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Deuterium permeation properties of Er_2O_3/Cr_2O_3 composite coating prepared by MOCVD on 316L stainless steel

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HIGHLIGHTS

- Grain sizes of the coatings enlarged with increasing thickness of Cr_2O_3 layer.
- Er_2O_3/Cr_2O_3 (80 nm) composite coating showed the maximum reduction in deuterium permeability.
- The Er_2O_3/Cr_2O_3 (80 nm) composite coating showed larger adhesion force value 9.2 N than the Er_2O_3 coating.
- Impurity layer formed at the interface of the Er_2O_3 coating due to element diffusion.

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ABSTRACT

In this work, an Er_2O_3/Cr_2O_3 composite coatings on 316L stainless steel were prepared by metalorganic chemical vapor deposition (MOCVD). Effect of Cr_2O_3 layer on the microstructure, mechanical properties and deuterium permeation properties of Er_2O_3 coating was investigated. It was found grain sizes of the coatings enlarged with increasing the thickness of Cr_2O_3 layer. The Er_2O_3/Cr_2O_3 (80 nm) composite coating showed larger adhesion force value 9.2 N than the Er_2O_3 coating. The Cr_2O_3 layer adding could significantly enhance the deuterium permeation inhibition property of the coatings. The single-layer Er_2O_3 coating exhibited the minimum reduction in deuterium permeability, and the permeation reduction factor (PRF) values were in the range of 95–146 at 823–973 K. The maximum reduction in deuterium permeability was obtained from the Er_2O_3/Cr_2O_3 (80 nm) composite coating, and the PRF values were in the range of 463–206 at 823–973 K. With further increasing thickness of the Cr_2O_3 layer to 120 nm, the hydrogen permeation inhibition performance of the composite coating lower instead. Furthermore, apparent delamination of coating was illustrated on the single-layer Er_2O_3 coating after the permeation measurement, and this might be the main reason for the transformation to diffusion limiting process.

1. Introduction

Hydrogen diffusion and permeation at high pressure are detrimental to the integrity of structural components for hydrogen storage and distribution [1–4]. 316L stainless steel is widely used in fields of hydrogen store devices and fusion reactors [5–7]. However, 316L stainless steel is susceptible to hydrogen embrittlement due to high hydrogen permeation rate at elevated temperature. The general solution is to use tritium permeation barriers (TPBs) on the inner wall of constructional materials to reduce tritium loss [8–12]. Some oxide ceramic coatings are chosen as important candidates for hydrogen permeation barrier due to their abilities for permeation barrier and good mechanical properties. Among the coating materials that have been considered, Al_2O_3 is a major candidate for research today because of its high permeation reduction factor and stability at high temperature [13,14]. Recently, Er_2O_3 is selected as a candidate materials for TPB coatings because it carries over excellent properties of α-Al_2O_3 [15]. It has been found that Er_2O_3 coatings can suppress deuterium permeation to an extent similar to Al-based coatings, which were the main focus of previous studies [15,16]. Moreover, it shows good mechanical stability under thermal load when Er_2O_3 is in contact with other materials and more appropriate capabilities, such as lower Gibbs free energy of formation [17]. However, working at high temperature may induce thermal cracks in coating due to different thermal expansion

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coefficients of Er_2O_3 and 316L stainless steel. According to our previous research, Cr_2O_3 could act as interlayer between Al_2O_3 coating and 316L stainless steel substrate because of gradient distribution of thermal expansion. By adding Cr_2O_3 interlayer, Al_2O_3/Cr_2O_3 composite coating exhibited much lower permeability than single-layer Al_2O_3 coating with the same thickness [18]. In addition, TPB coatings, including Er_2O_3 coating and Er_2O_3/Cr_2O_3 composite coating, often work in hydrogen isotopes-containing harsh environments, especially under high temperature and high pressure hydrogen conditions. It would incite microstructure change of the coatings. Therefore, for ensuring the effectiveness of TPB coatings, the performance evolution in working environments should be considered. In this work, in order to investigate the evolution of the microstructure and of coatings in working environment. The high-temperature annealing in hydrogen atmosphere was used to simulate the working environments. In this study, Er_2O_3/Cr_2O_3 composite coatings, with different thickness of Cr_2O_3 layer, were deposited on 316L stainless steel by MOCVD. Effect of Cr_2O_3 layer on the phase, the morphology and the deuterium permeation properties of Er_2O_3 coating was investigated.

2. Experimental

2.1. Material synthesis

The Er_2O_3/Cr_2O_3 composite coating was deposited on 316L stainless steel substrates in a horizontal hot wall reactor, which is described elsewhere [19]. The 316L stainless steel disk was 29 mm in diameter and 0.5 mm in thickness. Erbium β-diketonates organometallic $Er(tmhd)_3$ and Chromium(III) acetylacetonate $Cr(acac)_3$ were used as precursors. $Cr(acac)_3$ was sublimated at 433 K, and $Er(tmhd)_3$ was sublimated at 419 K. H_2 was used as carrier gas with a flow rate of 20 sccm. The carrier gas H_2 was mixed with water vapor by flowing through a water bubbler before arriving at the precursor sublimation zone. Cr_2O_3 was deposited at 773 K first, and then Er_2O_3 was deposited at 873 K. The deposition time of Er_2O_3 coating was 120 min. The deposition time of Cr_2O_3 layer was from about 20 to 60 min. The as-deposited coatings were annealed at 973 K for about 5 h in hydrogen atmosphere.

