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Hydrogen transport through the V-Cr-Al alloys: Hydrogen solution, permeation and thermal-stability

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ABSTRACT

Hydrogen permeable V-Cr-Al alloys have been designed based on the lattice matching principle. To elucidate alloying effects of Cr and Al, the hydrogen solubility and hydrogen permeation flux have been characterized at temperatures between 523 and 673 K. V₉₀Cr₅Al₅ exhibits a highly reduced hydrogen solubility, which contributes to enhanced resistance towards hydrogen embrittlement, at the same time maintaining the high permeability as pure vanadium at 673 K. The stability of the V₉₀Cr₅Al₅ membrane during hydrogen permeation tests at several temperatures has been characterized: V₉₀Cr₅Al₅ shows a constant hydrogen permeation flux up to 500 h at 573 K. A small drop in permeation flux ($J \times d$) by 4% was observed at 623 K after 500 h, i.e. from 1.35×10^{-4} to 1.30×10^{-4} mol H₂ m⁻¹s⁻¹. Serious degradation in the hydrogen permeation flux during the long-term test was observed at the temperatures above 673 K. This is attributed to the formation of a new barrier layer caused by the interdiffusion between Pd and V₉₀Cr₅Al₅.

1. Introduction

Fossil fuels such as coal and oil account for about 80% of the primary energy supply in the world, resulting in a strong impact on the environment especially concerning the emissions of carbon dioxide and thus the greenhouse effect. Hydrogen, as an environmental-friendly energy carrier, has drawn fast-growing attention since the last decade. For production of high purity H₂ by separating and purifying H₂ from a gas mixture, for example from hydrocarbon reforming gas which contains CO₂, CO and so on besides H₂, membrane separation is one promising hydrogen separation and purification technique and attracting increasing interest. Materials ranging from polymers to metallic alloys have been developed as effective hydrogen separation membrane materials [1–10]. Among them, dense ceramic mixed proton-electron conducting (MPEC) membranes, which separate hydrogen as protons instead of molecules [1–3], exhibit 100% hydrogen selectivity with an infinite separation factor as the major advantage. Some dense MPEC

ceramic membranes exhibit reasonable proton conductivity up to 900 °C. However, overcoming the dilemma between the chemical stability and proton conductivity has been the main aim for high performance MPEC ceramic membranes. Dense metal membranes, such as Pd, V, Nb and Ta or their alloys and amorphous alloys are effective in separating ultrapure (5 N) H₂ from other gases at temperature ranging from 300 to 600 °C [4–10]. The hydrogen permeation through metal membranes proceeds via consequently adsorption and dissociation of H₂ to the H atoms, solution in the metal, diffusion, and re-association of H atoms to H₂ and desorption. At present, Pd-based membranes, either of pure Pd or Pd-based alloys, are widely used for the production of high purity hydrogen by hydrogen permeation and separation processes [4–8]. However, the high cost and limited working temperature are restricting their large-scale application. Decreasing the thickness of the Pd-based membranes and alloying of Pd with less costly elements e.g. Ag, Cu and Ni, are considered as effective strategies for development of Pd-based hydrogen permeation membranes. In addition, metals and

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alloys of Group VB (Nb, V and Ta etc.), which are of body-centered cubic (bcc) structure and exhibit higher hydrogen permeability, are considered as promising alternatives [9–36].

Among those metals, V exhibits excellent hydrogen permeability and malleability but suffers from severe hydrogen embrittlement (HE) induced by excessive hydrogen absorption [11–27]. For preventing HE by reducing the hydrogen content, a ductile-to-brittle transition hydrogen concentration was proposed as a criterion defining the changes from ductile fracture to brittle fracture behavior [35]. The hydrogen concentration 0.2 (H/M) was proposed as the critical hydrogen concentration for pure V at 673 K [35]. Improved the resistance to HE via reducing the hydrogen solubility of V-based membranes has been achieved by alloying and by adjusting the microstructure. Developing multiphase V-based alloys, for example, V-Ti-Ni [13–15] and V-Cu [24], was proven successful in hindering HE induced failure of membranes. This results from the reduced hydrogen solubility and the buffering effect from the eutectic structure. However, the presence of the second phase in such alloys, for example, B2-TiNi or fcc-Cu, which exhibits negligible hydrogen permeation, also induced much reduced hydrogen permeability. The solid solution in bcc phase using W, Ni, Al and Co at the same time can prevent the formation of the second phase e.g. B2-TiNi phase, which allows maintaining high hydrogen permeability while improving HE resistance [12,17,21–27]. However, reduced hydrogen diffusivity has been often found in combination with alloying, which comes from the lattice distortion after alloying [26]. By matching the lattice constant to the value of pure V, alloying of V simultaneously with Fe which contracts the V lattice and Al which expands the V lattice contributed to good hydrogen permeability and enhanced resistance to HE [26]. This mainly results from the negligible change in lattice parameters of bcc-(V) matrix after bi-alloying using Fe and Al, which contributes to much-reduced hydrogen solubility but with enhanced hydrogen diffusivity. The strategy, matching the lattice constant to the value of pure V, originated from Ref. [26] sheds a light on the development of robust single-phase V-based alloys of high hydrogen permeability using the empirical theory of lattice size matching. As reported in previous work [12], solely alloying of V with Cr leads to increasing lattice parameters of bcc-(V) phase, and solely alloying of V with Al exhibits the opposite trend. Hence, a comparable lattice parameter as that of pure V will probably occur after proper simultaneous alloying with Cr and Al, similar as that occurred to V-Fe-Al system [26]. In the present work, bi-alloying of V using Cr and Al was performed aiming for simultaneous improvement in HE resistance and hydrogen permeability.

