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Preparation of Mg and Al phosphate coatings on ferritic steel by wet-chemical method as tritium permeation barrier

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ABSTRACT

Layers of Mg or Al phosphate were prepared on type 430 ferritic stainless steel (SS430) by wet-chemical methods as tritium permeation barrier. Disk-type specimens of SS430 were first coated with ZrO_2/ZrO_2 or ZrO_2/Al_2O_3 layers (100 nm) by sol–gel and electrolytic deposition techniques. Then, the phosphate layers were prepared by dip-coating method; the total thickness of coating was 200 nm. The permeation rate of hydrogen was measured at 300–600 °C under driving pressure of 0.1 MPa. The Mg or Al phosphate layers provided significant barrier effects, and the permeation reduction factor observed under the present conditions was 200–3000 against that of Pd coated 430 specimen. Further investigation, however, was required to improve the stability at high temperatures.

1. Introduction

Development of permeation barrier coatings on structural materials is a feasible solution to limit uncontrolled tritium transport in fusion reactor. Ceramic coatings have been studied extensively due to economical advantages and small permeability of hydrogen isotopes [1–3]. Wet-chemical methods, such as sol–gel method, slurry coating and electrochemical deposition, are suitable to prepare ceramic coatings on structural metals, because of their capability for coating complicated geometries and low processing temperatures.

Several researchers have examined barrier effects of coatings prepared by wet-chemical methods [4–12]. Terai et al. [4] and Nakamichi et al. [5,6] have prepared chemically densified Cr_2O_3–SiO_2 coatings on type 316 stainless steel (SS316) and measured permeation rate of tritium [4] or deuterium [5,6]. They reported that this type of coating provided only limited barrier effects, and permeation reduction factor (PRF), which is defined as the ratio of permeation rate of uncoated specimen in steady state to coated one, was 10–100 at 600 °C. Nevertheless, Nakamichi et al. [5,6] have found that addition of $CrPO_4$ by impregnation treatment in acid solution containing $CrPO_4$ and subsequent heat treatment led to significant improvement in barrier effects; PRF obtained for Cr_2O_3–SiO_2 coating including $CrPO_4$ on SS316 was 1000 under the similar conditions. These observations indicated that post-treatment with appropriate materials improves barrier effects of coatings derived by wet-chemical method. Kulsartov et al. [7] and Nakamichi et al. [8] have studied the effects of similar coating (Cr_2O_3–SiO_2 + $CrPO_4$) prepared on low-activation ferritic steel F82H. Although low-activation ferritic steels are primary candidates of structural materials of fusion blankets [13], the barrier effects obtained for F82H was smaller than that for SS316. The permeation reduction factor (PRF) for F82H was 400 [7] and 292 (in-pile test) [8] at 600 °C and much smaller at lower temperatures. Chikada et al. [10] and Yao et al. [11] have used a sol–gel method (spin coating) to prepare Er_2O_3 films on SS316, but they have not applied this technique to ferritic steels.

Films prepared by wet-chemical methods are prone to be porous due to volatilization of solvent during drying processes and cracking caused by different thermal expansions between coating materials and substrate metals during subsequent heat treatments. In our previous study [12], an electrolytic deposition technique, so-called electrochemical deposition-pyrolysis (ECDP) [14,15], was applied to seal sol–gel derived ZrO_2 coatings on a ferritic steel. Thin films of ZrO_2 (50 nm) were prepared on type 430 stainless steel (SS430) by a conventional sol–gel method, and pores in this film were sealed with ZrO_2 or Al_2O_3 by ECDP technique. The significant reduction in permeation rate was observed after sealing process by ECPD technique, and PRF of 1000 was obtained at 600 °C as the maximum value. The properties of coating, however, were not well reproducible, and further improvement was required.

