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Influence of microstructure on the hydrogen permeation of alumina coatings

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ABSTRACT

In this work, the influence of microstructure on the hydrogen permeation property of alumina coatings was investigated. The different microstructures were obtained by annealing coatings at 700 °C or 900 °C. The permeation measurements showed that the 700 °C annealed coating exhibited lower hydrogen permeability than the 900 °C annealed coating. The 700 °C annealed coating was amorphous alumina. While, the 900 °C annealed coating had the spinel $MnCr_2O_4$ phase and γ-alumina. This spinel $MnCr_2O_4$ formed a network on the coating surface compared with the fine and smooth surface of the 700 °C annealed coating. The $MnCr_2O_4$ network in the 900 °C annealed coating formed short-cut for hydrogen diffusion, and thus resulted in high permeability. Furthermore, apparent delamination of coating was illustrated on the 900 °C annealed coating after the permeation test, and this was another reason for the high permeability of coating.

1. Introduction

Hydrogen can dissolve and permeate in most materials, and the permeation of hydrogen may cause various problems. For example, the hydrogen diffusion and permeation at high pressure are detrimental to the integrity of structural components for hydrogen storage and distribution [1]. In the vacuum solar receivers, the decomposition of heat transfer oil in steel pipe at 400 °C leads to the release of hydrogen, and this hydrogen permeates through the steel pipe and enters the annular space between the glass tube surrounding the central steel pipe, causing significant increase of heat loss [2,3]. Moreover, the future fusion reactors use deuterium and tritium as fuel, and the permeation of tritium through first wall and tritium breeding blanket reduces the economic viability of operation and raises radiological hazards [4–6]. Therefore, the suppression of hydrogen permeation is essential in the hydrogen related fields.

The application of hydrogen permeation barriers on structural materials is an effective and practical route to reduce hydrogen permeation [4–16]. In general, ceramics are widely investigated as permeation barrier materials for their low hydrogen permeability, such as SiC [7], TiAlN [8], ZrO_2 [9,10], Er_2O_3 [11] and Al_2O_3 [12–16] etc. Among these materials, alumina is a promising barrier material because of its high thermal stability, hardness and low hydrogen permeability. The alumina coatings were stable against corrosions by Pb–17Li liquid from thermodynamic calculation at 500 °C [17] and corrosion experiment conducted at 550 °C for 5000 h [18]. Alumina coatings offered effective reduction to hydrogen permeation [4,12], e.g. the 1 μm thick alumina coating exhibited a deuterium permeation reduction factor of 10^3 at

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temperatures 700–800 °C [12]. The hydrogen permeation properties of coatings may not only relate to the material itself, but also depend much on the coating microstructure [11,19,20]. Chikada et al. [11] investigated the relationship between structure and permeation property of Er_2O_3 prepared by MOCVD. It was found that a $(Fe,Cr)_2O_3$ surface layer on ferritic/martensitic steel caused defects and degradation in the Er_2O_3 coating during hydrogen permeation measurements at 500–600 °C, while the coating yielded reduction factors of 500–700 at 500–700 °C without $(Fe,Cr)_2O_3$ layer. It was believed that the Er_2O_3 coating was damaged during the temperature change because of the inhomogeneous $(Fe,Cr)_2O_3$ layer.

In our previous works, alumina coatings were prepared by MOCVD on 316L [15,16]. The coatings showed permeation reduction factor of 106 at 600 °C, and the hydrogen permeation suppression performance was not apparently affected after thermal cycling at 700 °C for 30 times. However, there is still limited knowledge on the microstructure change during the coating formation and consequently the hydrogen permeation behavior of coating. In this work, alumina coatings were deposited on 316L substrate by MOCVD. Different microstructures were obtained by changing heat treatment conditions. Hydrogen permeation measurements were performed to evaluate the effect of microstructure on the permeation properties of coatings as hydrogen permeation barriers.

