Y_2O_3 coating by the atmospheric spraying method and a 160 μm thick 410SS undercoating by the vacuum spraying method using particles of 10–45 μm was the best in thermal shock resistance. This result was consistent with the metallographical observations [4].

Also in this study, measurement of electrical resistance, verification tests of open pore and compatibility tests as characterization were performed.

2. Specimens

The surface of the 316SS substrate was degreased by methyl alcohol and Al_2O_3 grit blasted to improve the adhesion between the 316SS substrate and 410SS undercoat. The undercoating of 410SS was coated about 160 μm thick by the vacuum plasma spraying method. The particle size of 410SS ranged from 10 to 45 μm. The spraying conditions of the 410SS undercoating are shown in Table 1.

* Corresponding author. Tel.: +81-29 264 8417; fax: +81-29 264 8480: e-mail: masaru@jmtr.oarai.jaeri.go.jp.

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Table 1
Spraying conditions of 410SS undercoat by vacuum plasma spray

Spraying apparatus: Plasma-Technik AG A-2000 V
Plasma gases
Ar: 7.5×10^{-4} m^3/s
H_2: 1.3×10^{-4} m^3/s
Plasma current: 685 A
Plasma voltage: 64 V
Spray distance: 275 mm
Pressure in chamber: 5.9 kPa

Table 2
Spraying conditions of Y_2O_3 coating by atmospheric plasma spray

Spraying apparatus: Plasma-Technik AG A-3000S
Plasma gases
Ar: 7.0×10^{-4} m^3/s
H_2: 2.0×10^{-4} m^3/s
Plasma current: 550 A
Plasma voltage: 74 V
Spray distance: 120 mm

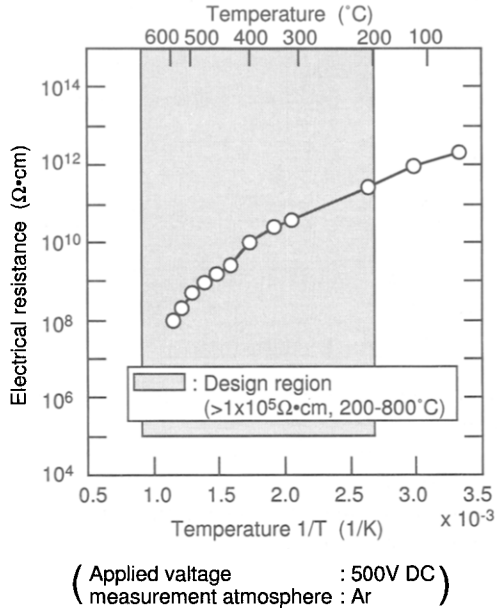


Fig. 2. Electrical resistance of the Y_2O_3 coating vs. temperature.

The Y_2O_3 (purity: 99.95 wt%, particle size: 10–45 μm) was coated about 50 μm thick by the atmospheric plasma spraying method. The spraying conditions of the Y_2O_3 coating are given in Table 2. The Y_2O_3 coating was densified by impregnation with the $Y(NO_3)_3$ solution ($Y(NO_3)_3$: 36.5 wt%) and fired up for one hour at 500°C in order to close open pores. The rates of heating and cooling were 500 and 50°C/h, respectively. Furthermore, densification treatment was repeated six times. In the specimens for compatibility testing, ceramic slurry was applied on the top of the specimens for reinforcement of the Y_2O_3 coating. The ceramic slurry was a solution of Y_2O_3 particles (purity: > 99.9 wt%, average particle size: 2.53 μm) and an $Y(NO_3)_3$ solution ($Y(NO_3)_3$: 36.5 wt%) and H_2O in the ratio of 1:1:1 (weight). The specimen with ceramic slurry was heated for one hour at 500°C. The rates of heating and cooling were 500°C/h and 100°C/h, respectively.