In addition to the high permeability and HE resistance, another essential property of metal membranes is the stability at elevated operating temperatures and pressures. Lundin et al. [37] reported the depression of the hydrogen flux through Pd membranes at 623 K and 673 K, which was induced by the morphological changes of the Pd surface that affected its hydrogen absorption rate. Besides, the interdiffusion between the membrane and the porous stainless steel support was reported inducing permeability decline of Pd-Cu alloy membranes [38]. Dolan et al. [39] reported the permeability decay of Pd-coated tubular V membranes at 573 K and 613 K. Similar permeability degradation has been observed in other Pd-coated non-Pd alloy membranes [40–50]. The decrease in permeability is usually induced by the following reasons: the surface rearrangement of the Pd layer, the interdiffusion between the Pd layer and support components, and mass transfer limitations at the upstream side. For the plate-type membranes, especially for V-based membranes, the focus is usually on high permeability and less attention is paid to stability. Therefore, the development of appropriate V-based hydrogen separation membranes still requires further research to enhance the permeability and stability. In the present work, the stability of V-Cr-Al alloy membranes was characterized, and the decay mechanism of hydrogen permeability was discussed.

2. Experimental

2.1. Sample preparation and microstructure characterization

As-cast ingots of pure V, V₉₅Cr₅, V₉₅Al₅, V₉₅Cr₅Al₅ and V₈₅Cr₁₀Al₅ alloys of 30 g were prepared by arc melting under a pure argon atmosphere from pure V, Cr and Al ($\geq 99.9\%$ purity), during which a water-cooled segmented copper crucible was used. After loading the pure elements into the copper crucible, the chamber was first evacuated till 8×10^{-3} Pa and charged with high purity Ar (9 N). The elements were then melted using a non-consumable tungsten electrode with a maximum direct current of 500 A. Strong convection was imposed during the melting and solidification process. In combination, the melting and solidification process was performed at least 5 times for each ingot to reach macro-scale homogeneity.

For characterizing the hydrogen solubility and permeability of the alloys, disks of 16 mm in diameter and 0.8 mm in thickness were cut from the as-cast ingots by a spark erosion wire-cutting machine. Grinding was performed to get rid of the contamination until the thickness was 0.6 mm, followed by the final polishing using liquid suspension composed of Al₂O₃ particle of 0.5 μ m in diameter. Each side of the disk was coated with a Pd layer by electroless plating. Pd coating layers of 900 nm in thickness were applied to promote H₂ dissociation and recombination and also to avoid oxidation. Before the electroless plating, the surfaces of the membrane were activated in a PdCl₂ and HCl solution at room temperature. This step lasted 20 min until the surface of the disk lost the metallic luster and became dark. Then electroless plating in a special ethylene diamine tetraacetic acid (EDTA)-based solution was performed at 323 K. More details can be found in previous work [51].

The constituent phase of the membranes before and after hydrogen permeation tests were characterized by X-ray diffraction analysis (XRD-Rigaku MiniFlex 600) with the Cu-K α radiation by the step rate of 0.1°/min (with the step size of 0.02°) in 2θ range of 20–100°. The microstructure of the membranes was characterized using a scanning electron microscope (SEM-FEI Quanta 250F) equipped with energy diffraction X-ray (EDX) analysis. An accelerating voltage of 15 kV was used for the images and the EDX analysis. For characterizing the interdiffusion between Pd and V after long-term hydrogen permeation tests, the Pd/V/Pd membrane was clamped tightly by a house made metallic holder and then the cross section was grinded and polished. Linear EDX analysis across the Pd/V interface was performed with a step interval of 20 nm.

2.2. Hydrogen solubility and permeability

The hydrogen solubility of as-cast V, V₉₅Cr₅, V₉₅Al₅, V₉₅Cr₅Al₅ and V₈₅Cr₁₀Al₅ alloys was measured using a Sieverts-type apparatus [24] with hydrogen pressure ranging from 0.01 up to 0.80 MPa at temperatures ranging from 523 to 673 K. The amount of absorbed hydrogen was calculated based on the measured pressure drop in a constant inner volume chamber. The hydrogen permeable properties of the V₉₅Cr₅Al₅ and V₈₅Cr₁₀Al₅ membranes under pure hydrogen atmosphere were characterized using a gas permeation apparatus as in Ref. [51]. The membrane was sealed by copper gaskets during the permeation test. Before the hydrogen permeation tests, both the feed side (upstream side) and permeate side (downstream side) of the membrane were first swept using a continuous N₂ flow introduced to the upstream side. Then the membrane was heated to the desired measuring temperature under pure N₂. For checking the intact of the membrane, pure N₂ up to 0.7 MPa was introduced to the upstream side, and at the same time the N₂ at the downstream side was kept at a pressure of 0.1 MPa. In case of detected N₂ flow by the flow meter, which indicates the presence of cracks or pores in the membrane, a new membrane will be used for hydrogen permeation test. Before each hydrogen permeation test, an air activation step was performed to promote the dissociation and absorption of hydrogen [52]. Then, the feed side and the permeate side

