INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 9794–9799

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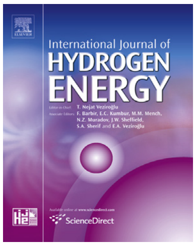

# Hydrogen transport properties of several vanadium-based binary alloys

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ARTICLE INFO

*Article history:*
Received 11 February 2013
Received in revised form
2 May 2013
Accepted 7 May 2013
Available online 24 June 2013

*Keywords:*
Hydrogen
Membrane
Alloy
Vanadium
Chromium
Aluminium

ABSTRACT

Vanadium-based alloys are an emerging alternative to palladium alloys for use in hydrogen-selective alloy membranes. The tendency of vanadium to embrittle, due to its high hydrogen absorption, means it lacks the robustness required for industrial hydrogen separation applications. Alloying vanadium with certain elements reduces hydrogen absorption, but also influences the diffusivity of hydrogen through the bulk material. Consequently, diffusivity and absorption data must be decoupled in order to fully evaluate the influence of various alloying additions on the hydrogen transport properties of vanadium alloys. To address this need, the hydrogen transport properties of V–Al ($V_{95}Al_5$, $V_{90}Al_{10}$, $V_{85}Al_{15}$, $V_{80}Al_{20}$, $V_{75}Al_{25}$, expressed as atom%) and V–Cr ($V_{95}Cr_5$, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$) alloys have been compared through a series of absorption and flux measurements. Pd-coated alloy disks were formed from arc melted and sectioned ingots, and each alloy was subjected to a microstructural analyses and a detailed examination of hydrogen absorption and permeation properties. Additions of Al and Cr reduce the hydrogen absorption and diffusivity of vanadium, with V–Cr alloys exhibiting the greatest hydrogen diffusivity for a given hydrogen feed pressure. The diffusivity of each alloy showed strong concentration dependence. Diffusivity-concentration results have been overlayed with an isoflux curve corresponding to a target flux of 1.0 mol $m^{-2}$ $s^{-1}$, enabling prediction of the thickness and pressure required to achieve this target flux target for a given alloy.

## 1. Introduction

The high hydrogen permeability of Group V metals is well established, particularly through the work of Steward [1], and later by Buxbaum [2,3], Nishimura [4–6], Yukawa [7–9], and others [10–13]. High permeability, largely attributable to the high hydrogen absorption of these metals and their alloys, make them of obvious interest for high-temperature $H_2/CO_2$ separation membranes, and in membrane reactors for the water–gas-shift and reforming reactions. Their relatively low cost compared to the benchmark metal, Pd, further increases the potential economic case for these materials.

Excessive hydrogen absorption, however, has been the major limitation of these materials [14], with the resulting lattice expansion and hydride precipitation making these alloys significantly less robust than Pd-based alloys. Options open to developers of Group V alloy membranes have included alloying to reduce absorption, and/or operating these membranes only in narrowly-defined pressure gradient and temperature windows.

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http://dx.doi.org/10.1016/j.ijhydene.2013.05.073

Another interesting aspect of these materials is the strong concentration-dependence of hydrogen diffusion. Most studies have simply used permeability (as mol $m^{-1}$ $s^{-1}$ $Pa^{-0.5}$) as a correlating property, which has its origins in ideal Fickian behaviour. This assumes diffusivity is concentration-independent, and that absorption is proportional to the square root of pressure, conditions which hold only at near-zero hydrogen concentrations.

High hydrogen absorption leads to considerable deviations from 'ideal' Sieverts'-type behaviour (where absorption is proportional to the square root of pressure). Studies of hydrogen diffusion through V–Ni [15] and V–Ni–Ti [16] alloys showed a significant concentration dependence, with the concentration-dependent hydrogen diffusion coefficient ($D_H$) increasing with increasing dissolved hydrogen concentration. Furthermore, the Sieverts' exponent decreases from its ideal value of 0.5 as the alloy approaches hydrogen saturation.

Hydrogen permeability, by definition, is independent of feed and permeate pressures. That this phenomenon is approximately observed in vanadium alloys [15] is in fact serendipitous, with the non-ideal effects of diffusivity and pressure-dependent concentration roughly cancelling each other out. Nonetheless, independent verification of diffusivity and hydrogen concentration under realistic operating conditions is essential to fully understand hydrogen transport, and to design an appropriate alloy for a given application.

