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Hydrogen permeation through steel coated with erbium oxide by sol–gel method

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ABSTRACT

Er_2O_3 coating is formed on austenitic stainless steel 316ss by sol–gel method. The results showed good crystallization of coating by baking in high purity flowing-argon at 973 K, and indicated that a little oxygen in baking atmosphere is necessary to crystallization of coating. The best baking temperature could be thought as 973 K, to get good crystallization of coating and avoid strong oxidation of steel substrate. The deuterium permeation test was performed for coated and bare 316ss, to evaluate the property of Er_2O_3 sol–gel coating as a potential tritium permeation barrier. In this study, the deuterium permeability of coated 316ss is about 1–2 orders of magnitude lower than that of bare 316ss, and is about 2–3 orders of magnitude than the referred data of bare Eurofer97 and F82H martensitic steel.

1. Introduction

For the concept of fluid/steel blanket, in liquid Pb–Li [1] and Flibe [2] the tritium solubility is quite low, in reduced activation martensitic (RAM) steel as Eurofer97 [3] and F82H [4] the tritium permeability is higher about one order of magnitude than that of austenitic stainless steel 316ss [5]. Even for 316ss as a common structural material for fusion blanket, the tritium permeation level still cannot be accepted. Thus one of remaining critical issues is the permeation of tritium through the structure wall of metal duct, which once produced in fluid under neutron irradiation. This issue induces the loss of fuel and harm to environment. The promising way to solve this issue is to use coating as tritium permeation barrier (TPB) on metal duct [6].

To produce TPB coating on steel, some oxides were chosen as candidate materials. From original idea, Er_2O_3 coating has been studied widely as insulator to mitigate magneto-hydrodynamic (MHD) pressure drop for Li/V blanket [7]. However in coincidence, Er_2O_3 coating produced by filtered arc deposition method was found to have quite low deuterium permeability [8]. Therefore Er_2O_3 coating has potential to act as both TPB and insulator for various kinds of blanket.

Among many fabrication methods to produce Er_2O_3 coating, sol–gel is a candidate method which has advantages of high homogeneity and single composition for coating, controllable procedure and simple device for process [9]. Especially sol–gel method has possibility to produce coating on the wall of component with complex shape.

In this study, the fabrication process and characterization of Er_2O_3 coating by sol–gel method were described. The permeation reduction factor (PRF) of Er_2O_3 coating acting as potential TPB was estimated by measuring deuterium permeability of coated and bare 316ss.

2. Experimental

The sol–gel method has two branch techniques to produce coating, one is spin-coating (for plate shape substrate) and one is moving dipping (for pipe or wire shape substrate). In this study, for the basic research of sol–gel coating the spin-coating technique was applied to disc-shape substrate.

The substrate was 316ss disc with size of $\Phi\, 20 \times 0.5$ mm. Before deposition, the samples were polished to mirror surface, and clean in acetone and ethanol by ultrasonic bath. The spin-coating processes could be divided by three steps normally. At first, the coating was performed by spin-coater with droplet of metal organic deposition solvent, in air at room temperature (RT). The compositions of dip-coat precursor are erbium carboxylic acid, turpentine, *n*-butyl acetate, ethyl acetate and some stabilizer and viscosity adjustor. The equivalent content of erbium oxide in solvent is about 3%. The rotary speed of spin-coater was 500–2000 rpm for 10–30 s, in this step the coating shows as wet-sol. At second, the coating was dried in a dry-oven in air at 393 K for 10 min, in this step the wet-sol change to dry-sol then to dry-gel. To get thicker coating, the first and second steps need to be repeated alternately several times. At third, the coating was baked in various

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atmosphere by an infrared image furnace (respectively, high vacuum of ~10^{-5} Pa by turbo molecular pump (TMP); low vacuum of ~1 Pa by rotary pump (RP); 7 N (99.99999%) high purity hydrogen ($O_2 < 0.02$ ppm, $H_2O < 0.5$ ppm) with flow-rate of 50 ml/min; 6 N (99.9999%) high purity argon ($O_2 < 0.05$ ppm, $H_2O < 0.5$ ppm) with flow-rate of 50 ml/min) at 673–1173 K for 1 h, in this step the dry-gel change to Er_2O_3 crystallization.