were evacuated. The feed side was charged by high purity H_2 with upstream pressure (P_u) ranging from 0.15 to 0.70 MPa. At the same time, the hydrogen pressure at the downstream side (P_d) was kept at 0.10 MPa. The hydrogen flux, J , through the membrane was measured using a hydrogen flow meter. Intervals of 15 min were employed during measurements to ensure a steady-state hydrogen flux through the membrane. Hydrogen permeation tests for the long duration were performed to characterize the stability of the membranes, where the upstream pressure was kept at 0.7 MPa during the whole test.

The hydrogen solubility of the alloy, C , is normally expressed as [9],

$$C = K \cdot P^{0.5} \quad (1)$$

where K is the hydrogen solubility coefficient.

The steady-state hydrogen permeable flux (J) through the membranes is calculated using the first Fick's law,

$$J = -D \times \frac{\Delta C}{L} \quad (2)$$

where D is the hydrogen diffusion coefficient, and L is the thickness of the membrane.

Combining Eqs. (1) and (2), the steady-state hydrogen permeable flux (J) can be described as follows:

$$J = \frac{D \times K (P_u^{0.5} - P_d^{0.5})}{L} = \frac{\Phi \times \Delta P^{0.5}}{L} \quad (3)$$

where P_u and P_d are the hydrogen pressure at the upstream and downstream side, and Φ is the hydrogen permeability. This implies that the hydrogen permeability, Φ , of the present alloys in a hydrogen pressure range at a certain temperature can be calculated based on the measured hydrogen solubility and hydrogen permeable flux.

3. Results and discussion

3.1. Microstructure and phase constituent of as-cast $V_{95-x}Cr_xAl_5$ ($x = 0, 5, 10$) alloys

Fig. 1 shows the XRD patterns of the as-cast ingots of V, $V_{95}Al_5$, $V_{95}Cr_5$, $V_{90}Cr_5Al_5$ and $V_{85}Cr_{10}Al_5$ alloys before the hydrogen permeation tests. Only diffraction peaks corresponding to bcc-V phase were observed, and no secondary phases were detected in all the samples. Single-phase microstructure was also confirmed by backscattered electron (BSE), as shown by the inset image in Fig. 1. This is consistent with the fact that V and Cr exhibit unlimited mutual solubility across the entire system [53], and that V exhibits a high solid solubility of Al

up to ~54 at% [54]. The same brightness over the whole sample indicates the homogeneous distribution of Al and Cr in the bcc phase. A shift of diffraction peaks to lower angles was observed for $V_{95}Al_5$, indicating an increase in the lattice parameter of bcc(V) after Al alloying, as shown in the inset local magnification of the XRD patterns in Fig. 1. The opposite trend was observed beyond a Cr alloy content of 5%, indicating a decrease in the lattice parameter of bcc(V). After simultaneous alloying using Al and Cr of 5at%, the $V_{90}Cr_5Al_5$ alloy exhibits nearly identical diffraction pattern as pure V, indicating a negligible change in the lattice parameter. However, with the further increase of Cr content, i.e. $V_{85}Cr_{10}Al_5$ alloy, the location of the diffraction peaks shifts to higher angles in comparison with pure V, similar to those of $V_{95}Cr_5$. The calculated lattice parameters of V-Cr-Al alloys follow the trend: pure V (3.0376 Å) > $V_{90}Cr_5Al_5$ (3.0330 Å) > $V_{85}Cr_{10}Al_5$ (3.0215 Å). Such a shift is induced by the interactive effect of Cr and Al dissolved into the V lattice. According to the lattice matching principle [26], $V_{90}Cr_5Al_5$ is supposed to exhibit comparable hydrogen diffusivity as pure V resulting from nearly the same lattice parameter.

