



Article Improved High-Temperature Stability and Hydrogen Penetration through a Pd/Ta Composite Membrane with a TaTiNbZr Intermediate Layer

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Abstract: In the hydrogen separation membrane, a dense TaTiNbZr amorphous layer was prepared between Pd and Ta to form a Pd/TaTiNbZr/Ta membrane system to prevent the reaction between Pd and Ta at high temperatures. The structural and chemical stability of the Pd/TaTiNbZr/Ta film system at high temperatures were investigated by annealing at 600 °C for 24 h. The high-temperature hydrogen permeation properties of the Pd/TaTiNbZr/Ta film systems were investigated by hydrogen permeation experiments at 600 °C after heat treatment for 6 h. The TaTiNbZr layer was significantly hydrogen-permeable. With the increase in the thickness of the barrier layer, the hydrogen permeability of Pd/TaTiNbZr/Ta decreased, but its hydrogen permeation flux was smaller than that of the highest value of Pd/Ta when it reached the steady state. The presence of the TaTiNbZr layer effectively blocks the interdiffusion between Pd and Ta to form TaPd₃, improving the sustained working ability of the Pd/TaTiNbZr/Ta membrane system. The results show that TaTiNbZr is a candidate material for the intermediate layer to improve the high-temperature stability of metal-composite hydrogen separation membranes.

Keywords: hydrogen permeation; barrier layer; high-entropy alloy

1. Introduction

Against the backdrop of today's growing energy challenges, hydrogen energy is attracting attention as a clean and efficient form of energy. There are still many challenges to realizing the widespread use of hydrogen energy in the energy transition, including technical issues in the production, purification, storage, transportation and utilization of hydrogen [1,2]. Among them, hydrogen purification has been receiving a lot of attention from researchers. Hydrogen separation membranes are key components of membrane reactors for the separation of hydrogen and its isotopes, e.g., for the recovery of deuterium and tritium from fusion reactors and for the steam reforming of natural gas. In previous studies [3–6], researchers have proposed solid alloy membrane separation technology to improve the recovery of hydrogen isotopes. Alloy film separation of hydrogen is characterized by high hydrogen selectivity, high hydrogen permeability, and good chemical stability [7–9]. Therefore, the development of new alloy membranes for the extraction and purification of hydrogen-permeable isotopes is a hot topic in current research.

Thick Pd layers reduce the rate of hydrogen penetration and have a high material cost [10]. Therefore, the development of new ultrathin films with good mechanical properties is the main goal of many researchers in this field. This goal is usually achieved by incorporating a thin Pd layer on the surface of the alloy [3–6,11–15]. Group V transition metals theoretically have a higher permeability to hydrogen atoms than Pd, a feature that has been experimentally demonstrated in a number of systems [4]. Cooney et al. showed



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). that the high permeability of group V transition metals is attributed to their more open body-centered cubic (BCC) structure with greater hydrogen solubility and faster diffusion rates [4]. In addition, the cost of these metals is much lower than that of pure Pd. Due to the high H₂ permeability and low cost of these BCC metals, thicker films can be used as support materials. When Pd/Ta multilayers were subjected to hydrogen permeation experiments at 500 °C, the decrease in the hydrogen permeation ability of Pd/Ta was mainly due to the formation of compounds by the interdiffusion of Pd and Ta, leading to a loss of the catalytic ability of Pd [4-6,14]. Therefore, inserting a diffusion barrier layer between Pd and Ta is a strategy that can prevent the formation of PdTa alloys. Nozaki et al. [16] chose to use hafnium nitride (HfN) as a barrier layer and developed a Pd/HfN/Tamembrane system, and after annealing at different temperatures, the results showed that the HfN layer exhibited significant hydrogen permeability, with the shortcoming that the hydrogen permeability of HfN was smaller than that of Pd and Ta. Nozaki et al. [14] analyzed the effect of the thickness of the interlayer HfN on the hydrogen permeability and showed that HfN samples with a thickness of 50 nm had a better blocking effect than those of 20 nm. However, for temperatures above 600 °C, HfN cannot effectively block Ta-Pd interdiffusion. In interconnect structures, a diffusion barrier with high thermal stability is very important to inhibit Ta-Pd interdiffusion. Because of the microstructural defects of these conventional barrier materials, higher requirements are placed on suitable barrier layers. A large numbers of reports [17–19] revealed that multi-principal component alloys with amorphous structures are outstanding diffusion barriers, and that amorphous highentropy alloys (HEAs) have excellent properties as diffusion barriers. Based on the above research, a Pd/TaTiNbZr/Ta multi-layer was constructed to suppress the interdiffusion between the Pd and Ta membrane in the current work. According to previous studies and theoretical calculations, The group V transition metals (Ta, Ti, and Nb) have better hydrogen permeability than Pd [20]. Jayalakshmi et al. [15] investigated that a Ni-Nb-Zr-Ta alloy with a low Zr content demonstrated a larger dilatation of the amorphous structure upon hydrogen charging. Dock-Young Lee et al. [21] also found that Zr has a large atomic size, and the introduction of Zr in the amorphous matrix increases the free volume, which is conducive to the diffusion of hydrogen. Therefore, a TaTiNbZr high-entropy alloy was prepared as a barrier layer to inhibit the interdiffusion of Pd and Ta. The TaTiNbZr amorphous alloy has the characteristics of complicated compositions, hysteretic diffusion, and serious lattice distortion. In addition, TaTiNbZr amorphous alloys with free grain boundaries can be used as a diffusion barrier layer [22]. Nevertheless, there is the question as to whether the TaTiNbZr intermediate layer could inhibit the hydrogen permeability on account of its distinct sluggish diffusion effect for the solute or solvent atoms, even in high-temperature conditions.