The cross-section of coated 316ss was observed by scanning electron microscopy (SEM). The depth profile of elements was analyzed by X-ray photoelectron spectroscopy (XPS) with Ar ion sputtering. The phase states of coating were identified by X-ray diffraction (XRD).

The deuterium which has low background noise to quadrupole mass spectrometer (QMS) detector was working gas for permeation test, as the substitute of hydrogen. The deuterium permeability of coated and bare 316ss disc was measured by gas permeation apparatus which was described detailedly in Ref. [3]. During measurement, the deuterium upstream pressures were about 10^4–10^5 Pa, and sample temperatures for 316ss coated with Er_2O_3 were at 773, 873 and 973 K and for bare 316ss were at 673, 773 and 873 K.

3. Results and discussion

Fig. 1 shows a SEM image of the cross-section of 316ss with sol–gel coating. The coating was baked in low vacuum of ~1 Pa at 973 K for 1 h. It is obvious that a layer with fairly uniform thickness of about 0.3 μm. The coating has no cracks and good adhesion with substrate. By repeating the spin-coating process and control rotary speed and time of spin-coater, the coating thickness was achieved flexibly 0.1–10 μm or more.

Fig. 2 shows the elemental depth profile by XPS with Ar-sputtering of 316ss with sol–gel coating showed in Fig. 1. The surface layer is enriched with erbium and oxygen. The atomic ratio between erbium and oxygen is about 1:2 in the coating, which is smaller than 2:3 of ideal Er_2O_3. Perhaps the shortage of erbium in coating means a weak crystallization. The signal of iron might be from a disturbance of substrate, it would be thought that the coating had invisible cracks. By combining with the SEM cross-section observation once, the sputtering rate of Ar ions was calibrated as ~14 nm/min. Thus the thickness of coating was ~0.3 μm in Fig. 2, which corresponds to SEM observation in Fig. 1 well.

Fig. 3 shows the phase states by XRD of 316ss with sol–gel coating formed in various baking atmosphere with different oxygen potential at 973 K for 1 h. The quite strong peaks at 44°, 51° and 75° correspond to Fe–Cr–Ni–Mo phases of 316ss substrate. Fig. 3(a) shows the coating baking in high vacuum of ~10^{-5} Pa as amorphous. Fig. 3(b) shows the coating baked in low vacuum of ~1 Pa as weak crystallization with quite wide peak. Fig. 3(c) shows that the coating baked in high purity (7 N) flowing-hydrogen has the peaks at diffraction angle around 29° corresponding to Er_2O_3 (222) and around 49° to Er_2O_3 (440), respectively, but the peaks still are not sharp. The aim to baking in high purity hydrogen is to get Er_2O_3 crystallization while avoid oxidation of steel substrate. But hydrogen is strongly reductive to lower the oxidation of substrate and crystallization of coating simultaneously. Fig. 3(d) shows that the coating formed in high purity (6 N) flowing-argon has sharp peaks of Er_2O_3 (222) and Er_2O_3 (440) which means good crystallization. Although the peak around 33.5° for oxide appears, the oxidization of substrate could be mitigated by choosing

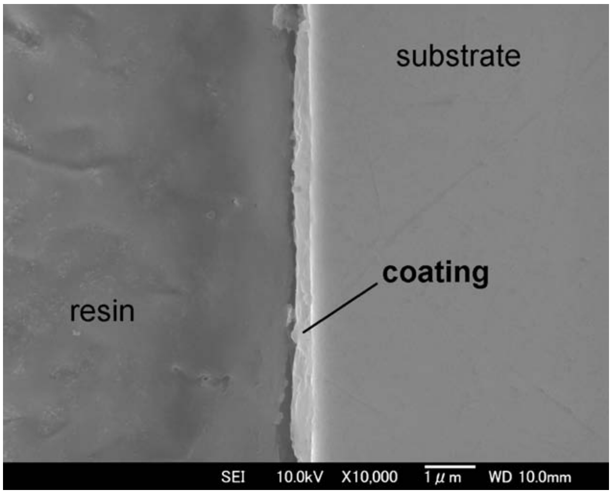

Fig. 1. SEM image of cross-section of 316ss with sol–gel coating.