3.2. Hydrogen solubility of as-cast $V_{95-x}Cr_xAl_5$ ($x = 0, 5, 10$) alloys

The pressure-composition-isotherms (PCT) curves of as-cast V-Cr-Al alloys at 673 K are shown in Fig. 2(a). The PCT curve of pure V in the present work is close to that from the literature [12]. After alloying using Al/Cr, a decrease in the hydrogen solubility was observed, as shown in Fig. 2(a). $V_{95}Cr_5$ and $V_{95}Al_5$ exhibited similar hydrogen solubility. However, after bi-alloying using Cr and Al up to 5 at%, i.e. $V_{90}Cr_5Al_5$, a large decrease in the hydrogen solubility in comparison with $V_{95}Cr_5$ was observed. Similarly, $V_{85}Cr_{10}Al_5$ showed a further decrease in the hydrogen solubility. When the pressure above 0.1 MPa, the hydrogen solubility of $V_{90}Cr_5Al_5$ is close to the value of the $V_{90}Fe_5Al_5$ [55]. The observed reduced hydrogen solubility in comparison with pure V after alloying with Al and Cr is consistent with previous work [12,17], that Al/Cr alloying in V is prone to inhibit the hydrogen absorption. The decreased hydrogen solubility is due to the change in the electronic structures and strain energy of dissolved hydrogen, which results from the existence of interstitial sites of a different size in the bcc matrix. The concept of site blocking [56] cannot well explain the highly reduced hydrogen solubility of $V_{90}Cr_5Al_5$, because $V_{90}Cr_5Al_5$ has similar lattice parameters as that of pure V. It can be concluded that other than the content of the alloying elements, the interactive effects of those elements, for example, the mixing rule [26,56], plays a critical role.

The PCT curves of the as-cast $V_{90}Cr_5Al_5$ and $V_{85}Cr_{10}Al_5$ at temperatures between 523 and 673 K are shown in Fig. 2(b). The hydrogen solubility of the two alloys increases with decreasing temperature under a certain H_2 pressure. This is consistent with the exothermic nature of hydrogen solubility of group V metals. $V_{85}Cr_{10}Al_5$ exhibits lower hydrogen solubilities than $V_{90}Cr_5Al_5$ under the same pressure and temperature. For H_2 pressures above 0.1 MPa, deviation of PCT curves ($P^{0.5} \sim r(H/M)$) from the linear relationship, i.e. the Sieverts' law, was detected for all the alloys, which is due to the change of elastic and electronic properties of V and the effect of the absorption of interstitial hydrogen atoms [24,55,57–59]. The nearly linear relationship between the hydrogen solubility, $r(H/M)$ and $P^{0.5}$ only holds when the H_2 pressure is lower than 0.1 MPa. This is similar to the previous work on the V-based alloy membranes [19,60–63].

3.3. Hydrogen permeability of $V_{95-x}Cr_xAl_5$ ($x = 5, 10$) membranes

A normalized hydrogen permeation flux $J \times d$ (where J is the hydrogen permeation flux measured during the test, and d is the thickness of the membrane) of $V_{90}Cr_5Al_5$ and $V_{85}Cr_{10}Al_5$ alloy membranes is characterized, as shown in Fig. 3(a). A nearly linear relationship between the normalized hydrogen permeation flux and $\Delta P^{0.5} (= P_u^{0.5} - P_d^{0.5})$ is observed for temperatures ranging from 523 K to

Fig. 1. XRD patterns of as-cast pure V and V-Cr-Al alloys. The inserted pictures show the microstructure of as-cast $V_{90}Cr_5Al_5$ alloy and the local magnified XRD patterns highlighting the shift of the main peak.

Fig. 2. PCT curves of as-cast pure V and several V-Cr-Al alloys at 673 K [12,55] (a), and PCT curves of as-cast V₉₀Cr₅Al₅ and V₈₅Cr₁₀Al₅ at temperatures between 523 and 673 K (b).

Fig. 3. Dependence of the normalized hydrogen permeation flux ($J \times d$) of as-cast V₉₀Cr₅Al₅ and V₈₅Cr₁₀Al₅ membranes on $\Delta P^{0.5} = P_u^{0.5} - P_d^{0.5}$ (a); hydrogen permeability of pure V, Pd [50] and different V-based alloy membranes [12,15,26,41] (b).

673 K, during which P_d was kept at 0.1 MPa. A small deviation from linearity was discerned for higher upstream H₂ pressures, especially for V₉₀Cr₅Al₅ at lower temperatures. This indicates that bulk diffusion through the V₉₀Cr₅Al₅ alloy membrane is the rate limiting step, although Sieverts' law does not hold at higher H₂ pressures. The slope of

the curves can be regarded as the hydrogen permeability. Overall, V₉₀Cr₅Al₅ exhibits a higher hydrogen permeability than V₈₅Cr₁₀Al₅ at the same temperature. For each membrane, the hydrogen permeability and the hydrogen permeation flux increase with increasing temperature. A normalized hydrogen permeation flux of 1.61×10^{-4} mol H₂ m⁻¹ s⁻¹ was reached for the V₉₀Cr₅Al₅ membrane at 673 K with a H₂ pressure drop of 0.6 MPa. This is nearly the same as the reported $J \times d$ of a V₉₅Cr₅ alloy membrane at similar feed pressure [12]. Keeping the lower hydrogen solubility of V₉₀Cr₅Al₅ comparable to V₉₅Cr₅ in mind, bi-alloying with Cr and Al is advantageous for improved mechanical stability while maintaining the same hydrogen permeability.

