The Effect of Thermal History on Microstructure of Er_2O_3 Coating Layer Prepared by MOCVD Process*)

Masaki TANAKA, Makoto TAKEZAWA, Yoshimitsu HISHINUMA[1)], Teruya TANAKA[1)], Takeo MUROGA[1)], Susumu IKENO[2)], Seungwon LEE[3)] and Kenji MATSUDA[3)]

Graduate School of Science and Engineering for Education, University of Toyama, Toyama 930-0855, Japan
[1)]*National Institute for Fusion Science, Toki 509-5292, Japan*
[2)]*Hokuriku Polytechnic College, Uozu 937-0856, Japan*
[3)]*Graduate School of Science and Engineering for Research, University of Toyama, Toyama 930-0855, Japan*

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Er_2O_3 is a high potential candidate material for tritium permeation barrier and electrical insulator coating for advanced breeding blanket systems with liquid metal or molten-salt types. Recently, Hishinuma *et al.* reported to form homogeneous Er_2O_3 coating layer on the inner surface of metal pipe using Metal Organic Chemical Vapor Deposition (MOCVD) process. In this study, the influence of thermal history on microstructure of Er_2O_3 coating layer on stainless steel 316 (SUS 316) substrate by MOCVD process was investigated using SEM, TEM and XRD. The ring and net shape selected-area electron diffraction (SAED) patterns of Er_2O_3 coating were obtained each SUS substrates, revealed that homogeneous Er_2O_3 coating had been formed on SUS substrate diffraction patterns. Close inspection of SEM images of the surface on the Er_2O_3 coating before and after thermal cycling up to 700°C in argon atmosphere, it is confirmed that the Er_2O_3 particles were refined by thermal history. The column-like Er_2O_3 grains were promoted to change to granular structure by thermal history. From the cross-sectional plane of TEM observations, the formation of interlayer between Er_2O_3 coating and SUS substrate was also confirmed.

Keywords: Er_2O_3, thermal history, MOCVD process, SEM, TEM

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1. Introduction

It has been reported that Er_2O_3 has excellent electrical resistance and a permeation controlling effect from various ceramic materials. Hishinuma *et al.* [1] succeeded in forming Er_2O_3 film by metal organic chemical vapor deposition (MOCVD) process as a new technology for large area coating on broad and complicated shaped components [2]. MOCVD process is a concise procedure to form homogeneous and large area coating layer synthesized from a metal organic complex.

Breeding blanket system of nuclear fusion reactor needs developments of advanced coating for controlling a leakage of tritium and reducing magneto hydrodynamic pressure drop (MHD). In breeding blanket system, materials for MHD insulating coating need to fulfill five conditions. 1. No breakdown at high temperature. 2. Low reactivity with Li as a coolant. 3. High electrical resistivity and insulating. 4. Easy controlling tritium permeation. 5. Coating thickness of 2 µm or more.

In this work, it was investigated the change of microstructure by thermal cycles of the Er_2O_3 coating layer fabricated by MOCVD process on stainless steel 316 (SUS316) plate.

author's e-mail: ikenolab@eng.u-toyama.ac.jp

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2. Experimental Procedure

Three SUS316 plates were prepared as a substrate and coated with Er_2O_3 film using MOCVD process at 500°C for 3 h. Samples were deposited at the substrate temperatures of (A) 450°C and (B) 550°C. One sample, (C), that was deposited at 500°C using substrate temperature of 550°C, was undergone 30 times of thermal cycle tests in argon atmosphere to avoid oxidation. Sample condition is summarized in Table 1. One thermal cycle assumed as one year of thermal exposure at nuclear fusion reactor, in Fig. 1. Scanning Electron Microscope (SEM) with EDS and SLEEM mode were carried out to observe surface morphologies using HITACHI S-3500 H. Trans-

Table 1 Sample conditions.

