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Hydrogen transport through $V_{85}Ni_{10}M_5$ alloy membranes

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ABSTRACT

Despite their inherent high permeability, unalloyed body-centred cubic (BCC) metals are prone to brittle failure due to their excessive hydrogen solubility. The primary challenge for BCC metal membrane development is therefore to control the solubility to a point where embrittlement is inhibited, while increasing the rate of hydrogen diffusion through the alloy. This can be potentially achieved through alloying, with several V-based BCC alloys exhibiting much improved resistance to embrittlement compared to pure vanadium, while maintaining higher hydrogen permeabilities than palladium alloys. While several binary and ternary V-based alloys have been investigated, a systematic approach is needed to properly evaluate potential alloying elements. In response, alloys of the general formula $V_{85}Ni_{10}M_5$ (atom%), where M is Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, or Al have been fabricated, coated with 500 nm of Pd, and their microstructure, hydrogen permeability and hydrogen solubility evaluated. The results obtained showed small compositional variations can lead to large changes in permeability, whereas diffusivity is less-dependent on composition. Formation of multi-phase microstructures can enhance the permeability by increasing the vanadium content and hydrogen solubility of the BCC primary phase. The multiphase $V_{85}Ni_{10}Ti_5$ alloy exhibited a hydrogen permeability of 9.3×10^{-8} mol m^{-1} s^{-1} Pa$^{-0.5}$ at 400 °C.

1. Introduction

Dense alloy membranes are expected to play a major role in the future production of H_2 from carbon-based fuels, either as stand-alone separators or incorporated into membrane reactors. Alloy membranes separate pure H_2 from mixed gas streams at temperatures associated with water-gas-shift [1–3] and reforming [4–6] reactions, making them particularly suited to the membrane reactor applications.

With reasonable permeabilities, good durability, tolerance to syngas species, alloys of Pd are rightfully considered the benchmark alloy membrane material. The high cost of Pd remains a concern, having been as high as $US 579 per oz. [7] within the last 5 years, which equates to ~$US 250/m^2(μm) thickness. To meet the 2015 DOE target for cost (<~1000/m^2) [8], Pd membranes must be very thin, or contain only a small amount of Pd at each surface to catalyse the dissociation and recombination of hydrogen.

Body-centred cubic alloys are one of the leading alternatives to Pd alloys. The high permeability of BCC V, Nb and Ta has been acknowledged for some time [9–13], but in pure form these metals embrittle rapidly due to their high hydrogen solubility (which is an order of magnitude greater than face-centred cubic Pd alloys) [14].

Increasing the hydrogen solubility is favourable from the perspective of increasing the hydrogen flux (which is equal to the product of the solubility and diffusion coefficient), but this must be balanced against embrittlement resistance and durability. Several research groups have examined the performance of V-based BCC alloys, including V–Ni [15–19], V–Al [20], V–Ni–Al [21], and V–Pd [22]. In each of these cases, the observed permeability is much lower than that of pure V, and this can be attributed largely to the reduced solubility of hydrogen in the alloy. Importantly, however, the embrittlement resistance and durability of these alloys are much better than the pure metal, while the permeability is still greater than the leading palladium alloy [22].

Vanadium-based solid solutions with the BCC structure can be formed with a wide range of elements. Given the large number of possible alloy substituents, the present work aims to evaluate the effect of systematic elemental substitutions on the microstructure, permeability, solubility, diffusivity and embrittlement resistance of V-based BCC membranes. Previous interest in the $V_{85}Ni_{15}$ alloy makes this a suitable reference alloy to which substitutions can be made. Alloys of the general formula $V_{85}Ni_{10}M_5$ (atom%), where M is Si, Mn, Fe, Co, Cu, Pd, Ag, or Al, were fabricated and evaluated. The selected M species were selected to provide a range of hydrogen solubilities [23], atomic radii [24] and thermal stabilities (from varying bond valences) [25].

Permeability and solubility were measured independently, allowing calculation of the hydrogen diffusion coefficient. Com-

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Table 1
Crystallographic summary of $V_{85}Ni_{10}M_5$ alloys.

Nominal composition (atom%)	Measured phase composition (atom%)	Space group	Lattice parameters (Å)
$V_{85}Ni_{10}Al_5$	$V_{85.0}Ni_{10.0}Al_{5.0}$	*Im*3*m* (229)	*a*: 3.0159 ± 0.0003
$V_{85}Ni_{10}Si_5$	$V_{90.5}Ni_{6.4}Si_{3.1}$ $V_{77.0}Ni_{4.9}Si_{18.1}$ $V_{72.0}Ni_{17.7}Si_{9.4}$	*Im*3*m* (229) *P*42/*mnm* (136) $P4_2/mnm$ (136)	*a*: 3.0141 ± 0.0004 *a*: 9.087 ± 0.0034 *b*: 4.706 ± 0.0027 Not determined
$V_{85}Ni_{10}Ti_5$	$V_{92.1}Ni_{5.1}Ti_{2.8}$ $V_{16.4}Ni_{52.1}Ti_{31.5}$	*Im*3*m* (229) *P*21/*m* (11)	*a*: 3.0058 ± 0.0003 Not determined
$V_{85}Ni_{10}Mn_5$	$V_{85.0}Ni_{10.0}Mn_{5.0}$	*Im*3*m* (229)	*a*: 3.0171 ± 0.0003
$V_{85}Ni_{10}Fe_5$	$V_{85.0}Ni_{10.0}Fe_{5.0}$	*Im*3*m* (229)	*a*: 2.9966 ± 0.0003
$V_{85}Ni_{10}Co_5$	$V_{85.0}Ni_{10.0}Co_{5.0}$	*Im*3*m* (229)	*a*: 3.0005 ± 0.0003
$V_{85}Ni_{15}$	$V_{85.0}Ni_{15.0}$	*Im*3*m* (229)	*a*: 3.0093 ± 0.0003
$V_{85}Ni_{10}Cu_5$	$V_{85.0}Ni_{10.0}Cu_{5.0}$	*Im*3*m* (229)	*a*: 3.0143 ± 0.0004
$V_{85}Ni_{10}Pd_5$	$V_{85.0}Ni_{10.0}Pd_{5.0}$	*Im*3*m* (229)	*a*: 3.0137 ± 0.0004
$V_{85}Ni_{10}Ag_5$	$V_{89.3}Ni_{10.7}$	*Im*3*m* (229)	*a*: 3.0122 ± 0.0003