The purpose of the present study is to examine barrier effects of Mg and Al phosphates against permeation of hydrogen through ferritic steel. Because of their environment-friendliness, refractoriness, and chemical stability, these phosphates have been used as binders of refractory ceramics [16–19], sealants of plasma-sprayed oxide coatings [20,21], and anti-corrosion/oxidation coatings [18,22,23]. The permeability of hydrogen isotopes, however, has

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been scarcely examined. In this study, capping layers of Mg and Al phosphates were prepared by dip-coating on ZrO_2/ZrO_2 or ZrO_2/Al_2O_3 films formed on SS430 by sol–gel and ECDP techniques, and hydrogen permeation rate was measured at 300–600 °C. The preparation of phosphate layer resulted in significant reduction in permeation rate, and PRF reached 3000 at 500 °C.

2. Experimental

Disk-type specimens of SS430 (20 mm diameter, 0.5 mm thickness) were polished with diamond powder and cleaned in ultrasonic bath with ethanol and de-ionized water. Thin films of ZrO_2 (50 nm) were first prepared on the specimens with a conventional sol–gel method, and these ZrO_2 films were sealed with ZrO_2 or Al_2O_3 by ECDP technique in the manner described elsewhere [12]. The thickness of coating was 100 nm after ECDP processes. The layer of ZrO_2 prepared by sol–gel method is hereafter denoted as ZrO_2(SG), and that sealed with ZrO_2 or Al_2O_3 by ECDP technique is ZrO_2(ED)/ZrO_2(SG) or Al_2O_3(ED)/ZrO_2(SG).

Then, the phosphate capping layers were prepared by dip-coating method. For preparing Mg phosphate layers, 2.5, 5 and 10 mass% $Mg(H_2PO_4)_2$ aqueous solution was prepared. At first, a specimen was dip-coated with 2.5 mass% solution at extraction rate of 0.5 mm s^{-1} and dried at 200 °C in air for 20 min. After heating at 500 °C in air for 1 h, the specimen was processed with 5 mass% solution for two times and heat-treated at 400 °C. At last, the specimen was processed with 10 mass% solution for one time and heat-treated at 300 °C in air for 1 h. For preparing Al phosphate layer, simplified processes were adopted, i.e. only 5 mass% $Al(H_2PO_4)_3$ aqueous solution and 500 °C heat treatment were applied.

Depth profiles of constituent elements of the coatings were measured by glow discharge optical emission spectroscopy (GD-OES). Cross-section morphology of the coatings was observed by a field emission scanning electron microscope (FE-SEM). Permeation rate of hydrogen through the specimen was measured with a vacuum device evacuated to 10^{-6} Pa by a turbomolecular pump and an oil-sealed rotary pump. The device was separated into two chambers, i.e. up- and downstream chambers, by the specimen sealed with metal gaskets (U-Tightseal, Usui Kokusai Sangyo Kaisha, Japan). The pressure of hydrogen in the upstream chamber was kept at 0.1 MPa, and that of hydrogen permeating through the specimen into the downstream chamber was measured by a quadrupole mass analyzer and a capacitance manometer; the pressure in the downstream chamber was maintained to be sufficiently low in comparison with the upstream. Detection limit of permeation rate controlled by pressure of residual gases was 1×10^{-8} m^{-2} s^{-1}. Each permeation measurement was started at the lowest temperature (300, 400 or 500 °C), and then the specimen temperature was raised in a step-by-step manner to 600 °C.

3. Results and discussion

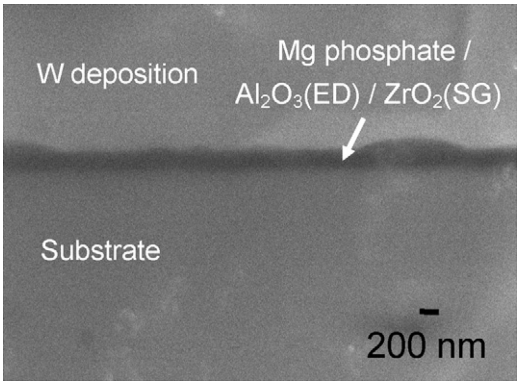

Fig. 1. Cross-section of Mg phosphate/Al_2O_3(ED)/ZrO_2(SG) coating.

