Improvement of high temperature stability of Pd coating on Ta by HfN intermediate layer

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ABSTRACT

Hafnium nitride (HfN) was chosen as a material for non-porous intermediate layer to improve the high temperature stability of Pd–Ta composite membranes for hydrogen separation. A layer of dense HfN (70 nm) was prepared between Ta substrate and thin Pd film (300 nm), and the high temperature stability of Pd coating was examined by hydrogen absorption experiments at 573 K after the heat treatments at 873 and 973 K. The HfN layer showed obvious hydrogen permeability, though the permeation rate in HfN appeared to be smaller than that in Pd and Ta. In addition, the degradation in coating effects of Pd at elevated temperatures was substantially retarded by HfN layer. Such improved stability was ascribed to retardation of open porosity development in Pd films and interdiffusion between Pd and Ta. It was concluded that HfN is a potential candidate material for intermediate layer to improve high temperature stability of Pd-group 5 metal composite hydrogen separation membranes.

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1. Introduction

Hydrogen separation membranes are key components of membrane reactors for production of hydrogen via, for example, steam reforming of natural gas [1]. A modern reforming system with Pd alloy membranes has nominal hydrogen production capacity of 40 Nm^3/h and energy efficiency of 70–76% [2]. Group 5 metals (V, Nb and Ta) have higher hydrogen permeabilites [3], lower cost and richer natural resources than Pd. Hence, membranes of group 5 metals have the potential to provide improved performance of reforming systems at reduced cost.

The surfaces of group 5 metals are reactive not only to hydrogen but also to other impurities such as oxygen. Therefore, almost all separation membranes based on group 5 metals

reported in literature are coated with Pd films as protection layers against oxidation [4–29]. Such composite membranes are sufficiently stable at/below 573 K [13,15,16]. At the typical operation temperatures of reforming systems (ca. 773–823 K [2]), however, the Pd coatings degrade quickly. Edlund et al. [8,9] observed significant reduction in permeation rate through Pd-coated V membranes at 973 K together with interdiffusion between Pd and V. Interdiffusion was observed also for the Pd–Ta system after the permeation experiments at temperatures from 557 to 662 K [11]. Rothenberger et al. [14] reported the development of open porosity and delamination of Pd films on Ta after hydrogen permeation experiments at temperatures from 623 to 1173 K. Hatano et al. [30] observed a marked reduction in hydrogen absorption rate accompanied by the development of open porosity in Pd films for Pd–Nb system

after heating above 623 K. Similar porosity development in the Pd–Nb system was also reported by Busnyuk et al. [31]. In order to prevent the interdiffusion between V and Pd, Edlund et al. [8,9] developed porous oxide intermediate layers. It is, however, difficult to prepare thin and dense Pd films on porous intermediate layers. Indeed, the thickness of Pd films employed in their study was rather large (25 μm) and comparable with that of conventional Pd alloy membranes. Benefits obtained by using such composite membranes cannot be significant. From these viewpoints, Hatano et al. [30,32] employed dense Nb carbide layers as intermediate layer between thin Pd film (100 nm) and Nb substrate. The high temperature stability of the Pd film was obviously improved by insertion of Nb carbide layers but this was still insufficient for long-term operation at temperatures above 773 K.

In the present study, layers of dense HfN were deposited between thin Pd films and Ta substrates as an intermediate layer. Due to their high chemical and thermodynamic stabilities and electronic properties, the nitrides of group 4 metals (Ti, Zr and Hf) have been used as diffusion barriers and adhesion promoters in electronic devices [33–35]. The free energy of formation of HfN is more negative than that of TiN and ZrN [36], and hence the stability of HfN on group 5 metals should be superior to TiN and ZrN. Hydrogen permeation through the nitrides, however, has scarcely been studied. Shu et al. [37] have prepared a thin TiN layer as diffusion barrier of composite hydrogen permeation membrane consisting of Pd–Ag alloy film and porous stainless steel substrate. In this case, however, the TiN layer was also porous, and hence the hydrogen permeability through the bulk of TiN was not an issue. Recently, Kim and Hong [38] prepared membranes of TiN-5 wt.%Ni by spark plasma sintering and observed hydrogen permeability higher than $Pd_{77}Ag_{23}$ at 473, 573 and 673 K. Although the rate-limiting step of permeation was considered to be the diffusion process in TiN-5 wt.%Ni, this type of membrane was also porous and the permeation mechanism has not been understood in detail; the specific surface area of the TiN-5 wt.%Ni membrane was as high as 0.92 m^2 g^{-1} [38]. The objectives of the present study are to examine (1) whether a dense HfN intermediate layer is permeable to hydrogen or not, and (2) influence of a HfN intermediate layer on the high temperature stability of the Pd film. Sheet-type Ta specimens with HfN intermediate layers (70 nm thick) and Pd films (300 nm) were heat-treated in vacuum at 873 and 973 K, and then hydrogen absorption by the substrate Ta through the Pd film and HfN intermediate layer was examined at 573 K. Changes in morphology and surface state by the heat treatments were also studied.

