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Study on influence factors of permeation reduction factor of Al_2O_3-hydrogen isotopes permeation barriers

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
4 January 2016
Accepted 5 January 2016
Available online 2 February 2016

Keywords:
Al_2O_3-HIPB
Hydrogen energy
Deuterium permeation reduction factor
Coating thickness
Annealing temperature

ABSTRACT

Hydrogen isotopes permeation barriers (HIPB) play an important role in reducing hydrogen isotopes permeation and leakage in hydrogen energy and thermonuclear fusion energy. In this study, the Al_2O_3-HIPB were prepared on 316L stainless steel by RF magnetron sputtering. The impacts of coating thickness and annealing temperature of as-deposited coatings on deuterium permeation reduction factor (D-PRF) are studied in detail. With increasing thickness of coatings from 0.2 μm to 1.6 μm, the D-PRF did not rise significantly, which indicated that coating surface, for thin coatings, played more important role in impeding deuterium permeation than coating interior. As a result of further crystallization and grain growth, the 700 °C-annealed Al_2O_3 coatings had stronger ability to impede deuterium permeation than 600 °C-annealed Al_2O_3 coatings. This further proofs that grain boundaries may be a short-cut path for deuterium diffusion in Al_2O_3 coatings. The D-PRF drastically decreased when the annealing temperature reaches 800 °C, which might be ascribed to the new phases form and the coating cracks appearance after 800 °C annealing.

Introduction

Hydrogen energy is the promising green energy and an important alternative to fossil energy. The hydrogen isotopes leakage and resulting constructional materials crisp are urgent problems [1–6]. The general solution is to prepare hydrogen isotopes permeation barriers (HIPB) on the inner wall of constructional materials. HIPB have wide application in many fields related to hydrogen energy [7]. HIPB are prepared on inner wall of construction materials to impede the deuterium and tritium permeation from circle tubes in thermonuclear fusion such as ITER [8]. In the vacuum solar receivers, the releasing hydrogen as a result of decomposition of heat transfer oil in steel pipe at 400 °C may permeate through the steel pipe and enters the annular space between the glass tube surrounding the central steel pipe and cause significant increase of heat loss. The existence of HIPB could efficiently

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http://dx.doi.org/10.1016/j.ijhydene.2016.01.018
0360-3199/

reduce the hydrogen permeation [9]. In the hydro-cracking reactor of petroleum industry, hydrogen with scores of atmosphere pressure and 300–500 °C temperature would easily permeate into steel and react with carbon to form CH_4. The CH_4 bubble may form and grow at the place such as inclusion and grain boundary, further cause the steel embrittlement, which can be significantly inhibited by HIPB [10]. As a promising HIPB, Al_2O_3 coatings have been mentioned in previous literature. Zhang et al. prepared the Al_2O_3 coating by a three-step method, i.e. ambient temperature melts salt electroplating followed by heat treating and artificial oxidation at 700 °C. The 11–13 μm coatings were made on HR-2 steel and the deuterium permeation rate was reduced by 2–3 orders of magnitude at 600–727 °C [11]. He et al. studied the effect of substrate roughness and thermal cycling to the deuterium permeation of the MOCVD derived alumina coatings. The result showed that substrate with low roughness was favored to obtain the low permeability and high thermal cycling resistance of coatings [12]. He et al. also investigated the influence of microstructure on the hydrogen permeation of alumina coatings. It was found that the 900 °C-annealing coatings exhibited the lower ability to impede the deuterium permeation as a result of formation of spinel $MnCr_2O_4$ [13]. In addition, other research were also carried in previous papers [14–19], involving the preparation process, permeation reduction factor (PRF), the resistivity and the compatibility between the HIPB with construction materials. Furthermore, these theory calculations were also performed [8,20–22]. However, the impacts of coating thickness and annealing temperature of thin Al_2O_3-coatings on deuterium permeation reduction factor (D-PRF) have hardly been mentioned in previous studies.