In this study, Pd/TaTiNbZr/Ta multilayers were prepared using the magnetron sputtering technique. The hydrogen permeability, structure, and chemical stability of the Pd/TaTiNbZr /Ta films were investigated at 600 °C. The purpose of this study is to test whether the high-entropy alloy TaTiNbZr barrier layer can penetrate hydrogen, as well as the effect of the high-entropy alloy TaTiNbZr barrier layer on the high-temperature stability of Pd films. The Pd/TaTiNbZr/Ta samples with different barrier thicknesses (50 nm, 100 nm, 150 nm) were heat-treated under vacuum at 600 °C, and the hydrogen absorption of Pd/TaTiNbZr/Ta with barrier thickness of 50 nm and 100 nm was measured at 600 °C. The changes in the morphology and surface state of the alloy after heat treatment were also studied.

2. Experimental Details

2.1. Specimen Preparation

For the study of structural and chemical stability, Pd/TaTiNbZr/Ta multilayer thin film samples were prepared by magnetron sputtering on a single-crystal silicon substrate (Si). For the study of hydrogen permeability, Pd/TaTiNbZr/Ta multilayer films were prepared using a 300 μ m Ta sheet as a substrate. The substrate was put into acetone and anhydrous

ethanol, respectively, and cleaned in an ultrasonic cleaning machine for 10 min. After the ultrasonic cleaning was completed, the substrate was repeatedly rinsed with deionized water and dried for use. At room temperature, Pd/TaTiNbZr/Ta films were deposited on the substrate surface by magnetron sputtering. Before the deposition experiment, the vacuum chamber pressure was controlled below 4.0×10^{-4} Pa and then stabilized at 0.4 Pa through 38 sccm pure argon gas. The TaTiNbZr target was prepared by powder metallurgy, and the target raw materials were 99.99% pure titanium (Ti), zirconium (Zr), niobium (Nb), and tantalum (Ta) powder. The sputtering powers of the Pd, Ta, and TaTiNbZr targets were all 200 W, and deposition distance was 10 cm. The load bias was -60 V. The thickness of the TaTiNbZr barrier layer was regulated by controlling the deposition time, and three kinds of samples were prepared: #1: Pd/TaTiNbZr (50 nm)/Ta, #2: Pd/TaTiNbZr (100 nm)/Ta, and #3: Pd/TaTiNbZr (150 nm)/Ta.

2.2. Annealing and Hydrogen Permeation Test

The deposited multilayer film was selected for an annealing experiment. The annealing experiment was carried out in a vacuum tube furnace instrument. The annealing vacuum was 4×10^{-4} Pa, the heating rate was $10 \,^{\circ}$ C/min, the annealing temperature was 600 $\,^{\circ}$ C, and the holding time was set to 24 h. There are three reasons for using 600 $\,^{\circ}$ C for the experiment. First, hydrogen embrittlement tends to occur at temperatures below 350 $\,^{\circ}$ C, and this temperature is high enough to effectively avoid the effects of hydrogen embrittlement [23,24]. The second is that the interdiffusion between Ta and Pd becomes very obvious above 400 $\,^{\circ}$ C, and choosing 600 $\,^{\circ}$ C will make this diffusion easier to observe [25,26]. The third is that at 350 $\,^{\circ}$ C–600 $\,^{\circ}$ C, Pd can catalyze the cracking of carbon and hydrogen isotopes in alkanes, which can be applied to the extraction of deuterium and tritium from the treatment of exhaust gas in fusion reactors [27,28].