Fig. 1 shows micrograph of cross-section of the specimen with Mg phosphate layer on Al_2O_3(ED)/ZrO_2(SG) as a typical example. The specimens for the cross-sectional observation were prepared by a focused ion beam (FIB) technique, and a layer of tungsten (W) was deposited to avoid the sputtering of coating during the specimen preparation. The coating has uniform thickness of about 200 nm. No crack is observed at the interface between coating and substrate. Depth profiles of constituent elements in Mg phosphate/ZrO_2(ED)/ZrO_2(SG) coating are shown in Fig. 2(a). The coating had two-layer structure of phosphate layer and oxide layer even after the heat treatment in air. Before preparing phosphate layers on ZrO_2(ED)/ZrO_2(SG) and Al_2O_3(ED)/ZrO_2(SG) coatings, peak of Cr was observed at the interface between substrate and oxide coatings as shown in Fig. 2(b). This Cr peak indicated the formation of Cr oxide at the interface during the heat treatment in air. The profile of Cr in Fig. 2(a) has no peak and shows the absence of Cr oxide at the interface. These observations showed that Mg phosphate/ZrO_2(ED)/ZrO_2(SG) coating had better barrier effects against penetration of oxygen to the interface than ZrO_2(ED)/ZrO_2(SG) and Al_2O_3(ED)/ZrO_2(SG); porosity in Mg phosphate/ZrO_2(ED)/ZrO_2(SG) coating should be lower than that in other types of coating. Similar profiles were also observed for Al phosphate/ZrO_2(ED)/ZrO_2(SG) and Mg phosphate/Al_2O_3(ED)/ZrO_2(SG) coatings.

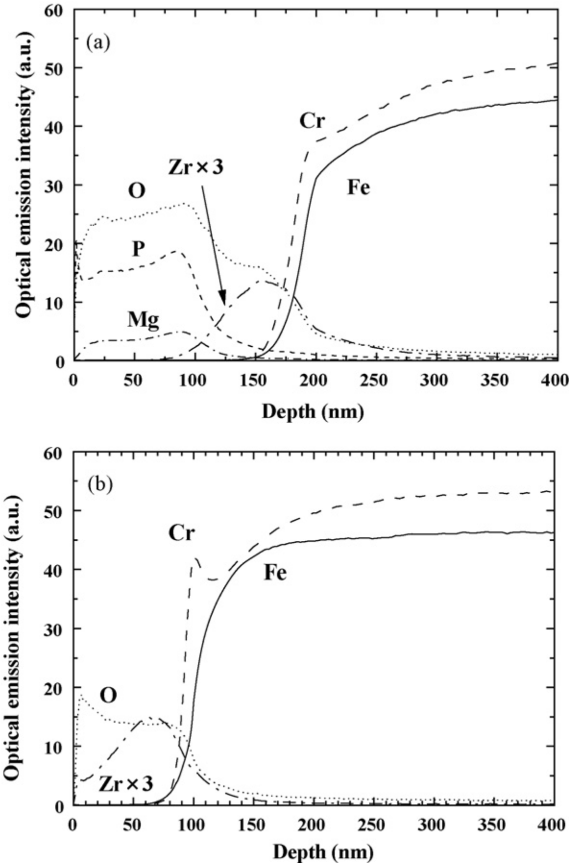

Fig. 2. Depth profiles of constituent elements in (a) Mg phosphate/ZrO_2(ED)/ZrO_2(SG) and (b) ZrO_2(ED)/ZrO_2(SG) coatings measured with GD-OES, where Zr × 3 means that the plot of Zr was made after multiplying the values of emission intensity by 3 because original intensity was too small.