A comparison of the hydrogen permeability between as-cast V₉₀Cr₅Al₅, V₈₅Cr₁₀Al₅ and other V-based alloy membranes from literature [12,15,26,41] is shown in Fig. 3(b). V₉₀Cr₅Al₅ exhibits the highest hydrogen permeability among the reported V-based alloys [12,15,26,41], for example 3.05×10^{-7} mol m⁻¹ s⁻¹ Pa^{-0.5} at 673 K. This value is one order higher than that of pure Pd (1.6×10^{-8} mol m⁻¹ s⁻¹ Pa^{-0.5}) at the same temperature. Therefore, for reaching the same hydrogen permeation flux, a V₉₀Cr₅Al₅ membrane can be 16 times thicker than a pure Pd membrane. V₈₅Cr₁₀Al₅ exhibits lower hydrogen permeability than that of V₉₀Cr₅Al₅, which is still higher than the reported value from Ref. [51]. This may result from the air treatment before the permeation test.

3.4. Hydrogen diffusion coefficient of as-cast V_{95-x}Cr_xAl₅ ($x = 5, 10$) alloys

The apparent diffusion coefficient has been recognized as a pseudo-value [63] because of the effect of the infiltration distance of hydrogen atom throughout the membranes. Extensive efforts have been done to modify the "Arrhenius" equation of diffusion by introducing a concentration-independent diffusion coefficient D_H^* . Nevertheless, the concentration-dependent diffusion coefficient D from the classical Fick's first law can still provide a criterion for evaluating the diffusion of hydrogen throughout the membranes. Based on the experimentally characterized dependence of hydrogen solubility on hydrogen pressure $P^{0.5}$ (Fig. 2), the hydrogen solubility difference between the upstream side (0.1 to 0.7 MPa) and downstream (maintained as 0.1 MPa) side (ΔC) was obtained. Correlating the dependence of hydrogen flux on hydrogen pressure (Fig. 3), the concentration-dependent diffusion coefficient D was calculated based on Eq. (2). The D values of as-cast V₉₀Cr₅Al₅ and V₈₅Cr₁₀Al₅ membranes at 523–673 K was calculated, which are shown in Fig. 4(a) and (b). An increasing trend of the calculated hydrogen diffusion coefficients (D) on the hydrogen solubility is found for each temperature, which is consistent with previous studies on V-based alloy membranes [12,58]. V₈₅Cr₁₀Al₅ exhibits lower D values than V₉₀Cr₅Al₅ under the same condition. This indicates that Cr

Fig. 4. Dependence of the diffusion coefficients on hydrogen concentration for $\text{V}_{90}\text{Cr}_5\text{Al}_5$ (a) and $\text{V}_{85}\text{Cr}_{10}\text{Al}_5$ (b) membranes at temperatures between 523 and 673 K, and a comparison of the average hydrogen diffusion coefficients ($\bar{D}$) of several V-based alloy membranes [12,26,41,65] (c).

acts as defects in the substrate alloy V, which affects the distribution of hydrogen potential in V due to the change in the distribution of site energy and the jumping rate of hydrogen in V [64]. To compare the membranes of different alloys, the average hydrogen diffusion coefficients, $\bar{D}$, which is the average value of the hydrogen diffusion coefficients of $\text{V}_{85}\text{Cr}_{10}\text{Al}_5$ and $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membranes at a certain temperature (Fig. 4(a) and (b)), are illustrated in Fig. 4(c). An Arrhenius relationship between the average hydrogen diffusion coefficients ($\bar{D}$) and the temperature in the temperature range 523–673 K is confirmed. The average hydrogen diffusion coefficients of the V-based alloys fall between the values of pure V and pure Pd, and the $\text{V}_{90}\text{Cr}_5\text{Al}_5$ exhibits the highest $\bar{D}$ value among listed membranes in the temperature range 523–673 K.

3.5. Stability of hydrogen permeation flux of $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membranes

Hydrogen permeation tests of as-cast $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membrane up to 500 h were performed in the temperature range between 573 and 753 K, during which the H_2 pressure at the upstream and downstream

Fig. 5. Normalized hydrogen permeable flux of $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membrane during the long-term test at 573–753 K (a); a comparison of the degradation in hydrogen permeation flux of some V-based alloy membranes [20,49] (b).

side was kept at 0.7 MPa and 0.1 MPa, respectively. The measured hydrogen permeation flux is illustrated in Fig. 5(a). At 673 and 753 K, a fast decrease in the hydrogen permeation flux during the long-term test was observed. At 753 K, the normalized hydrogen permeation flux ($J \times d$) decreases dramatically from 1.85×10^{-4} to $1.10 \times 10^{-4} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1}$, i.e. a reduction of $\sim 38\%$. At 673 K, $J \times d$ decreases from 1.6×10^{-4} to $1.2 \times 10^{-4} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1}$ corresponding to a reduction of 25%. In comparison, only a slight decrease of 4% in the hydrogen permeation flux up to 500 h is observed at 623 K, and the hydrogen permeation flux remains constant at 573 K. The decreasing tendency of the as-cast $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membrane during the long-term test is illustrated in Fig. 5(b), along with several V-based alloy membranes [20,49]. In comparison with pure V [49], the decreasing rate of the rest alloys in the hydrogen permeation flux at 673 K is much lower. This less deleterious effect is supposed to come from the reduced diffusion coefficient of Pd in V matrix after alloying using Cr and Al, or segregation of some alloying element(s) at the grain boundary, which further hinders the fast diffusion along the grain boundaries [20]. With the temperature increase up to 753 K, despite the fast degradation of the hydrogen permeation flux, the degradation rate of the $\text{V}_{90}\text{Cr}_5\text{Al}_5$ membrane is still slower than that of the $\text{V}_{85}\text{Ni}_{15}$ membrane at 753 K and that of pure V at 673 K.

