



Suppression of the critical temperature in binary vanadium hydrides



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ABSTRACT

The tendency of vanadium-based alloy membranes to embrittle is the biggest commercialisation barrier for this hydrogen separation technology. Excessive hydrogen absorption and the $\alpha \rightarrow \beta$ hydride transition both contribute to brittle failure of these membranes. Alloying is known to reduce absorption, but the influence of alloying on hydride phase formation under conditions relevant to membrane operation has not been studied in great detail previously. Here, the effect of Cr, Ni, and Al alloying additions on V–H phase equilibrium has been studied using hydrogen absorption measurements and in situ X-ray diffraction studies. The addition of 10 mol% Ni increases the critical temperature for $\alpha + \beta$ hydride formation to greater than 400 °C, compared to 170 °C for V. Cr also increases the critical temperature, to between 200 and 300 °C. The addition of 10 mol% Al, however, suppresses the critical temperature to less than 30 °C, thereby enabling this material to be cycled thermally and hydrostatically while precluding formation of the β -hydride phase. This is despite Al also decreasing hydrogen absorption. The implication of this finding is that one of the mechanisms of brittle failure in vanadium-based hydrogen-selective membranes has been eliminated, thereby increasing the robustness of this material relative to V.

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1. Introduction

1.1. Background

Hydrogen-selective alloy membranes are an emerging gas separation technology with potential application to a number of hydrocarbon-to-hydrogen processes, including integrated gasification – combined cycle power generation [1] and natural gas reforming [2]. While thin, supported palladium alloy membranes have entered semi-commercial production [3,4], the high cost of palladium (~\$US 250/m²/μm [5]) has continued to drive the development of lower-cost alternatives. Most notable amongst these are vanadium alloys [6], but to achieve commercial viability, alloy membranes must exhibit a number of desirable properties which are best illustrated through a number of performance targets established by the US Department of Energy [7]. Among these DOE targets, it is the cost, hydrogen flux and lifetime which can be considered most important, and meeting all three of these simultaneously presents a significant challenge. Cost is one of the key advantages of vanadium over palladium for this application, but development has been tempered by significantly reduced durability and lifetime *c.f.* palladium.

1.2. Mass transfer rates

Alloy membranes transport hydrogen via a solution-diffusion mechanism, whereby molecular hydrogen adsorbs on the feed (high-pressure) surface and dissociates into atomic hydrogen. The dissociated hydrogen then dissolves into the alloy and migrates across the membrane via interstitial sites, driven by a concentration gradient. At the permeate (low-pressure) surface, the hydrogen recombines and desorbs from the surface in molecular form.

Hydrogen flux is dependent on the intrinsic permeability of the alloy, which in turn is dictated by the hydrogen absorption and diffusivity characteristics. Vanadium, and other BCC metals like Nb and Ti, exhibit hydrogen permeabilities well over an order of magnitude greater than Pd at 400 °C [8,9]. Despite this, the poor mechanical stability of these group IV and V metals under hydrogen has necessitated the development of more stable alloys, achieved primarily by reducing hydrogen absorption. Along with several other groups, we have reported the diffusion and absorption characteristics of a number of binary (V–Ni, [10–13] V–Al, [14,15] V–Cr [14]) and ternary (V–Al–Fe, [16] V–Ti–Ni, [17–19] V–Ti–Al, [20] V–Ti–Cr [21]) vanadium alloys, showing that while these alloying additions reduce absorption (as intended), they also reduce diffusivity which is unfavourable. The optimum alloy from a mass transport perspective is one with the greatest diffusivity/absorption ratio.

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1.3. Durability

The durability of an alloy membrane in a separation or conversion process is, like mass transfer rates, strongly linked to hydrogen absorption. The intended operating conditions for a water–gas-shift membrane reactor ($\sim 400^\circ\text{C}$ and large trans-membrane pressure) can readily be achieved in the absence of hydrogen by a $100\ \mu\text{m}$ -thick alloy tube, but the absorption of hydrogen degrades the mechanical properties to a point where catastrophic failure can occur. Yukawa [22] determined that a ductile–brittle transition occurs when the hydrogen to metal (H/M) ratio exceeds 0.2. Durability can therefore be improved simply by reducing absorption (which also reduces permeability), but the influence of alloying additions on hydride phase stability must also be considered.