In this study, the Al_2O_3 hydrogen isotopes permeation barriers (Al_2O_3-HIPB) were prepared on 316L stainless steel by RF magnetron sputtering. The influencing factors of D-PRF including coating thickness and annealing temperature of as-deposited Al_2O_3 coatings are studied in detail.

Experimental

Sample preparation

The Al_2O_3 coatings were prepared on 316L stainless steel disks with 25 mm diameter and 0.5 mm thickness. All these disks were ground with 2000 grit sandpaper, and then cleaned ultrasonically at 80 °C according to the following order: In sodium hydroxide solution for 15 min, deionized water for 15 min and alcohol for 15 min. These disks were blown to be dry. The radio frequency magnetron sputtering was utilized to deposit Al_2O_3 coatings with 60 mm target–substrate distance. The sputtering chamber was vacuumed to 8×10^{-4} Pa, and then the 99.99% argon and 99.995% oxygen were introduced into the sputtering chamber in which the total gas pressure was kept at 1.2 Pa. The flux ratio of argon to oxygen was 3:1. After deposition at 300 °C, these samples were annealed in argon. For studying the impact of annealing temperature on D-PRF, the samples coated with Al_2O_3 were annealed at 600 °C, 700 °C and 800 °C in vacuum, respectively. The annealing was used for crystallization of Al_2O_3.

Characterization

Permeation reduction factor (PRF) is the most important parameter of the HIPB, which is used to evaluate the ability of coatings reducing hydrogen isotopes permeation. The PRF is defined as the ratio of the flux through the uncoated sample to that through the coated one. The higher PRF means the stronger ability reducing hydrogen isotopes permeation. The permeation apparatus was assembled according to the description in Ref. [4]. The parts and integral permeation samples are shown in Fig. 1. After coating and annealing, the coated samples were welded together with these parts by laser and the integral permeation samples were made. For avoiding the coatings were destroyed, the distance between welding position and coating is far than 2 mm. After welding, the leak hunting was carried out for ensuring that there was no deuterium leakage in permeation process. After the integral permeation sample was installed on the permeation apparatus, the apparatus was divided into two parts by sample, i.e., the low-pressure part and high-pressure part. The apparatus was pumped until the pressure reached 10^{-6} Pa and the deuterium ion current of quadrupole mass spectrometer was also lower than 10^{-12} A. Then, the permeation gas was introduced into the high-pressure part with pressure of about 120 kPa at the set temperature. The ion current was recorded when the permeation reach stable and the PRF could be obtained. It took 3.5 h to finish a permeation cycle from 600 °C to 300 °C. Considering high abundance of hydrogen in nature which results in the high ion current background and radioactivity of tritium, the deuterium was selected as permeation gas and the corresponding PRF was called D-PRF.

The morphologies of the Al_2O_3-HIPB were observed through scanning electron microscopy (SEM, ZEISS SUPRA 55). The element analysis of Al_2O_3 coatings was carried by EDS which was attached to SEM. The phase compositions were characterized by X-ray diffraction (XRD, RIGAKU D/MAX-RB).

Results

Fig. 2 (a) and (b) show the SEM images of the surface and cross-section of the Al_2O_3-HIPB. It is found that the surface is smooth and grains are fine, the grain size is about 20 nm. There are no cracks and pours on the surface of the coatings. The cross-section image shows that the coating is compact and the thickness is uniform. It is also observed that the coatings consist of spherical grains.

Fig. 3 shows the ion currents of deuterium permeating samples with different-thickness Al_2O_3 coatings. The ion currents of deuterium permeating the sample coated with 0.2 μm, 0.8 μm and 1.6 μm Al_2O_3 coatings are showed in curve (a), (b) and (c), respectively. By comparing ion current value of deuterium which permeates uncoated samples and coated samples, it is known that the Al_2O_3 coatings impede the deuterium permeation. The D-PRF of Al_2O_3 coatings are showed in the bottom of Fig. 3. It is observed that the D-PRF does not rise significantly although the coatings have increased from 0.2 μm to 1.6 μm. Considering that the pressure