3. Measurement of electrical resistance

Electrical resistance of the Y_2O_3 coating was measured from room temperature to 600°C in Ar gas. Specimen and outline for electrical resistance measurement is shown in Fig. 1. An Ag paste was applied on the Y_2O_3 coating, and heated for 20 min at 150°C. The applied voltage was DC 500 V. The results of the electrical resistance measurement are shown in Fig. 2. Electrical resistance of the Y_2O_3

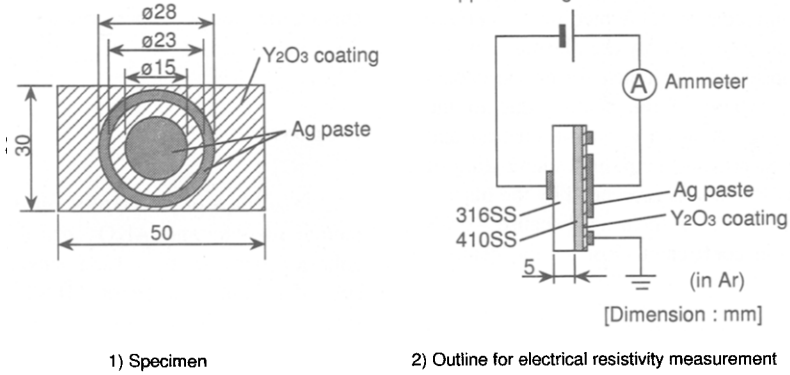


Fig. 1. Specimen and outline for electrical resistance measurement of the Y_2O_3 coating.

coating is 3.8×10^{10} and 1.0×10^{8} Ω cm at 213 and 593°C, respectively, which satisfies the ITER design guideline ($> 1.0 \times 10^{5}$ Ω cm, from 200°C to 800°C).

4. Verification test of open pore

A verification test of open pores in the Y_2O_3 coating was performed. In this test, 316SS/410SS/densified Y_2O_3 coating and 316SS/410SS/no-densified Y_2O_3 coating were used as specimens. The reagent was $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, NaCl and H_2O in the ratio of 1:1:6:100 (weight). The filter paper (20 (width) × 40 (length) mm) impregnated the reagent place on the surface of Y_2O_3 coating. Sn plates (20 (width) × 40 (length) mm) were placed on the filter paper with the reagent, and a weight of 200 g was added as a load. Holding time is 10 min. The specimen were dried up after full washing in water.

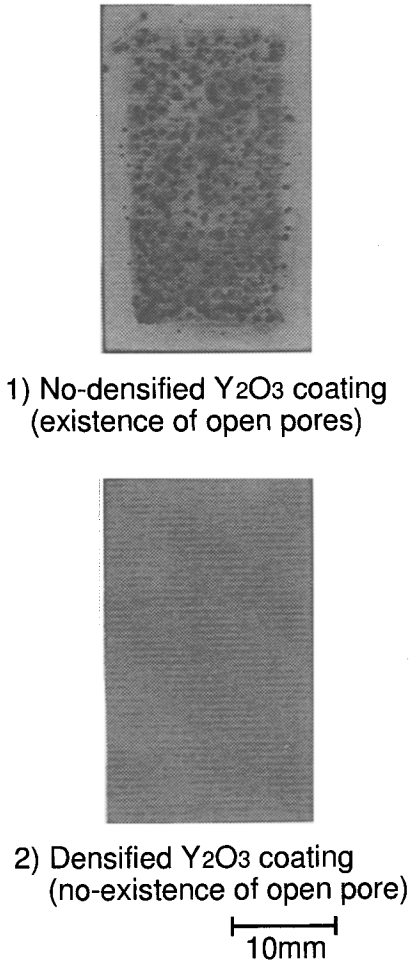


Fig. 3. Appearance observation after the verification test of the open pore.

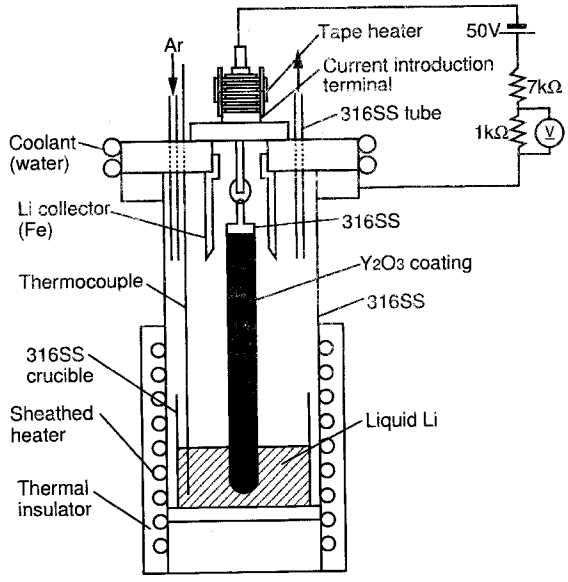


Fig. 4. Outline of the compatibility test.

$Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ appears as small spots in the Y_2O_3 coating at the existence of open pores.

A photograph of appearance after the verification test of open pores was shown in Fig. 3. No-densified Y_2O_3 coating has open pores, but open pores could be enclosed by densification treatment.

5. Compatibility test

An outline of the compatibility test was shown in Fig. 4. Lithium and specimen were equipped in a glove box in Ar atmosphere. The concentrations of oxygen and nitrogen were about 10 ppm at room temperature in lithium. It was supposed that the concentration of oxygen was less than 1000 ppm at 500°C, because Li_2O was not observed in lithium after the compatibility test up to 500°C heating. Lithium (about 30 g) in the 316SS crucible was placed in

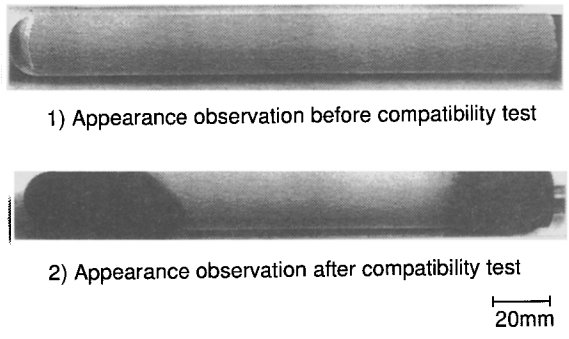
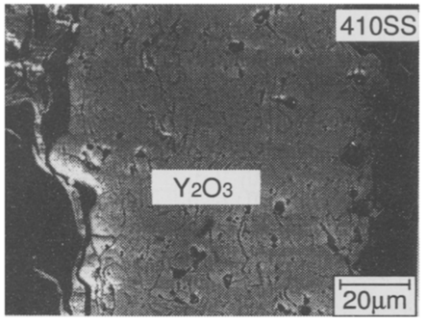
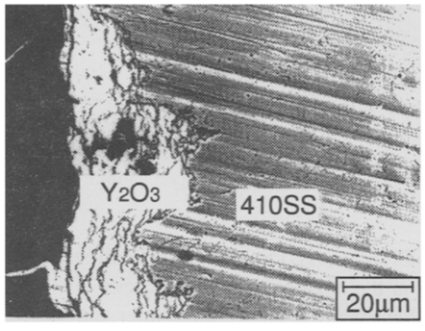


Fig. 5. Appearance observation before and after the compatibility test.



1) Scanning electron microscope (SEM) photographs of a cross section in the Y2O3 coating out of contact with lithium



2) Scanning electron microscope (SEM) photographs of a cross section in the Y2O3 coating in contact with lithium

Fig. 6. Scanning electron microscope (SEM) photographs of a cross-section in the Y_2O_3 coating without, and in contact with lithium.

the bottom of a testing vessel. In the vessel, lithium collector (Fe) was set up for the collection of evaporated lithium. The specimen was soaked about 30 mm in lithium. The applied voltage was DC 50 V. The testing temperature was raised to 500°C. This compatibility test was performed under severe conditions.

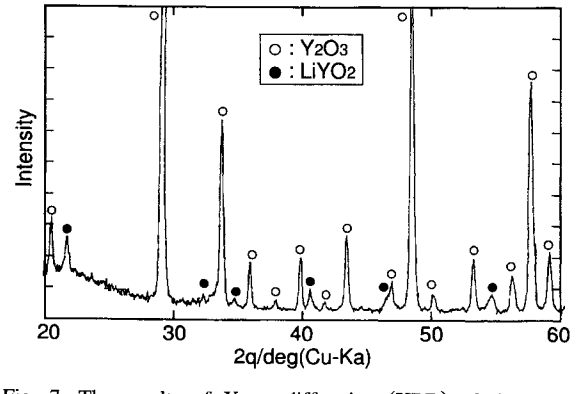


Fig. 7. The results of X-ray diffraction (XRD) of the Y_2O_3 coating in contact with lithium.