2.2. Material characterization

The phase and morphology of the films were examined by X-ray diffraction (XRD, Rigaku-D/max2500) and scanning electron microscopy (SEM, Hitachi-S4800). Chemical composition and binding states are examined by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM). Deuterium permeation properties were measured by a self-made apparatus. Before taking permeation measurements, the uncoated side of 316L stainless steel was polished in order to eliminate the influence of surface oxide layer formed during thermal processing. The permeation chamber was divided by the coated disk into two parts: the upstream chamber and the downstream chamber. The coated side of the sample is mounted facing the upstream side. Before the permeation measurement, the upstream chamber was repeatedly poured with deuterium gas and then pumped for three times to eliminate residual impurity gas. Then deuterium was used as permeation gas and introduced into the upstream chamber at 40–100 kPa using a needle valve. The pressure of deuterium was monitored by a quartz vacuum gauge (10–100 kPa, DL-10, Beijing Xinhengjiu Tech.). During the permeation measurement, the downstream chamber was continuously pumped to maintain the pressure at 2×10^{-5} Pa. The pressure of the downstream chamber was measured by an ionization gauge (6×10^{-8}–10^{-1} Pa, DL-7, Beijing Xinhengjiu Tech.). The flux of deuterium permeating through the sample from the coated side in the upstream chamber to the downstream chamber was measured by a quadrupole mass spectrometer (QMS, Hiden HPR30). The measurement temperatures for deuterium permeation were 823 K–973 K. The measurement procedure is described in detail elsewhere [19].

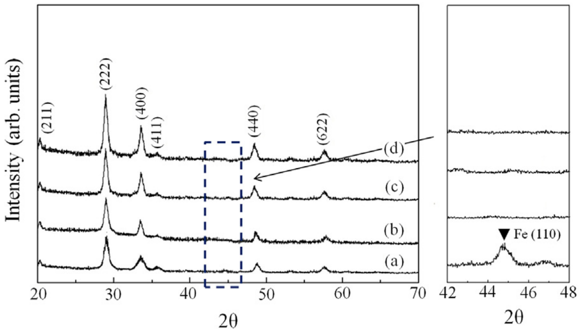

Fig. 1. X-ray diffraction patterns of (a) S1, (b) S2, (c) S3 and (d) S4. The inset showed the enlarged XRD pattern with diffraction angle 2θ between 42° to 48° marked by rectangle.

Table 1
The grain sizes, the thicknesses of Cr_2O_3 layer and Er_2O_3 layer of the single-layer Er_2O_3 coating Er_2O_3/Cr_2O_3 composite coatings.

Sample	Grain size (nm)	Thickness (nm)	
		Cr_2O_3 layer	Er_2O_3 layer
S1	35	0	604
S2	56	44	609
S3	73	82	605
S4	81	118	597

3. Results and analysis

Fig. 1 shows the grazing incidence XRD (GIXRD) patterns of the single-layer Er_2O_3 coating and the Er_2O_3/Cr_2O_3 composite coatings with increasing thickness of Cr_2O_3 layer. The incident angle of GIXRD was set at 1°. In the experiment, the thickness of the Cr_2O_3 layer was around 40 nm, 80 nm or 120 nm. For convenience, The single-layer Er_2O_3 coating and the Er_2O_3/Cr_2O_3 coating with the Cr_2O_3 layer thickness of 40 nm, 80 nm, 120 nm were denoted as S1, S2, S3 and S4 respectively. All the diffraction peaks of the samples could be indexed to the powder-diffraction file for erbium oxide. Moreover, the intensity of the diffraction peaks increased, and the full width at half maximum (FWHM) of the diffraction peaks decreased after adding Cr_2O_3 layer, indicating the increase of crystallite sizes after adding Cr_2O_3 layer. However, the Fe (110) diffraction peak at 44.7° [20] was detected on the coating S1. It meant that trace amount of impurity phase exist after annealed in hydrogen atmosphere for the coating S1. According to the Scherrer equation $D = K\lambda/\beta\cos\theta$, where K is scherrer constant, λ is wavelength, β is intrinsic width and θ is Bragg angle. β can be expressed by the FWHM of peaks, the grain size D was calculated, and the results were listed in Table 1. Here, X-ray slow scan mode with speed 0.1°/min was used to test a characteristic peak such as (222) diffraction peak. The results were based on the statistics data of (222), (400) and (440) characteristic peaks.

The surface morphologies of the single-layer Er_2O_3 coating and the Er_2O_3/Cr_2O_3 composite coatings, measured by SEM, are shown in Fig. 2. It was found that the coatings exhibited a surface morphology with angular grains, and the grain sizes of the coatings enlarged with increasing thickness of the Cr_2O_3 layer, which consistent with the results observed in the XRD pattern.

High-precision profilometer was used to measure the thicknesses of the samples. Fig. 3(a) and (b) shows the profilometer measurement curves of the S1 and S3, respectively. According to

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