Given that high hydrogen absorption incurs a mechanical penalty, whereas rapid diffusion does not, a, excellent criterion for rating prospective alloy materials is the ratio of hydrogen diffusivity to concentration. Our previous study of the V–Ni system showed a clear reduction in hydrogen diffusivity for a given hydrogen concentration with increasing Ni content. The present work builds on this foundation by extending the approach to V–Al and V–Cr binary alloys within the compositional range for body-centred cubic solid solution formation, with the aim of identifying the best alloy for high-temperature hydrogen separation. The present work is one of three prime considerations when selecting an alloy for a hydrogen-selective membrane application, the others being phase stability and mechanical formability, each of which will be examined separately.

## 2. Methods

Several binary V–Al ($V_{95}Al_5$, $V_{90}Al_{10}$, $V_{85}Al_{15}$, $V_{80}Al_{20}$, $V_{75}Al_{25}$, expressed as atom%) and V–Cr ($V_{95}Cr_5$, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$) alloys were selected so as to ensure formation of a single-phase body-centred cubic solid solution. Circular membranes were prepared by sectioning arc-melted ingots using electrical discharge wire machining. Alloy compositions were verified chemically and were within 2% (relative) of the nominal composition. The preparation method, including surface preparation and the deposition of 500 nm-thick Pd catalyst layers, has been described in detail previously. [15] Membranes were approximately 900 μm thick to ensure bulk diffusion was the rate-limiting step in hydrogen permeation.

Images of alloy microstructure were recorded using optical microscopy at a magnification of 5×. Alloy fragments were mounted and polished to reveal a cross-section, and etched to show grain detail.

Hydrogen flux was measured using the constant pressure method. Membranes were sealed compressively using copper gaskets inside an inconel module which was heated to 400 °C under an inert atmosphere and held for 12 h. A mixture of 10% $CO_2$ in $H_2$ was supplied to the feed surface at rates sufficient to prevent concentration polarisation. Ar was fed to the opposing surface, also at rates sufficient to prevent concentration polarisation. Each condition was maintained for around 1 h to ensure the attainment of steady-state flux conditions. The feed pressure was progressively increased from ~1 to ~10 bar(a), while the sweep pressure was maintained at ~1.5 bar(a) throughout the experiment. The $H_2$ content in the permeate stream was measured using a gas chromatograph calibrated against certified standard gas mixtures. Flux was then calculated based on the permeate $H_2$ concentration, and the flow rate of Ar. The detection of $CO_2$ in the permeate stream was indicative of a membrane defect, and the experiment was terminated accordingly.

The hydrogen absorption of each alloy was measured manometrically. Samples were held at 400 °C for 24 h under vacuum to ensure any residual $H_2$ from the flux measurement was purged from the sample. Isotherms were then generated between ~15 and 0 bar, using an initial 15 bar absorption step followed by stepwise desorption steps.

Lattice parameter measurements were made after permeation and absorption testing. Alloys were ground into a powder using a Philips planetary mini mill. These powders were sealed into glass tubes under vacuum, followed by a stress-relief annealing at 450 °C for 16 h. A Bruker D8 Advance X-ray Diffractometer using CuKα radiation (40 kV, 40 mA) equipped with a LynxEye silicon strip detector was employed to obtain the XRD patterns. The powder samples were scanned over the $2\theta$ range 20°–130° with a step size of 0.02° $2\theta$ and a count time of 3.2 s per step. Lattice parameters were determined using the software package Diffrac.Topas (Bruker AXS).

## 3. Results

Fig. 1 shows optical micrographs (5× magnification) for $V_{95}Al_5$ and $V_{95}Cr_5$. These alloys form a polyscrystalline microstructure with grains around 1 mm in diameter. Given the thickness of the prepared membranes (~900 μm), hydrogen diffusion will be mostly intra-granular and grain boundary influences can be considered negligible.

X-ray diffraction measurements confirmed each alloy was a single-phase, vanadium solid solution ($V_{SS}$). Measured lattice parameters are shown in Fig. 2. Both alloy series follow Vegard's law, with substitution of V by Al increasing the lattice parameter of V by a small amount, and substitution of V by Cr decreasing the lattice parameter significantly. These trends are expected given the reported atomic radii of V (0.132 [17]/0.134 [18] nm), Al (0.143 [17] nm) and Cr (0.125 [17]/0.130 [18] nm). The general trend for V–Cr is also in agreement with a recent first-principles study [19].

Fig. 3 shows the variation in measured flux with hydrogen partial pressure in the feed ($p_1$) for alloys in the V–Al and V–Cr series at 400 °C. In each case flux has been normalised