The hydrogen permeation experiment was carried out on a plasma gas-driven hydrogen permeation device independently designed and developed by the Advanced Nuclear Energy Laboratory of Sichuan University. The hydrogen permeation flux was obtained by detecting the changes in H⁺ ion flow in the downstream chamber by means of a quadrupole mass spectrometer. The hydrogen penetration chamber is divided into an upper chamber and a lower chamber. The background vacuum degree of the upper chamber is pumped to ~10⁻⁴ Pa, and the background vacuum degree of the lower chamber is kept at 10⁻⁵ Pa~10⁻⁶ Pa. Then, after the sample was kept at 600 °C for 6 h, hydrogen was injected into the upper chamber so that the hydrogen pressure in the upper chamber was maintained at 90 kPa; the temperature during hydrogen penetration was 873 K and the inner diameter of the sample film was 20.5 mm.

2.3. Micro-Structure Characterization

The phase structure of the Pd/TaTiNbZr/Ta multilayer films was analyzed using a small-angle grazing-incidence X-ray diffractometer (GIXRD, Bruker D8 Advanced, Billerica, MA, USA). The analysis conditions were as follows: the Cu target K α ray wavelength was 0.15408 nm, the scanning speed was 4°/min, and the step size was 0.02°. Scanning electron microscopy (SEM, FEI Inspect F50, Hillsboro, OR, USA) was used to observe the surface morphology and cross-section morphology of the Pd/TaTiNbZr/Ta multilayer films, and an energy-dispersive spectrometer (EDS, FEI Thermo Scientific EDAX EDS, Waltham, MA, USA) was used to detect the distribution and content of elements in the multilayer films.

3. Results and Discussions

3.1. Influence of Annealing Temperature on Microstructure of Multilayer Films

Figure 1 shows the GIXRD patterns of samples with three different barrier layer thicknesses before and after annealing. It was observed that after annealing at 600 °C for 24 h, the diffraction peaks of Pd and Ta of the three multilayer film samples were basically consistent with the deposited state and had the same crystal structure. Moreover, no TaPd₃ diffraction peak was found in the GIXRD pattern of the annealed samples, indicating

that TaTiNbZr barrier layers can effectively prevent the formation of TaPd₃ compounds under this annealing condition. The deposited TaTiNbZr multi-principal component showed a wide diffraction peak with a span of about 10° at 37°, and no obvious peak was observed, indicating that the deposited TiTaNbZr multi-principal component alloy film had an amorphous structure. Previous studies have shown that amorphous barrier layers have better blocking properties [13]. Furthermore, the thickness of the barrier layer has a significant impact on the hydrogen permeability of the material [14,16], and the three kinds of TaTiNbZr barrier layers can prevent the formation of TaPd₃. Therefore, Pd/TaTiNbZr (50 nm)/Ta is mainly used as the research object in the subsequent study.



Figure 1. (**a**–**c**) XRD patterns of Pd/TaTiNbZr (50 nm)/Ta, Pd/TaTiNbZr (100 nm)/Ta, Pd/TaTiNbZr (150 nm)/Ta before and after annealing at 600 °C for 24 h.

Figure 2 shows the SEM images between annealed Pd/TaTiNbZr (50 nm)/Ta multilayers and deposited Pd/TaTiNbZr (50 nm)/Ta multilayers. It can be observed from Figure 2a that the surface of the film system is covered by a dense Pd layer without exposing the underlying barrier layer. After annealing 24 h at a temperature of 600 °C, the surface Pd layer has a flocculent structure (Figure 2b,c), the agglomeration of Pd film occurs after annealing, and there is no membrane separation phenomenon. Nozaki et al. [14,16] observed that

Pd/Ta after high-temperature treatment became porous in structure, and Daniel et al. [4] found that one of the reasons for the failure of a Pd/Ta multilayer film was that the Pd layer would be stratified after annealing, which reduced the effective contact area between Pd and hydrogen. Neither of the above changes appeared in our experiment. Through the flocculent structure of the Pd film in Figure 2d,e, it can be seen that the TaTiNbZr barrier layer surface below is still intact, and no Pd diffusion into the barrier layer is observed.



Figure 2. (a) The sedimentary surface morphology of Pd/TaTiNbZr (50 nm)/Ta sample. (b–e) The surface morphology of Pd/TaTiNbZr (50 nm)/Ta sample after annealing at 600 °C for 24 h.