	Substrate Temp. °C	Deposition Temp. °C	Thermal Cycle Test
(A)	450		None
(B)	550	500	None
(C)	550		30 times

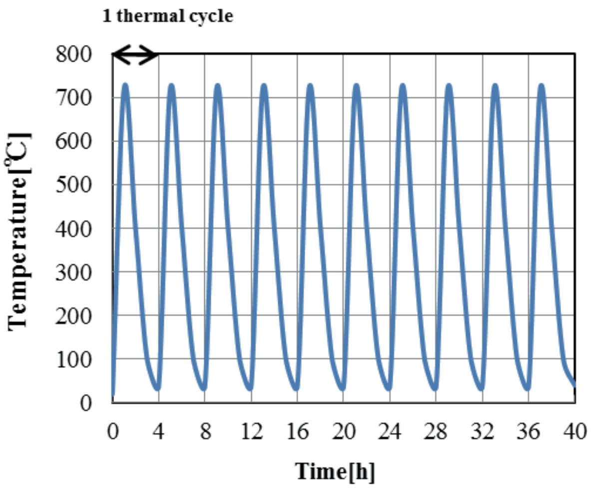

Fig. 1 Diagram of thermal history test.

mission Electron Microscope (TEM) sample for cross-sectional observation were prepared by Focus Ion Beam method (FB-2100, HITACHI) operating at 40 keV using gallium ion. TEM observations and TEM-EDS analyses were conducted using TOPCON EM-002B operating at 200 keV. XRD analyses with θ-2θ scan mode were carried out using Philips X'pert system diffractometer using Cu-Kα X-Ray irradiation.

3. Results and Discussion

Figure 2 shows SEM images of surface morphologies. With inspection of SEM images, surface morphology of Er_2O_3 thin film was changed significantly with increase of substrate temperature. Er_2O_3 formed networks in Fig. 2 (a), however, Er_2O_3 particles covered the whole surface in Fig. 2 (b). Er_2O_3 grains were refined after thermal cycle test in Fig. 2 (c).

Figure 3 shows TEM bright field images with SAED patterns taken from central part of Fig. 2 by FIB method. Figure 3 (a) shows TEM bright field images and SAED pattern of the sample was deposited when substrate temperature was 450°C. Er_2O_3 structure are consistent to surface morphology of Fig. 2 (a). SAED patterns formed ring due to the formation of nano-sized Er_2O_3. With increase of substrate temperature to 550°C, Er_2O_3 thin films formed columnar structure in Fig. 3 (b). Average thickness of Er_2O_3 thin film was 1.4 μm, and column width was 0.32 μm. Furthermore, Er_2O_3 net-shaped diffraction pattern was obtained. With close analysis, the grain growth direction of Er_2O_3 can be suggested as [123]. In Fig. 3 (c), average thickness of Er_2O_3 thin film and column width decreased to 0.82 μm and 0.21 μm, respectively. With inspection of SAED pattern, the grain growth direction of Er_2O_3 can be suggest as [110] during thermal cycle test. It can be noted that the Er_2O_3 thin film maintains its structure with acceptable thickness after thermal cycle test.