2. Experimental

2.1. Coating preparation

316L stainless steel disks of 29 mm in diameter and 0.5 mm in thickness were used as substrates. Deposition of alumina coating was performed in a MOCVD system, as described elsewhere [15]. Aluminum acetylacetonate ($Al(acac)_3$, ≥99.8%, Xingye Chemical) was sublimated at 120 °C and the vapor was transported to the furnace by carrier gas H_2. The flow rate of H_2 was 20 sccm. The alumina coating was deposited on one side of the substrate at 350 °C for 2 h with pressure of 1.2–1.4 kPa in the chamber. The as-deposited coatings were annealed in argon at 700 °C and 900 °C.

2.2. Coating characterization

Phases of coatings were examined by X-ray diffraction (XRD, Rigaku-D/max2500). The microstructure of coatings was examined by scanning electron microscope (SEM, Hitachi-S4800).

The hydrogen permeation properties of coatings were measured by a self-made apparatus [15]. The permeation chamber was divided by the alumina coated disk into two parts: the upstream and downstream chamber. Deuterium was used as permeation gas in the upstream chamber. The coated side faced the upstream chamber to avoid oxidation of the uncoated side due to the oxidizing contaminations in deuterium. The permeated deuterium through sample was measured by quadrupole mass spectrometer (QMS, Hiden HPR30).

The steady state permeation flux of hydrogen through material can be expressed by the following equation [14]:

$$J = \frac{P \cdot p^n}{d}$$

where P is the permeability, p is the hydrogen pressure, n is the pressure exponent, and d is the sample thickness. The rate limiting process for permeation is hydrogen diffusion when the pressure exponent n equals to 0.5, while when n equals to 1, the surface process is the rate limiting process.

3. Results and analysis

Fig. 1 shows the hydrogen permeabilities of the alumina coatings as a function of temperatures. It was apparent that the 900 °C annealed alumina coating exhibited substantially higher permeabilities than the 700 °C annealed coating. The permeation reduction factor (PRF) was calculated by dividing the permeability of 316L by that of the alumina coating. For the 700 °C annealed coated sample, the PRF values were in the range of 65–139 at temperatures 600–700 °C. While, for the 900 °C annealed coating, the PRF values were 11 and 6 at 600 °C and 650 °C. There was an apparent drop of PRF values for the 900 °C annealed coating compared with the 700 °C annealed coating.

To evaluate the hydrogen permeation regime, the driving pressure dependence of the permeation flux of the coatings annealed at 700 °C and 900 °C was investigated and the results were presented in Fig. 2. Double logarithmic plots of the data well followed a linear relationship. The pressure exponent reflected the rate limiting process of hydrogen permeation. In general, pure surface process limited hydrogen permeation is expected for defect-free oxide coatings. However, the oxide coatings usually suffer from various kinds of defects, e.g. pinholes, pores, cracks or delamination of coating etc., and the hydrogen permeation is thus controlled by both the surface process and hydrogen diffusion. In Fig. 2a, the pressure exponent of the 700 °C annealed coating was 0.75–0.78, which indicating both the surface process and hydrogen diffusion as the rate limiting process for permeation. However, in Fig. 2b, the pressure exponent of the 900 °C annealed coating was 0.71 at 600 °C, while the value decreased to 0.52 at 650 °C, indicating that the permeation changed to hydrogen diffusion limited regime.

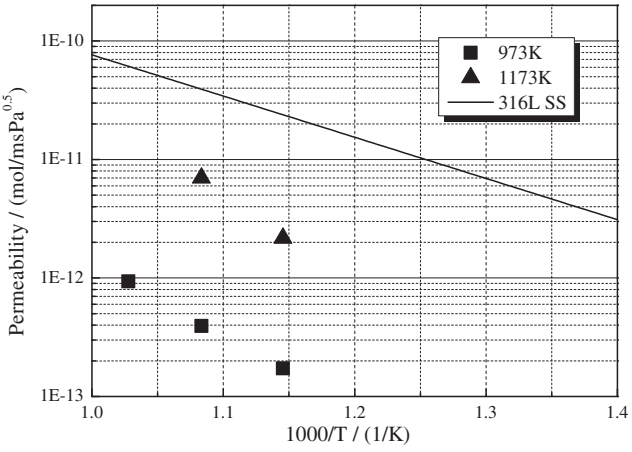

Fig. 1 – Arrhenius plots of hydrogen permeabilities of alumina coatings.