3.6. Interdiffusion between Pd and $\text{V}_{90}\text{Cr}_5\text{Al}_5$ substrate

Considering that the thickness of the Pd catalytic layer in the

Fig. 6. Morphology of the surface Pd-coating layer (a–c) and the concentration profile across the Pd/V₉₀Cr₅Al₅ interface (d–f) before and after permeation test; (a), (d) pre-test, (b), (e) 623 K/500 h, (c), (f) 673 K/500 h.

present work is 900 nm, the rate of hydrogen transport through the Pd layer is supposed to be controlled by the surface reaction, i.e. dissociation and association of H₂ molecules at the upstream and downstream sides [6,24]. The rate limiting step for the hydrogen permeation through the Pd/V/Pd membrane is the bulk diffusion through the V-based membrane material. According to previous work on V-Pd alloys [40,58], V-Pd alloys with Pd content about 10 at% exhibit lower hydrogen permeability than that of pure V but higher than that of pure Pd [50]. For example, V-10 at%Pd alloy exhibits a hydrogen permeability of $3.86 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ at 400 °C, which is higher than that of pure Pd, $8.8 \times 10^{-9} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$, but lower than that of pure V, $3.6 \times 10^{-7} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$, by one order. Hence, the degradation of the hydrogen permeation flux of Pd-coated bcc V-based membranes in the present work either comes from the degraded catalytic efficiency of Pd layer or from the formation of the layer of deteriorated hydrogen permeability than that of V-based substrate as a result of interdiffusion [49,54].

The surface morphology of the Pd catalytic layer before and after hydrogen permeation tests is shown in Fig. 6(a)–(c). A dense and intact Pd-coating layer was confirmed before the hydrogen permeation test, as shown in Fig. 6(a). After hydrogen permeation at 623 K for 500 h, a slight change in the microstructure of the surface Pd layer such as local coarsening was observed. With the hydrogen permeation test temperature increased up to 673 K, besides the obvious Pd clusters, large Pd-V compound particles were observed locally on the surface Pd-coating layer, as illustrated by the arrows in Fig. 6(c). For characterizing the interdiffusion between the Pd and V₉₀Cr₅Al₅ during long-term hydrogen permeation tests, the cross section of the membranes was prepared, and linear EDX analysis starting from the Pd surface (defined as position 0) and crossing the Pd/V₉₀Cr₅Al₅ interface was performed. The composition profiles are shown in Fig. 6(d)–(f), in which the microstructure of the cross section of the membranes was illustrated by inset figures. It is worth noting that falling off of the big Pd-V compound particles occurred during metallographic preparation, and that an area of less destructive Pd layer (as illustrated by the inset pictures in Fig. 6(d)–(f)) was used for EDX analysis to get more details of the composition distribution across the Pd/V interface. Before the hydrogen

permeation test, a sharp change in composition across the Pd/V₉₀Cr₅Al₅ interface was confirmed, as shown in Fig. 6(d). After the hydrogen permeation test at 623 K for 500 h, an intermediate layer (~1 μm in thickness) formed between the Pd layer and V₉₀Cr₅Al₅ substrate, as shown in Fig. 6(e). The gradual variation in Pd concentration from 100% to null existed, indicating the interdiffusion between Pd and V₉₀Cr₅Al₅. The interdiffusion between Pd and V₉₀Cr₅Al₅ was more serious at 673 K, and a sharp decrease of the Pd content to ~65 at% occurred at the Pd surface, as shown in Fig. 6(f). This may lead to degraded catalytic efficiency of H₂ molecules at the upstream side. At the same time, the interdiffusion layer, which can be considered as V-Pd alloys of different Pd concentrations, is of lower hydrogen permeability than that of the V₉₀Cr₅Al₅ base membrane [40,58]. The degraded surface Pd catalytic layer and the formation of interdiffusion layer are supposed to lead to hydrogen permeation flux decline during the long-term test.

XRD analysis of the V₉₀Cr₅Al₅ membranes after the long-term hydrogen permeation tests was performed, as shown in Fig. 7. For the sake of comparison, the XRD pattern of the V₉₀Cr₅Al₅ membrane before the test is also shown. Two phases, fcc-(Pd) and bcc-(V), were confirmed for the membrane before the test. After hydrogen permeation tests at 573 and 623 K for 500 h, no new phase was detected. However, with the temperature increased up to 673 and 753 K, Pd₃V and some unknown phases were detected. Moreover, a shift of the diffraction peaks of bcc-V to lower angles and Pd peaks to higher angles were observed. This clearly confirms the interdiffusion between the Pd layer and V₉₀Cr₅Al₅ substrate. To maintain the integrity of the membrane after the test for further characterization, the membranes were cooled down under vacuum after the test. Hence, no hydride phase was detected in the membrane.

