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Title:

INFLUENCE OF SURFACE COATING ON THE PERFORMANCE OF VANADIUM–COPPER, VANADIUM–TITANIUM, AND TANTALUM MEMBRANES FOR HYDROGEN SEPARATION

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Influence of Surface Coating on the Performance of V–Cu, V–Ti, and Ta Membranes for Hydrogen Separation

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Abstract

Foils of $V_{0.95}Ti_{0.05}$, $V_{1-x}Cu_x$ (x = 0.01-0.12, atom fraction) and Ta coated with thin films of Pd or Pd alloys (Pd–Cu or Pd–Ag), and other metal interlayers were fabricated and tested for hydrogen permeability and stability at temperatures from 320-450°C. Vanadium-alloy or Ta foils were ion-milled and coatings between 30 and 250 nm thick were applied to both sides *in-situ* via electron beam evaporation. Membranes were between 40 and 75 µm thick and were completely permselective for hydrogen. Pt or Ni surface coatings on VTi_5 foils reduced the permeability by at least an order of magnitude while the membrane coated with the thinnest Pd layer (30 nm) exhibited the fastest hydrogen flux decline at 450°C. The hydrogen flux through a 75 µm thick $Pd/V_{0.99}Cu_{0.01}/Pd$ composite membrane with 100 nm Pd per side was 0.66 mol (STP)/m^2·s at 350°C and a transmembrane pressure differential (ΔP) of 3.5 atm compared to 0.44 mol (STP)/m^2·s for a 71 µm thick $Pd/V_{0.88}Cu_{0.12}/Pd$ membrane at the same conditions.

Foils of Ta were coated with layers of Ti, Mo and Pd to increase the hydrogen flux stability during operation above 400°C. Although the hydrogen flux through the coated Ta foils was generally an order of magnitude less than through the vanadium-alloy membranes, the hydrogen flux stability was greater. Metallic interdiffusion at different temperatures between various surface coatings and foils was characterized with AES depth profiles. Methods are being developed for welding the thin foil membranes into modules for testing.

1 Introduction

With increasing pressure on energy supplies and the threat of global climate change, more efficient and less polluting ways of utilizing fossil fuels are being explored. Metals such as vanadium, niobium, and tantalum have been considered since the 1960's as cheaper alternatives to palladium alloys for hydrogen separating membranes [1]. A catalytic coating is necessary on these metals to facilitate hydrogen entry and exit from the metal [2]. Metallic interdiffusion between Pd coatings and membrane supports has been recognized to cause a decrease in the hydrogen permeability of composite membranes around 400°C [3-6], while hydrogen embrittlement is known to cause premature failure of metal membranes [7]. Addition of alloying elements to reduce the solubility of hydrogen and prevent the formation of brittle hydrides can increase membrane strength [8; 9]. Therefore, alloys of V with Ti or Cu were investigated for hydrogen permeability and increased resilience, while various surface coatings were studied for resistance to metallic interdiffusion. For comparison, Ta foils with various surface coatings were also tested.

2 Experimental

High purity (99.9%) metals were electron beam (*e*-beam) melted into buttons in a vacuum furnace. The buttons were flipped and re-melted several times to ensure compositional uniformity. Buttons of roughly 250 g were sliced and cold rolled into ~5×15 cm strips with nominal thicknesses of 40-75 ±5 μm. Ta foil was obtained commercially.

The foils were washed with warm soap and water, rinsed with methanol, blown dry with nitrogen, mounted by clamping the ends of the foil strip, and loaded into the physical vapor deposition (PVD) chamber. After evacuation, argon was bled into the chamber to a pressure of $1.5 \cdot 10^{-4}$ Torr and the ion-gun was used to ion-mill each side of the foil for 60-90 min. The foil was visually inspected through a window during ion-milling to ensure removal of all remaining macroscopic contaminants. After ion-milling, the chamber was evacuated again to $1 \cdot 10^{-7}$ Torr and palladium was *e*-beam evaporated onto the foil to the desired thickness at 3-5 Å/s. A quartz crystal was used to monitor the thickness of metal deposited. The Pd–Ag films were deposited by sputtering from a $Pd_{0.50}Ag_{0.50}$ target. In all cases, the same metal coating was deposited onto both sides of each foil.