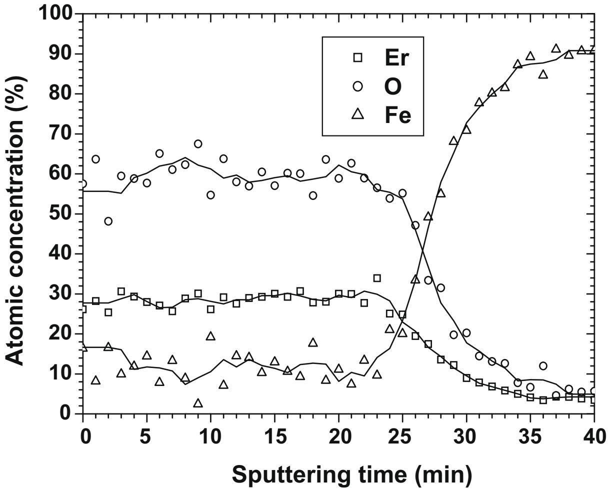

Fig. 2. Elemental depth profile by XPS with Ar-sputtering of 316ss with sol–gel coating.

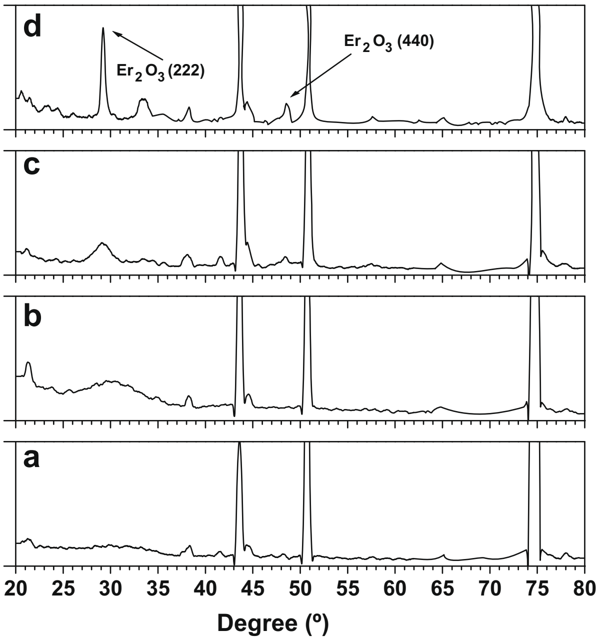

Fig. 3. Phase states by XRD of 316ss with sol–gel coating formed in various baking atmosphere. (a) ~10^{-5} Pa vacuum by TMP; (b) ~1 Pa vacuum by RP; (c) 7 N flowing H_2; (d) 6 N flowing Ar.

suitable fabrication technics for large components. It indicates that a little of oxygen in baking atmosphere is necessary to get good crystalline coating.

Fig. 4 shows the phase states by XRD of 316ss with sol–gel coating formed at various baking temperature. The coating was baked at 673–1173 K for 1 h in high purity (6 N) flowing-argon. The quite strong peaks at 44°, 51° and 75° correspond to Fe–Cr–Ni–Mo phases of 316ss substrate. Fig. 4(a) shows a very wide and low peak to Er_2O_3 which means very weak crystallization at 673 K. Fig. 4(b) shows the Er_2O_3 (222) peak becomes a little high but still wide and (440) peak does not appear at 773 K, it means the crystallization still weak. Fig. 4(c) shows a sharp (222) peak and a wide (440) peak which means crystallization, however a peak to oxidization of 316ss appears at 873 K. Fig. 4(d) shows a quite sharp (222) peak and (440) peak means a good crystallization at 973 K. Fig. 4(e) shows also good crystallization for coating but strong oxidation of substrate at 1073 K. Fig. 4(f) shows an unacceptable oxidation of substrate, although good crystallization of coating at 1173 K. Therefore it could be thought that the best baking temperature will be 973 K.