3.7. Model

To clarify the effect of the interdiffusion between Pd and V₉₀Cr₅Al₅ on the hydrogen permeation flux, the equation taking consideration of the interdiffusion layer was used [46,49,54], as follows:

Fig. 7. XRD patterns of Pd-coated $V_{90}Cr_5Al_5$ membranes after the hydrogen permeation tests at 573–753 K for 500 h, where a shift of the diffraction peaks of bcc-(V) to lower angles and fcc-(Pd) peaks to high angles is illustrated by the inserted picture.

$$P_u = \frac{J}{Z_{H_2}} \left[\frac{1}{\alpha_u} + \left(\sqrt{\frac{1}{\alpha_d} + \frac{Z_{H_2}}{J} P_d} + \sqrt{4Z_{H_2}J} \sum_i \frac{L_i}{S_i D_i} \right)^2 \right] \quad (4)$$

where “u” and “d” refer to the upstream and downstream side of the membrane, P_u and P_d are the hydrogen pressure at the upstream and downstream side, J is the hydrogen permeation flux through the membrane, Z_{H_2} ($= \frac{3.2}{\sqrt{T}}$ mol H_2 /(m^2 s Pa) [54] is the gas kinetic theory coefficient, α_u represents the probability of the dissociative sticking of H_2 molecule to upstream surface followed by hydrogen solution in the metal lattice (sticking coefficient), α_d is the same for the downstream side, L_i is the thickness of each layer involved, i.e. the Pd-coating layer, substrate $V_{90}Cr_5Al_5$ and the interdiffusion layer, S_i and D_i are the hydrogen solubility and diffusivity of each layer. In the present work, for the sake of simplification, α_u and α_d are assumed identical ($\alpha_u = \alpha_d = \alpha$).

Taking the change in the structure of the Pd/ $V_{90}Cr_5Al_5$ /Pd membrane into consideration:

$$\sum_i \frac{L_i}{S_i D_i} = \left(\frac{L_{Pd}}{S_{Pd} D_{Pd}} \right)_u + \left(\frac{L_{int}}{S_{int} D_{int}} \right)_u + \left(\frac{L_V}{S_V D_V} \right) + \left(\frac{L_{int}}{S_{int} D_{int}} \right)_d + \left(\frac{L_{Pd}}{S_{Pd} D_{Pd}} \right)_d \quad (5)$$

where L_{Pd} , L_V , L_{int} , S_{Pd} , S_V , S_{int} , D_{Pd} , D_V , and D_{int} are the thickness, solubility and diffusivity of the Pd layer, V-based alloy and the interdiffusion layer respectively. In the present work, the thickness of the Pd coating layer, L_{Pd} , is 900 nm, and the thickness of the $V_{90}Cr_5Al_5$ substrate, L_V , is 0.6 mm. The hydrogen solubility and hydrogen diffusivity are based on the experimental results, as e.g. from Figs. 2–4. For the calculation at 673 K in the present work, $S_{Pd} \times D_{Pd} = 3.13 \times 10^{-8}$ mol H $m^{-1} s^{-1} Pa^{-0.5}$ from Ref. [54] is used. At 673 K, the hydrogen permeability in V-Pd compounds is ~ 10 times lower than that in pure V [40]. Hence, the layers formed due to the interdiffusion are expected to exhibit much lower hydrogen permeability than the original Pd coating layer, which plays a critical role in the degradation of hydrogen permeation flux shown in Fig. 5. However, the hydrogen solubility and diffusivity of the interdiffusion layer are not known, which makes it hard to do the calculation based on Eqs. (4) and (5).

For analyzing the influence of the interdiffusion on the hydrogen permeation behavior, experimentally, three different types of Pd/ $V_{90}Cr_5Al_5$ /Pd membranes were made and then submitted to hydrogen permeation tests at 673 K, as shown in Fig. 8. The membrane consisting of Pd layers on both sides of the $V_{90}Cr_5Al_5$ alloy, defined as pre-test membrane, is defined as #1. Considering the formation of the

Fig. 8. Dependence of the normalized hydrogen permeation flux ($J \times d$) through the membranes on the H_2 pressure, $P_u^{0.5}$ at 673 K. Solid dots – experimental datum, dotted line – the calculation with Eqs. (4)–(6) with different sticking coefficients.

interdiffusion layer of Pd/ $V_{90}Cr_5Al_5$ /Pd membranes during the hydrogen permeation test, membrane #2, which presents the state of membrane #1 but after annealing in the H_2 atmosphere with a H_2 partial pressure of 0.7 MPa at 673 K for 4 days, was prepared. The membrane #2 consists of surface Pd catalytic layer, the interdiffusion layer and the $V_{90}Cr_5Al_5$ layer, as shown by the inset illustration in Fig. 8. For recovering the catalytic effect of Pd layer, electroless plating of membrane #2 was performed to produce dense Pd-coating layers at both sides, and this membrane with new Pd catalytic layers was termed as #3, as shown in Fig. 8. The hydrogen permeation tests of the same procedure were carried out on the three membranes at 673 K. The duration of each test was 3 h. As shown in Fig. 8, membrane #1 exhibits the highest hydrogen permeation. The reduction of the hydrogen permeation flux between membrane #1 and #2 demonstrates the degradation induced by the formation of the interdiffusion layer and change in the surface Pd-coating layer. Membrane #3 exhibits a slightly improved hydrogen flux in comparison with membrane #2, but still lower than that of membrane #1. The slightly improvement in comparison with membrane #2, on one hand, indicates the recovery of the hydrogen dissociation/association due to the new dense Pd layer, and on the other hand, means that the hydrogen flux degradation of membrane 2 mainly comes from the formation of interdiffusion layer. The lower hydrogen flux of membrane #3 in comparison with membrane #1 suggests the degradation induced by the interdiffusion layer.