Table 3
Free energy and equilibrium constants between lithium and Y_2O_3

Temperature (°C)	Free energy, ΔG_f^0 (kJ/mol)	Equilibrium constant, K_p
400	58.257	3.02×10^{-5}
500	62.857	5.67×10^{-5}
600	67.455	9.22×10^{-5}

The specimen was applied with DC 50 V at the start of heating. Around the melting point of lithium (180.5°C), the electric current flew. The electric current flew about 1 μA at 250°C. After 30 min at 250°C, a short circuit was formed. After 6 h at 250°C, the testing temperature was raised to 500°C. The holding time was about 150 h at 500°C. The electric resistance of the specimen from 250°C to 500°C was only 0.03–0.08 Ω.

Photographs of the appearance before and after the compatibility test were shown in Fig. 5. The Y_2O_3 coating was changed from white to black and peeling of Y_2O_3 coating occurred in contact with lithium after the compatibility test. The black area of Y_2O_3 coating had no-insulation.

The photographs in the Y_2O_3 coating without contact and in contact with lithium were shown in Fig. 6 by scanning electron microscopy (SEM). In the Y_2O_3 coating in contact with lithium, peeling of the Y_2O_3 coating and cracks were observed. Cracks were observed in the Y_2O_3 coating not in contact with lithium. It was considered that peeling of the Y_2O_3 coating occurred by invasion of lithium along the cracks in the Y_2O_3 coating.

The results of X-ray diffraction (XRD) of the Y_2O_3 coating in contact with lithium was shown in Fig. 7. $LiYO_2$ was confirmed in addition to Y_2O_3 (see Fig. 7). From the results of XRD, it is clear that lithium invaded into the Y_2O_3 coating. However, the amount of $LiYO_2$ was smaller than the amount of Y_2O_3 from comparison of XRD peak intensity between $LiYO_2$ and Y_2O_3. Therefore, there is a possibility of change on the surface of the Y_2O_3 particle.

Free energy (ΔG_f^0) and equilibrium constants (K_p) between lithium and Y_2O_3 (see Eq. (1)) are given in Table 3 [10]:

$$2Li + \tfrac{1}{3}Y_2O_3 \rightarrow \tfrac{2}{3}Y + Li_2O. \quad (1)$$

The reaction between lithium and Y_2O_3 did not occur, because ΔG_f^0 is positive from 400°C to 600°C (see Table 3). However, ΔG_f^0 of the $LiYO_2$ generation is still unknown at all. It is necessary to elucidate ΔG_f^0 from the $LiYO_2$ generation.

Y_2O_3 was made oxygen deficient as Y_2O_{3-x} at high temperature in reducing atmosphere. In this test, the Y_2O_3 coating changed from white to black in color and lost its insulation properties upon reduction.

6. Conclusion

(1) Measurement of electrical resistance

Electrical resistance of the Y_2O_3 coating satisfies the ITER design guideline.

(2) Verification test of open pore

No-densified Y_2O_3 coating has open pores, but open pores could be enclosed by densification treatment.

(3) Compatibility test

In the Y_2O_3 coating in contact with lithium, peeling of the Y_2O_3 coating and cracks was observed. Cracks were observed in the Y_2O_3 coating not in contact with lithium. It was considered that peeling of the Y_2O_3 coating occurred by invasion of lithium along the cracks in the Y_2O_3 coating.

Y_2O_3 was made oxygen deficient as Y_2O_{3-x} at high temperature in reducing atmosphere. The Y_2O_3 coating changed from white to black in color and lost its insulation properties upon reduction.

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References

[1] M. Nakamichi et al., Fusion Tech. 1994 2 (1995) 1217.
[2] M. Nakamichi et al., JAERI-Tech 95-009, Mar. 1995.
[3] M. Nakamichi et al., Therm. Spraying 2 (1995) 1027.
[4] M. Nakamichi et al., Therm. Spraying 2 (1995) 815.
[5] M. Nakamichi et al., J. Nucl. Mater. 233–237 (1996) 1427.
[6] S. Malang et al., Fusion Eng. Des. 27 (1995) 399.
[7] J.-H. Park et al., J. Nucl. Mater. 233–237 (1996) 476.
[8] A. Perujo, K. Forcey, Fusion Eng. Des. 28 (1995) 252.
[9] A.A. Bauer, J.L. Bates, Battelle Mem. Inst. Rept., 1930, Jul. 31, 1974.
[10] The thermal measurement society of Japan, MALT (materials-oriented little thermodynamic data base), Kagaku gijyutsu sya, 1985.