Samples were handled using gloves and forceps. Discs (2 cm diameter) were laser cut from the foil or cut by hand from larger foil samples using clean scissors. The membrane foil was sandwiched between two Ni VCR gaskets (12.7 mm OD) and positioned in the fixture, a stainless steel VCR fitting adapted with an impinging flow design. A final helium pressurization test was performed to confirm the absence of leaks.

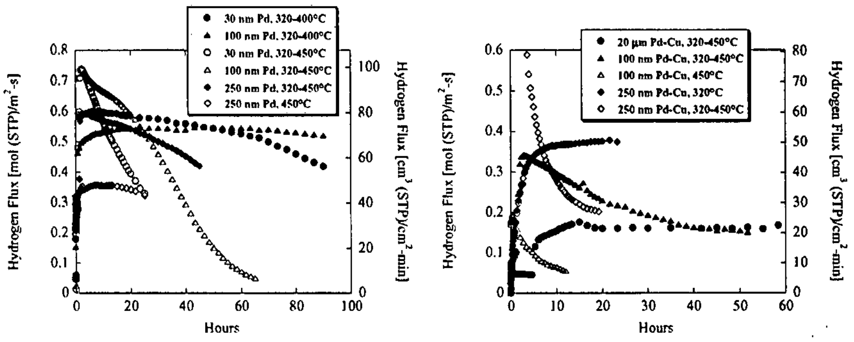
The membrane module was placed in a heater and connected to a gas plumbing and measurement system. Mass flow controllers metered the gas while 0-10,000 or 0-100 torr pressure transducers measured upstream and downstream pressures, respectively. All gases used were at least 99.999% pure and used without further purification. The membrane module was heated in the absence of hydrogen (vacuum at the feed and permeate sides). The inlet flow was 200 sccm of hydrogen during all tests. The feed pressure was set at 760 Torr and the retentate pressure ranged from 700 to 750 Torr. The permeate pressure was typically between 10 and 25 Torr. Sweep gas was not used during the permeation experiments.

Auger Electron spectroscopy (AES) results were obtained with a PHI 5600 System. Electron energy analysis was accomplished using a CHA with an OMNI Focus IV input lens system. AES results were obtained with a 5 keV electron beam. Background pressure was essentially 1×10^{-10} Torr. Elemental analysis should be considered to be semi-quantitative (± 20%). The built in SEM was used for sample imaging.

3 Results and Discussion

The hydrogen flux vs. time at 1 atm pressure differential through 40 μm thick $V_{0.95}Ti_{0.05}$ membranes with 30, 100, or 250 nm Pd coatings is shown in Fig. 1a. The flux through membranes coated with 30 or 100 nm of Pd were comparable at 400°C, while the flux through the membrane with a 30 nm Pd coating declined at a faster rate. In all cases the flux dropped much more quickly at 450°C. In the case of the membranes coated with 250 nm of Pd, one was tested for hydrogen flux at 320°C before testing at 450°C, while the other was heated directly to 450°C before introducing hydrogen. The formation of hydride at 320°C appeared to increase the hydrogen flux subsequently observed at 450°C (Fig. 1a).

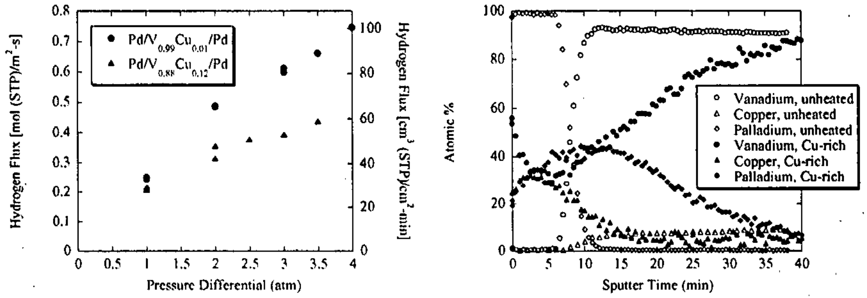
Hydrogen flux vs. time data for 40 μm thick $V_{0.95}Ti_{0.05}$ membranes coated with 100 or 250 nm of $Pd_{0.47}Cu_{0.53}$ are shown in Fig. 1b. While the fluxes were similar to the Pd coated membranes, the flux declined more quickly at 450°C. The flux was stable for a membrane tested at 320°C. Once again, a membrane first exposed to hydrogen at 320°C exhibited higher initial hydrogen flux at 450°C. The flux through a 20 μm thick $Pd_{0.47}Cu_{0.53}$ foil was constant at 450°C suggesting that the flux decline was related to interaction of the V–Ti foil with the surface coating. Coating the V–Ti foil with $Pd_{0.50}Ag_{0.50}$ resulted in higher initial flux than for the Pd–Cu coated membranes, however, similar flux decline with time at 450°C was observed (not shown). Interlayers of 30 or 90 nm of Ni or Pt between the $V_{0.95}Ti_{0.05}$ foil and the 100 nm Pd coating reduced the hydrogen flux to ≤0.5 cm^3(STP)/cm^2·min with no discernable increase in flux stability. The low flux may be attributed to the low hydrogen permeability of both Ni and Pt.