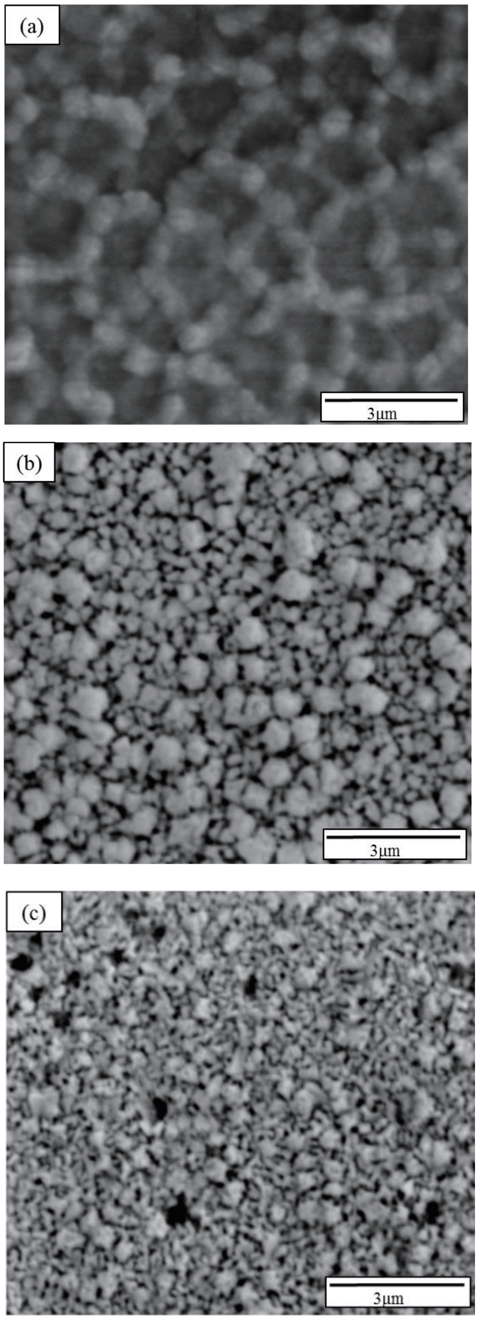

Fig. 2 SEM images of surface for Er_2O_3 film (a) substrate temperature is 450°C (A), (b) substrate temperature is 550°C (B) and (c) after thermal cycle test (C).

Figure 4 shows XRD profiles of sample (A)-(C) indexed with Er_2O_3. When substrate temperature is 450°C, peak intensities of Er_2O_3 were small in Fig. 4 (a). In the case of sample (B), intensities were larger than sample (A) with strong 400 peak. X-ray diffraction patterns of Er_2O_3 films after thermal history test didn't have the preferential peak, however, it still has Er_2O_3 peaks. This Er_2O_3 thin film could keep its crystal structure during thermal treatment, and it could be stable.