The deposited and annealed Pd/TaTiNbZr (50 nm)/Ta samples were analyzed by sectional scanning and energy spectrum analysis, as shown in Figure 3. It can be clearly observed from Figure 3a that the sample has a multi-layer structure. After annealing, the multi-layer structure remains intact, the interlayer interface is clear, and the structure is stable. The Pd/NbTiCo/Pd prepared by Xiao et al. formed a boundary layer between the Pd layer and Nb30Ti35Co35 substrate after annealing at high temperatures, which contributes to the fast declination of hydrogen flux from the beginning of the permeation process [11,29]. This indicates that after annealing at 600 °C for 24 h, the TaTiNbZr barrier layer with a thickness of 50 nm can effectively prevent the interdiffusion of Pd and Ta. Xiao et al. [29] indicated that HfN could only improve the permeability stability in the temperature range of 500-550 °C, and could not effectively prevent the diffusion of Pd at 600 $^{\circ}$ C. The distribution of various elements in Figure 3e shows the same distribution as the structure of the multilayer film, demonstrating a homogeneous distribution of elements. The EDS spectrum in Figure 3f scanned the distribution of Pd elements; only the surface had a high Pd content, and there was no Pd element inside the sample. In the reported Pd/NbTiCo/Pd film, Pd diffused significantly into the substrate after annealing at 600 °C [11,29]. This shows that TaTiNbZr barrier layers can effectively prevent Pd diffusion.







Figure 3. Cont.







Figure 3. (a,b) Depositional cross-section morphology of Pd/TaTiNbZr (50 nm)/Ta sample. (c,d) Cross-section morphology of Pd/TaTiNbZr (50 nm)/Ta sample after annealing at 600 °C for 24 h. (e) EDS surface scanning of Pd/TaTiNbZr (50 nm)/Ta samples after annealing at 600 °C for 24 h. (f) Pd distribution of Pd/TaTiNbZr (50 nm)/Ta sample scanned on EDS surface after annealing at 600 °C for 24 h.

The microstructural changes of the Pd/TaTiNbZr (50 nm)/Ta multilayers were mainly investigated after annealing at 600 °C for 24 h. The Pd on the surface after annealing changed from providing dense and uniform coverage on the sample surface in the asdeposited state to agglomeration on the sample surface. From the cross-section SEM, it can be seen that the TaTiNbZr high-entropy alloy and the supporting material, Ta, are dense and uniform, and the multilayer structure of the sample remains intact, with a clear interlayer interface and a stable structure. From previous studies on high-entropy alloys, it can be seen that new phases appear in XRD when the high-entropy alloys fail; for example, when FeCoBTiNb or NbMoTaW/TiVCr is used as a Cu/Si barrier layer, the Cu₃Si phase will appear when the barrier layer fails [30,31]. In this study, after annealing at 600 °C for 24 h, the amorphous structure of the high-entropy alloy is stabilized without the appearance of new phases, which is consistent with the phase of the as-deposited state.

3.2. Hydrogen Permeation through Pd/TaTiNbZr/Ta and Pd/Ta

In order to investigate the permeation behavior of hydrogen in Pd/TaTiNbZr/Ta multilayer films, gas-driven permeation behavior experiments of hydrogen through the multilayer films were conducted. The hydrogen-permeable samples were Pd/Ta, Pd/TaTiNbZr (50 nm)/Ta, and Pd/TaTiNbZr (100 nm)/Ta. A quadrupole mass spectrometer was used to detect changes in H⁺ ion flow. The hydrogen permeable flux at 600 °C was obtained by the following transformations:

The output data of the quadrupole mass spectrometer are the ion current (I), which can be converted into gas pressure by the following formula:

$$\mathbf{K} = \mathbf{I} \cdot \mathbf{P}^{-1} \tag{1}$$

where P is the lower chamber pressure in mbar and K is the sensitivity of the quadrupole mass spectrometer; in this work, $K = 9.66 \times 10^{-4}$ (A·mBAR⁻¹). The vacuum pumping speed of the lower chamber is S = 0.7 (m³·S⁻¹). The penetration rate, Q (Pa·m³·S⁻¹), can be calculated by the following formula:

$$Q = (P - P_{base}) \cdot S$$
⁽²⁾

where P_{base} is the pressure before penetration in the lower chamber, and the conversion of the permeability rate (Q) into permeability flux (F) (molecule $\cdot s^{-1}$) can be expressed as follows [32]:

$$1 \operatorname{Pa} \cdot \mathrm{m}^3 \cdot \mathrm{s}^{-1} = 10 \operatorname{cc} \cdot \mathrm{s}^{-1} = 10^{-5} \operatorname{m}^3 \cdot \mathrm{s}^{-1} / 24.5 \operatorname{Lmol}^{-1} \approx 4.08 \operatorname{mol} \cdot \mathrm{s}^{-1}$$
(3)

The total permeation flux (F) is obtained, and the planar diaphragm permeation flux (J) (mol·s⁻¹·m⁻²) passes through

I

$$= F/A \tag{4}$$

where A (m^{-2}) is the effective penetration area of the diaphragm.