(a) (b)

Figure 1: Influence of surface coating thickness and composition on hydrogen flux through 40 μm thick $V_{0.95}Ti_{0.05}$ membranes (a) coated with 30, 100 or 250 nm of Pd (b) coated with 100 or 250 nm of $Pd_{0.47}Cu_{0.53}$, plus results for a 20 μm thick $Pd_{0.47}Cu_{0.53}$ foil

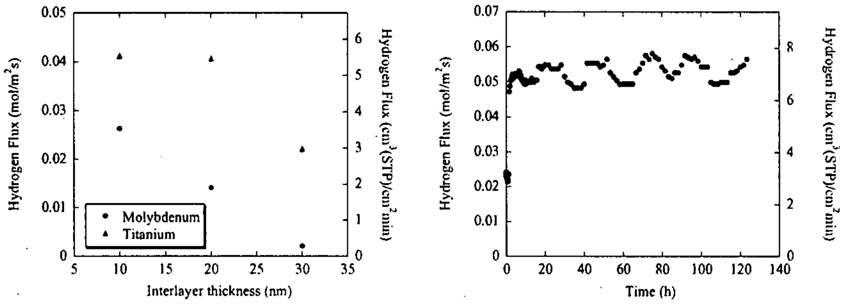
Hydrogen flux results for V–Cu membranes with 100 nm Pd coatings are displayed in Fig. 2a. After testing at 450°C for 75 hours, the hydrogen flux through the $V_{0.88}Cu_{0.12}$was reduced by 50%. An AES depth profile revealed that V and Cu had diffused to the surface while Pd had diffused into the membrane (Fig. 1b). SEM revealed the formation of light and dark regions on the membrane surface and AES indicated that Cu had segregated into Cu-rich regions, likely due to the low solubility of Cu in V. Tubular membrane modules have been fabricated by *e*-beam welding the Pd coated foil to itself in a special fixture and then to 6 mm VCR fittings.



(a) (b)

Figure 2: (a) Flux at 350 ℃ through V–Cu membranes coated with 100 nm of Pd (b) AES depth profile of $V_{0.88}Cu_{0.12}$ membrane before heating and of a Cu-rich region on the upstream side after testing at 450 ℃ for 75 hours

Ta has a much higher melting point than V (3014°C vs. 1902°C) although the hydrogen permeability is lower [10]. Fig. 3a presents hydrogen permeability vs. interlayer composition and thickness for 50 μm thick Ta foils coated on both sides with either Mo or Ti and then 200 nm of Pd. As expected, the hydrogen permeability was less than through the V-alloy membranes, and the hydrogen flux decreased with increasing interlayer thickness. Ti also appeared to have less of an impact on hydrogen flux through the membrane than Mo. The hydrogen flux was fairly stable through all of the Ta membranes tested, even for those without Ti or Mo interlayers. Hydrogen flux vs. time at 400°C through a 40 μm thick Ta membrane coated with 100 nm Pd is shown in Fig. 3b. The flux was essentially constant, with some drift, over a period of over 125 hours.



(a) *(b)*

Figure 3: (a) Hydrogen flux through 50 μm thick Ta at 400 °C vs. interlayer composition and thickness (coated with 200 nm Pd per side) (b) Hydrogen flux vs. time through 40 μm thick Ta at 400 °C (coated with 100 nm Pd per side)

4 Conclusions

The hydrogen flux and flux stability through $V_{0.95}Ti_{0.05}$, $V_{1-x}Cu_x$ ($x = 0.01$-0.12), and Ta foils coated with various thicknesses and compositions of surface coating was determined at 320-450°C. Based on AES depth profiles of a $Pd/V_{0.88}Cu_{0.12}/Pd$ composite membrane, the decline in hydrogen flux with time at 450°C was the result of metallic interdiffusion and Cu segregation.

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