2. Experimental

Specimens of pure Ta (12 × 22 × 0.5 mm, 99.95% purity) were prepared from a sheet supplied by Nilaco Co., Japan. The surfaces of specimens were polished with abrasive papers and finished with diamond powders (9 and 3 μm) and colloidal silica suspension. A layer of dense HfN was prepared on Ta specimen at 673 K by arc plasma gun (Ulvac Co., Japan) with Hf cathode under N_2 gas atmosphere of 0.3 Pa. The thickness of HfN layer reached 70 nm at 3600 pulses. The HfN layer thus

prepared showed typical gold-yellow color, and there were no cracks and open pores visible with a filed-emission scanning electron microscope (FESEM)(JEOL JSM-6701F). Analysis by means of glazing-angle X-ray diffraction technique (XRD) (Phillips PW3200) showed the presence of HfN in NaCl-type cubic structure; the diffraction pattern agreed well with that reported in Refs. [39,40]. Then the specimen was installed in a magnetron sputtering device to prepare the Pd film. After gentle sputtering of the specimen surface at room temperature for 30 s by rf-discharged Ar plasma (50 W) to remove contaminants, Pd film was formed by DC magnetron sputtering under Ar atmosphere of 0.5 Pa at 573 K. The thickness of Pd film reached 300 nm by sputtering for 600 s at 100 W. The specimens thus prepared are hereafter denoted as Pd/HfN/Ta. For comparison, the specimens without HfN layer were also prepared, and they are described as Pd/Ta.

In order to examine the high temperature stability of the Pd films, the specimens were first heat-treated for 3.6 ks (1 h) at 973 K in vacuum (10^{-5} Pa). Then, additional heat treatment was carried out in vacuum at 873 K for 18 ks (5 h). Hydrogen absorption experiments were carried out after each step of heat treatment with the vacuum apparatus described elsewhere [41]. First, the heat-treated specimen was cooled down to room temperature and exposed to air for 3.6 ks to form Ta oxides on the area not covered by Pd. Then, hydrogen absorption was examined at 573 K. Since the hydrogen absorption experiments were carried out in a closed vacuum system, the rate of hydrogen absorption was evaluated from that of pressure drop. The initial pressure of H_2 gas was adjusted to be 13.3 Pa. Under the above-mentioned conditions (573 K and 13.3 Pa), Ta sheet without Pd film showed no noticeable hydrogen absorption due to the presence of Ta oxides formed by the exposure to air. In other words, hydrogen absorption by Pd/Ta and Pd/HfN/Ta took place only through the Pd film (and HfN intermediate layer beneath it). Therefore, the hydrogen absorption rate after the heat treatment is sensitively dependent on the stability of the Pd film; it should decline substantially if the coating degrades. The above-mentioned value of initial H_2 pressure (13.3 Pa) is significantly smaller than the upstream H_2 pressures commonly employed in the permeation experiments in this field [4–29]. In general, however, the rates of hydrogen absorption and permeation become more sensitive to surface state as pressure decreases [42]. Hence, the experiments in the low H_2 pressure region appeared to be suitable to examine the effects of coating stability. After the heat treatments, the specimens were examined by means of FESEM, XRD, and Auger electron spectroscopy (AES) (Perki-nElmer 15-110B). A heat treatment at 873 K for 18 ks in addition to the above-mentioned one (36 ks in total at 873 K) was carried out in some cases to observe the clear difference between Pd/Ta and Pd/HfN/Ta.

3. Results and discussion

Fig. 1(a) shows typical hydrogen absorption curves observed at 573 K for Pd/Ta before and after the heat treatments at 973 K for 3.6 ks and additional heating at 873 K for 18 ks. Before heat treatment, the pressure of hydrogen dropped rapidly due to the absorption by the specimen. The rate of hydrogen