The Effect of Thermal History on Microstructure of Er$_2$O$_3$ Coating Layer Prepared by MOCVD Process*)

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Er$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ coating were obtained each SUS substrates, revealed that homogeneous Er$_2$O$_3$ coating had been formed on SUS substrate diffraction patterns. Close inspection of SEM images of the surface on the Er$_2$O$_3$ coating before and after thermal cycling up to 700°C in argon atmosphere, it is confirmed that the Er$_2$O$_3$ particles were refined by thermal history. The column-like Er$_2$O$_3$ 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$_2$O$_3$ coating and SUS substrate was also confirmed.

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1. Introduction

It has been reported that Er$_2$O$_3$ has excellent electrical resistance and a permeation controlling effect from various ceramic materials. Hishinuma et al. [1] succeeded in forming Er$_2$O$_3$ 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$_2$O$_3$ coating layer fabricated by MOCVD process on stainless steel 316 (SUS316) plate.

2. Experimental Procedure

Three SUS316 plates were prepared as a substrate and coated with Er$_2$O$_3$ film using MOCVD process at 500°C for 3h. 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-3500H. Trans-

Table 1 Sample conditions.

<table>
<thead>
<tr>
<th>Substrate Temp. °C</th>
<th>Deposition Temp. °C</th>
<th>Thermal Cycle Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 450</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>(B) 550</td>
<td>500</td>
<td>None</td>
</tr>
<tr>
<td>(C) 550</td>
<td>500</td>
<td>30 times</td>
</tr>
</tbody>
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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 Er₂O₃ thin film was changed significantly with increase of substrate temperature. Er₂O₃ formed networks in Fig. 2 (a), however, Er₂O₃ particles covered the whole surface in Fig. 2 (b). Er₂O₃ 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. Er₂O₃ structure are consistent to surface morphology of Fig. 2 (a). SAED patterns formed ring due to the formation of nano-sized Er₂O₃. With increase of substrate temperature to 550°C, Er₂O₃ thin films formed columnar structure in Fig. 3 (b). Average thickness of Er₂O₃ thin film was 1.4 μm, and column width was 0.32 μm. Furthermore, Er₂O₃ net-shaped diffraction pattern was obtained. With close analysis, the grain growth direction of Er₂O₃ can be suggested as [123]. In Fig. 3 (c), average thickness of Er₂O₃ 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 Er₂O₃ can be suggest as [110] during thermal cycle test. It can be noted that the Er₂O₃ thin film maintains its structure with acceptable thickness after thermal cycle test.

Figure 4 shows XRD profiles of sample (A)-(C) indexed with Er₂O₃. When substrate temperature is 450°C, peak intensities of Er₂O₃ 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 Er₂O₃ films after thermal history test didn’t have the preferential peak, however, it still has Er₂O₃ peaks. This Er₂O₃ 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 Er₂O₃ film (a) substrate temperature is 450°C (A), (b) substrate temperature is 550°C (B) and (c) after thermal cycle test (C).

4. Summary

The Er₂O₃ films consisted of small crystalline which had C-care earth structure from XRD, SEM and TEM analysis. After thermal history test, Er₂O₃ grains were refined and maintained its structure. Also, the average thickness and column width were decreased. The thickness of Er₂O₃ film decreases from 1.4 to 0.82 μm after 30 times of thermal cycles.