At the beginning of the hydrogen permeation experiment, hydrogen molecules are first adsorbed on the Pd surface. It can be seen from Figure 4 that Pd/Ta has a crystal structure, so H atoms can rapidly diffuse to the lower surface along the grain boundary. When hydrogen atoms dissolve in the metal material and diffuse into the near-surface region, they recombine with another near-surface hydrogen atom to form hydrogen molecules and escape from the lower surface [4-6]. The diffusion of H atoms in Pd/TaTiNbZr/Ta is a similar process. The difference is that when H atoms diffuse along the Pd grain boundary towards the barrier layer, due to the lattice distortion of the amorphous TaTiNbZr HEA, the diffusion distance increases, resulting in a longer diffusion time for H₂ to reach a steady state in Pd/TaTiNbZr/Ta [18,31,33,34]. The permeable flux of the three film samples is shown in Figure 5. From Figure 5, it can be seen that Pd/Ta shows excellent hydrogen permeation performance at the beginning of hydrogen permeation and can reach a steady state very quickly, and after keeping the steady state for a period of time, the hydrogen permeation performance decreases sharply. It can be seen from Figure 4 that this is because Pd and Ta form TaPd₃ at a high temperature of 600 $^{\circ}$ C, and Pd loses its catalytic performance. Pd/TaTiNbZr(50 nm)/Ta and Pd/TaTiNbZr(100 nm)/Ta reached a steady state after a long time after the initial introduction of hydrogen, but the permeability flux at steady state was lower than Pd/Ta, because the addition of a barrier layer affected the rate of hydrogen penetration. It can be seen from the GIXRD pattern in Figure 4 that Pd/TaTiNbZr(50 nm)/Ta does not form TaPd₃ after the hydrogen penetration experiment at a high temperature, indicating that the TaTiNbZr barrier layer can effectively prevent the mutual diffusion of Pd and Ta. The addition of the barrier layer will affect the hydrogen permeation flux, but effectively extend the continuous working ability of the multilayer film. When the experimental temperature and upstream pressure are kept constant, the thickness of the barrier layer is the main reason for affecting the hydrogen permeation flux, but the thickness of the barrier layer does not affect the continuous working ability of the sample.



Figure 4. XRD spectra of Pd/Ta and Pd/TaTiNbZr(50 nm)/Ta after hydrogen penetration.



Figure 5. Time evolution curve of gas-driven hydrogen permeation flux of Pd/Ta, Pd/TaTiNbZr (50 nm)/Ta, and Pd/TaTiNbZr (100 nm)/Ta at 600 °C.

In this study, the effect of adding a barrier layer and the thickness of the barrier layer on hydrogen permeability was discussed. It is well known that the experimental results of hydrogen permeation are subject to changes in pressure, temperature, and other parameters. The rate of hydrogen permeation usually increases as the pressure increases. This is because high pressure increases the frequency of collisions between gas molecules, thereby facilitating the rate at which hydrogen permeation also increases as the temperature increases because the increase in temperature increases the average kinetic energy of the gas molecules, thus giving them a higher penetration capacity [35].

4. Conclusions

- 1. After the addition of an amorphous TaTiNbZr barrier layer, Pd/TaTiNbZr/Ta can maintain structural and morphological stability before and after annealing.
- 2. The high-temperature hydrogen permeation experiment shows that the barrier layer can effectively increase the working time of the multilayer film. Pd/TaTiNbZr(50 nm)/Ta has better hydrogen permeation performance than Pd/TaTiNbZr(100 nm)/Ta, indicating that the thickness of the barrier layer is a key factor affecting the hydrogen permeation ability.
- 3. A layer of TaTiNbZr was inserted between a Ta substrate and a Pd film as a barrier layer. No TaPd₃ was produced after the hydrogen infiltration experiment at 600 °C, indicating that TaTiNbZr can effectively block the mutual diffusion of Ta and Pd.

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