bined with the observations of membrane behaviour during thermal cycling, this gives insight into the elements which are most suitable for increasing hydrogen diffusivity while abating the effects of hydrogen embrittlement.

2. Methods

2.1. Membrane preparation

High purity (99.9%) vanadium and nickel pellets were mixed with Ti, Mn, Fe, Co, Cu, Pd, Ag, Al or Si and melted on a water-cooled copper hearth using a vacuum/argon arc melter. All arc-melted ingots, each weighing ∼60 g, were turned over and re-melted several times to ensure compositional homogeneity. During melting, the chamber was evacuated to $<0.7 \times 10^{-3}$ Pa and then backfilled with high-purity argon gas up to a pressure of 100 kPa.

The arc-melted ingots were sectioned using electrical discharge machining (EDM), in which electrical discharge between a cutting wire and the sample was used to erode the alloy. Sample surfaces were polished using a 1 μm diamond compound to a thickness of ∼500 μm, then chemically cleaned and RF-sputtered with 500 nm of Pd to promote H_2 dissociation. This thickness was selected to minimize any effects associated with catalyst degradation so that the influence of bulk alloy properties could be isolated.

2.2. Microstructural analysis

The pre-permeation alloy microstructure was examined in back-scattered electron (BSE) mode a Quanta 400 FEG-SEM equipped with X-ray Energy Dispersive Spectroscopy (EDS). Surfaces were polished using diamond paste prior to analysis.

XRD measurements were made with a Bruker D8 Advance X-ray Diffractometer employing Cu-Kα radiation with a tube voltage of 40 kV and current of 40 mA. The sample was scanned over the 2-theta range 20–120° with a step size of 0.02° and a count time of 4 s. For several samples, diffraction measurements were made using metal filings to enhance the detection limits for secondary phases. Analyses were performed on the collected X-ray diffraction (XRD) data using the Bruker XRD search match program EVA. Crystalline phases were identified from the ICDD-JCPDS powder diffraction database.

Micro-XRD was employed to identify several minor phases that were present at levels below the detection limit of bulk XRD. A Bruker General Area Detection Diffraction (GADDS) X-ray micro-diffractometer was employed for minor phase analysis, equipped with a HiStar area detector, Cu-Kα radiation, and cross-coupled Goebel monochromating mirrors. The X-ray beam was collimated to a spot size of 300 μm using a pinhole collimator with a count time of 300 s. Micro-diffraction data were collected using Cu-Kα radiation at 40 kV and 40 mA. Two-dimensional intensity patterns collected across the area detector were converted to conventional XRD patterns which were analysed using the Bruker XRD search-match program EVA.

Quantitative composition analysis was performed on different areas of interest such as the V-matrix and secondary-phase compounds present in $V_{85}Ni_{10}Si_5$ and $V_{85}Ni_{10}Ti_5$ alloys using a JEOL 8500F electron microprobe. The intensity measurements were conducted at 12 kV accelerating voltage and a beam current of 30 nA.

2.3. Permeation testing

Hydrogen permeability was measured using the constant pressure method. Membranes were sealed in a custom inconel module using annealed copper gaskets with an internal diameter of 1.60 cm, giving an active area of 2.01 cm^2. During permeation testing, the feed-side was supplied with a 90% H_2 + 10% CO_2 mix at 200 ml/min at a pressure of 4.0 bar (a). Pressure was equalized on the permeate side with 200 ml/min Ar. The hydrogen content in the Ar stream was measured using a gas chromatograph, and from this value hydrogen flux was calculated. The integrity of the membrane was confirmed by the absence of CO_2 in the permeate stream. Permeability was calculated as the gradient of hydrogen flux against $(P_1^{0.5} - P_2^{0.5})$, where P_1 is the feed-side pressure and P_2 is the permeate-side pressure. At each temperature, each membrane surface was exposed to air for 1 h. This treatment had the effect of increasing permeability by ∼10%, presumably through impurity removal and oxidation of the Pd catalyst layers. At the conclusion of permeation testing, membranes were allowed to cool under the $(H_2 + CO_2)$/Ar test atmosphere, and fracture temperatures were recorded.

2.4. Solubility testing

The hydrogen uptake of several alloys with varying hydrogen pressure was measured via the Sieverts' method. Pd-coated samples of each alloy were used for the testing, and given the difference in total Pd thickness (1 μm) compared to the V-based alloy (∼500 μm), the contribution of the Pd to each solubility isotherm was negligible. Measurements were performed at 400 °C, and up to 12 bar (a). Little difference was observed between the increas-