Considering that the duration of the test for membrane #1 is 3 h, and a linear relationship between $J \times d$ and $P_u^{0.5}$ maintained until the end of the test, i.e. not obvious degradation of hydrogen flux, the formation of the interdiffusion layers and their influence were neglected. Eq. (5) was simplified as follows:

$$\sum_i \frac{L_i}{S_i D_i} = \left(\frac{L_{Pd}}{S_{Pd} D_{Pd}} \right)_u + \left(\frac{L_V}{S_V D_V} \right) + \left(\frac{L_{Pd}}{S_{Pd} D_{Pd}} \right)_d \quad (6)$$

Combining Eqs. (4) and (6), the hydrogen permeation flux through membrane #1 can be calculated based on the experimental results (Figs. 2–4). For membrane #1, a sticking coefficient $\alpha = 7 \times 10^{-4}$ was derived based on the experimental measurements, which is consistent with the work of Alimov et al. [46,49]. In the present work, the sticking coefficient α of membrane #3 is expected to be the same as that of membrane #1 due to the recoated Pd layer. Based on this assumption, the experimentally measured hydrogen flux of membrane #3, the value of $\left(\frac{S_{int} D_{int}}{L_{int}} \right)$, i.e. the influence of the interdiffusion layer, can be obtained. The inhibition of interdiffusion layers which causes the inevitable increase of the sum in Eq. (5) leads to 1.4 times (which is acquired from the fitting of the experimental results) of the sum of Eq. (6).

Due to the pronounced roughness of the Pd layer after electroless plating, similar as in the previous work [49], it is not straightforward to measure the thickness of the interdiffusion layer of the degraded membranes Pd (0.9 μm)/V₉₀Cr₅Al₅ (0.6 mm)/Pd (0.9 μm) after 4 days of heat treatment. This makes it difficult to characterize the hydrogen solubility and diffusivity of the interdiffusion layer. A sticking coefficient for membrane #2, $\alpha = 3.5 \times 10^{-4}$, was derived through Eqs. (4) and (5) based on the experimental results of membrane #2 and the value of $\left(\frac{S_{\text{int}}D_{\text{int}}}{L_{\text{int}}}\right)$ discussed above, as shown in Fig. 8, which follows the variation tendency of the sticking coefficient in Ref. [37,38]. It is worth noting that a deviation of the dependency between $J \times d$ and $P_u^{0.5}$ from the linear relationship was observed for membrane #2 and #3. With increasing upstream hydrogen pressure, the difference in hydrogen flux between membrane #2 and #3 becomes smaller, indicating a weak influence of Pd agglomeration or surface saturation on the hydrogen permeation flux under high hydrogen pressure. This is consistent with Refs. [46,49,66] that hydrogen prefers to chemisorb on the defects on the metal surface than on the clean metal surface. The barrier layer formed due to the interdiffusion between Pd and V-Cr-Al is the main reason for the decay in the hydrogen permeation flux at 673 K.

4. Conclusions

Alloying of V using Cr and Al based on the principle of lattice matching has been carried out, which has been demonstrated to reduce the hydrogen absorption while maintaining the high hydrogen permeability similar to pure vanadium. The V₉₀Cr₅Al₅ alloy exhibits a significantly reduced hydrogen solubility, but a slightly reduced hydrogen diffusivity in comparison with pure V, resulting from a similar lattice parameter as that of pure V. The long-term stability of the V₉₀Cr₅Al₅ membrane at temperatures of 623 and 673 K was investigated. Excellent stability at 623 K with a hydrogen permeation flux of $1.3 \times 10^{-4} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1}$ after 500 h was confirmed. With increasing operating temperature up to 673 K, a degradation of the hydrogen permeation flux was experimentally observed during long-term permeation tests. By analyzing the obtained experimental results, it is found that the formation of barrier layers at the Pd/V₉₀Cr₅Al₅ interfaces induced by interdiffusion between Pd and V₉₀Cr₅Al₅ is the main reason of the degradation in the hydrogen permeation flux.

CRedit authorship contribution statement

Feifei Huang: Investigation, Data curation, Writing - original draft. **Xinzhong Li:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Writing - review & editing, Project administration. **Xingrun Shan:** Investigation. **Jingjie Guo:** Resources. **Fausto Gallucci:** Resources, Writing - review & editing. **Martin van Sint Annaland:** Resources, Writing - review & editing. **Dongmei Liu:** Conceptualization, Supervision, Writing - review & editing.

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Declaration of Competing Interest

Authors declare that there is no potential conflict of interests.

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