1.3.1. Phase stability

Another important consideration is the phase stability of the vanadium hydride. Under the conditions of interest vanadium hydride can exist as α -hydride (adopting the BCC structure of the vanadium solid solution, and with interstitial hydrogen randomly distributed between octahedral and tetrahedral sites), β_1 -hydride and β_2 -hydride (low- and high-temperature V_2H phases respectively with ordered to octahedral sites [23,24]), and a fully hydrogenated, face-centred cubic γ -phase (first appearing at hydrogen concentration of $\text{VH}_{0.95}$ [25]). The β_1 -hydride forms at very low pressure (0.1 Pa) [26] and undergoes a first-order transition to the β_2 -hydride. The β_1 phase adopts a body-centred tetragonal structure if grown under applied stress [27], or a monoclinic structure if grown without applied stress [28]. The critical temper-

ature for V lies at approximately 170°C and 0.0001 MPa [29–31]. Above the critical temperature (T_C), the isothermal transition between the α and β phases occurs gradually with increasing hydrogen concentration, but below 170°C there exists a set of conditions under which both hydride phases can coexist. β -hydride precipitation under these conditions can have catastrophic consequences for membranes, as the stresses created along phase boundaries can lead to cracking [32,23,24], or at worst, pulverisation of the alloy.

Vanadium hydride phase equilibrium studies have been undertaken previously, but not under conditions of concern for membrane operation. For example, Yukawa's study [33] into the effect of alloying on the stability of vanadium hydrides showed the γ -hydride plateau pressure at 313 K to be greatest for Group VIII additions (Fe, Ru, Os), and decreasing systematically for elements from lower and higher groups.

For pure V the formation of β -hydride occurs far below the intended operating temperature of the membrane, but the membrane can undergo phase transitions during shutdown, when the membrane approaches ambient temperature. In the field of palladium-based membranes, it is known that the addition of 23 wt% Ag to Pd reduces the critical temperature to well below room temperature [34], thereby allowing these membranes to be cycled down to room temperature under hydrogen without risk of β -hydride formation. Understanding how prospective alloying additions influence the location of the α – β phase boundary will be an important consideration when selecting an alloy for a specific membrane application, and when implementing an appropriate operating procedure for plant start-up and shut-down.

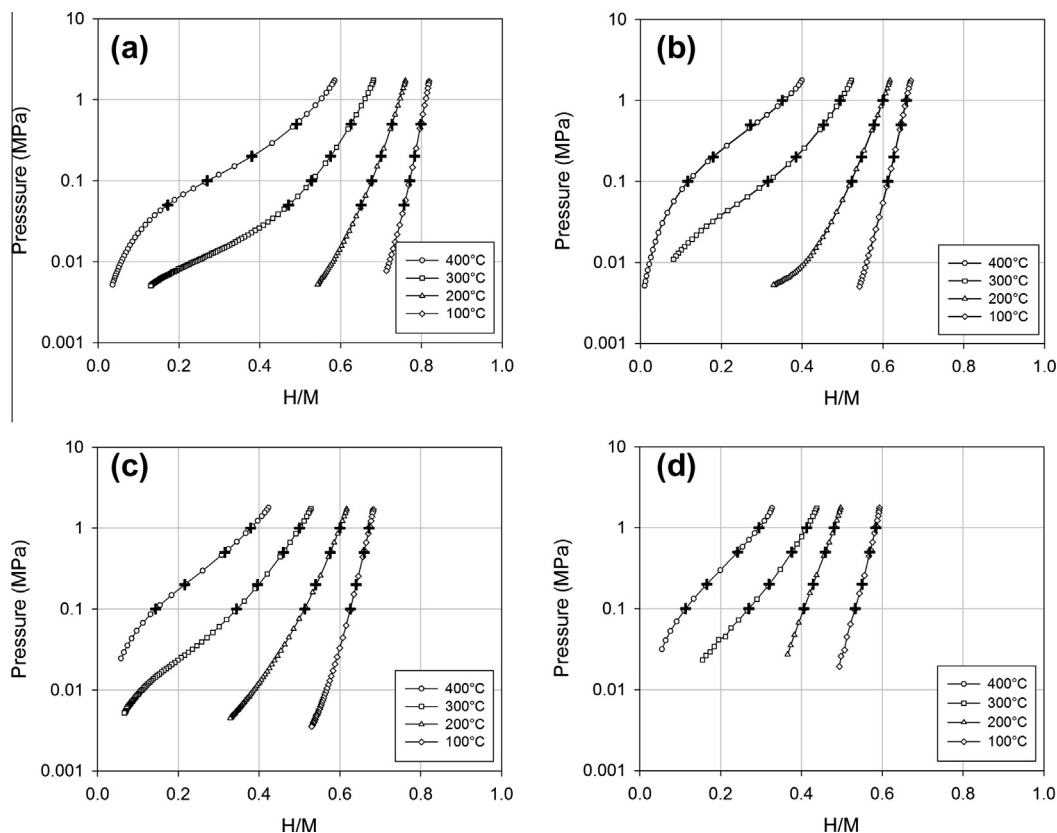


Fig. 1. Hydrogen absorption isotherms for (a) V, (b) $\text{V}_{90}\text{Cr}_{10}$, (c) $\text{V}_{90}\text{Ni}_{10}$ and (d) $\text{V}_{90}\text{Al}_{10}$. The crosses represent the experimental conditions for in situ diffraction measurements.

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