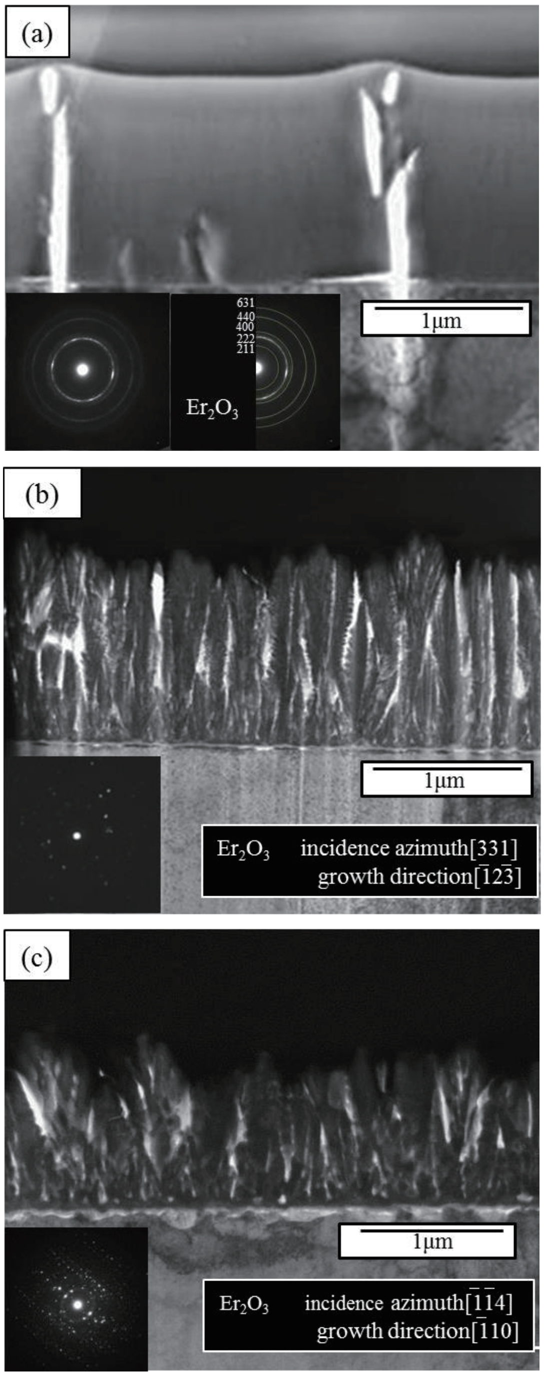

Fig. 3 Cross-sectional TEM bright field of surface for Er_2O_3 film (a) substrate temperature is 450°C (A), (b) substrate temperature is 550°C (B) and (c) after thermal cycle test (C).

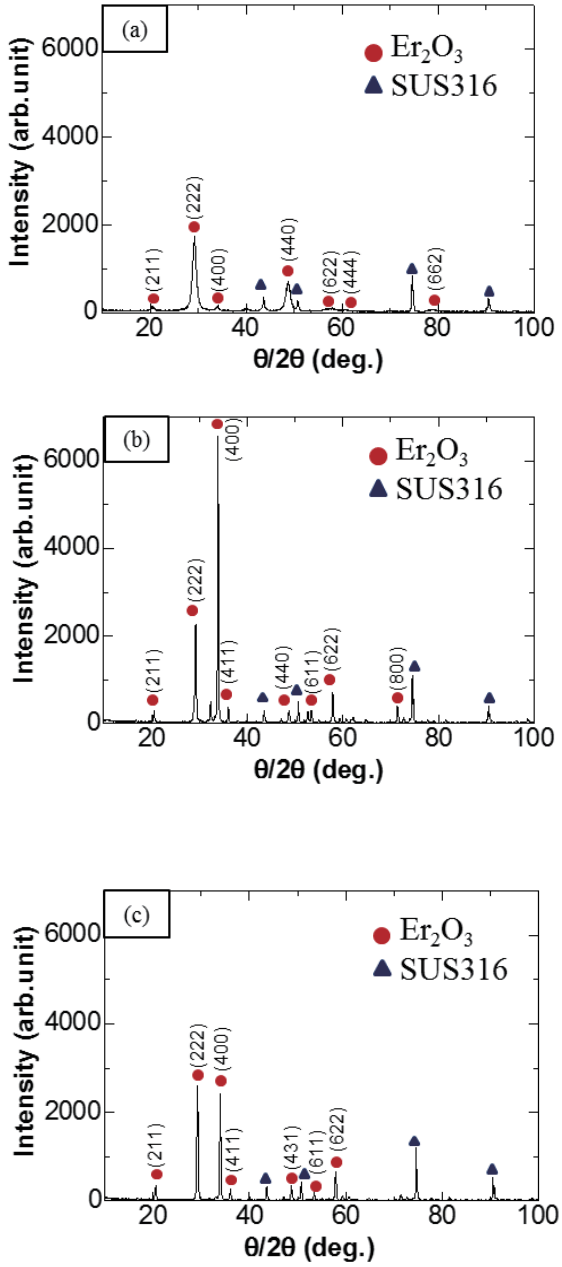

Fig. 4 XRD analysis of Er_2O_3film (a) substrate temperature is 450°C (A), (b) substrate temperature is 550°C (B) and (c) after thermal cycle test (C).

4. Summary

The Er_2O_3 films consisted of small crystalline which had C-care earth structure from XRD, SEM and TEM analysis. After thermal history test, Er_2O_3 grains were refined and maintained its structure. Also, the average thickness and column width were decreased. The thickness of Er_2O_3 film decreases from 1.4 to 0.82 μm after 30 times of thermal cycles.

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