Fig. 5 shows deuterium permeability of 316ss with Er_2O_3 sol–gel coating and bare 316ss. The coating was produced by spin-coater in air at RT, dried in air at 393 K for 10 min and baked in 6 N flowing-argon at 973 K for 1 h. To compare, the deuterium permeability data of bare Eurofer97 [3] and bare F82H [4] were referred. In figure, the data of solid symbols of coated and bare 316ss, and dish line of bare Eurofer97 were measure by same deuterium permeation device and sample shape. Because deuterium permeability through ceramic is much lower than that through metal, the apparent deuterium permeability of ceramic coated metal is decided by that of coating but not metal substrate. The efficiency of TPB coating on 316ss substrate will be applicable to RAM steel substrate. The deuterium permeability was gotten at 773–973 K for coated 316ss while 673–873 K for bare 316ss, because of insufficient QMS sensitivity to detect permeated deuterium at lower temperature. It shows that the deuterium permeability of RAM steels (bare Eurofer97 and bare F82H) are coincident well, and higher than ~50 factors at 673 K and ~30 factors at 773 K than that of bare austenitic 316ss. The reason could be explained as different phase structure between two kinds of steel, normally the deuterium permeation in martensitic steel is easier than that in austenitic steel. It shows that the deuterium permeability of 316ss with Er_2O_3 sol–gel coating is lower about 1–2 orders of magnitude than that of bare 316ss, i.e. the PRF value is ~60 at 773 K and ~30 at 873 K. Although not available data for bare 316ss at 973 K, the PRF value could be expected to ~10 at 973 K. Comparing with bare Eurofer97 and F82H, the deuterium PRF is 1700–2000 at 773 K and 600–1000 at 873 K. The expected PRF value is 80–120 at 973 K. Therese, an acceptable PRF value as TPB could be achieved by Er_2O_3 sol–gel coating.

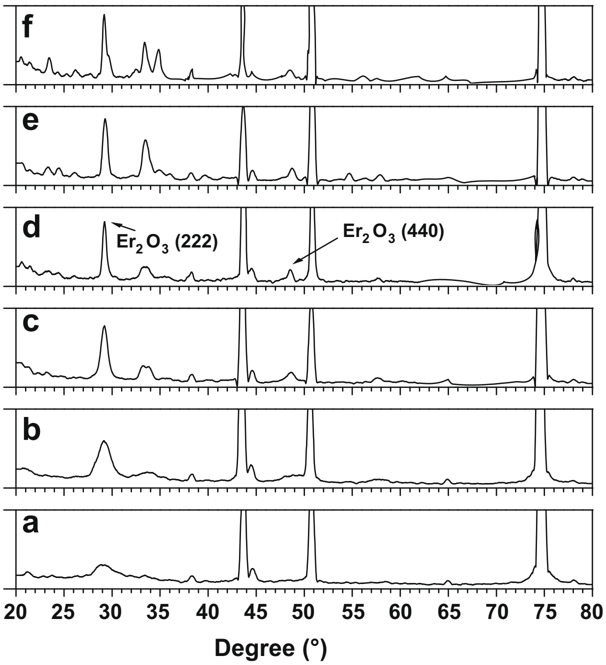

Fig. 4. Phase states by XRD of 316ss with sol–gel coating formed at various baking temperature. (a) 673 K; (b) 773 K; (c) 873 K; (d) 973 K; (e) 1073 K; (f) 1173 K.

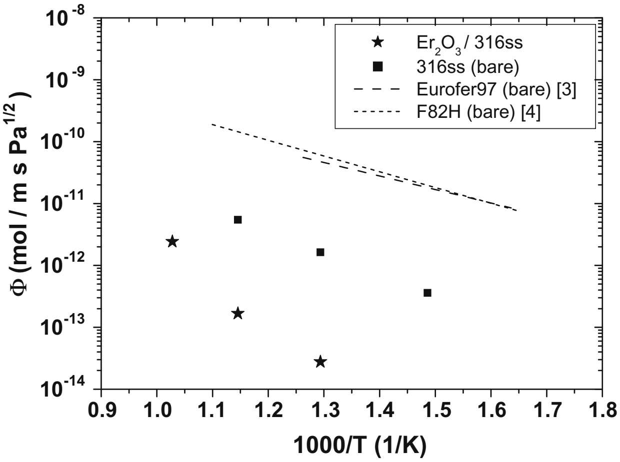

Fig. 5. Deuterium permeability of coated 316ss and bare 316ss. Data of bare Eurofer97 [3] and bare F82H [4] are also referred.

4. Summary

Er_2O_3 coating is formed on stainless steel by sol–gel method. The results showed the good crystallization of coating could be achieved by choosing suitable baking atmosphere and temperature. A little oxygen in baking atmosphere is necessary to crystallization. In this study, the deuterium permeability of coated 316ss is about 1–2 orders of magnitude lower than that of bare 316ss, and is about 2–3 orders of magnitude than the referred data of bare Eurofer97 and bare F82H steel. The study indicated that the sol–gel is a visible method to produce Er_2O_3 coating as a TPB.

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