Journal of Alloys and Compounds 509 (2011) 9322–9328

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

V–Ni–Ti multi-phase alloy membranes for hydrogen purification

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ARTICLE INFO

Article history:
Received 11 May 2011
Received in revised form 8 July 2011
Accepted 8 July 2011
Available online 2 August 2011

Keywords:
Hydrogen
Membrane
Alloy
Vanadium
Nickel
Titanium
Body-centred cubic

ABSTRACT

Hydrogen-selective membranes formed from body centred cubic alloys can exhibit very high hydrogen permeability, but are prone to brittle failure due to excessive hydrogen absorption. Until issues associated with this are overcome, these materials will not provide a viable alternative to Pd-based membranes. Multi-phase V–Ni–Ti alloys which contain a significant proportion of a BCC component show promise for this application. In order to examine this system in greater detail, alloys of the general form $V_{85-x}Ti_xNi_{15}$, in which x was varied between 0 and 30 (at.%), were fabricated via arc melting and electrical-discharge wire cutting. Hydrogen permeation measurements of Pd-coated samples at 400 °C showed a monotonic increase in permeability with increasing Ti, reaching a maximum of 1.0×10^{-7} mol H_2 m^{-1} s^{-1} $Pa^{-0.5}$ for the $V_{55}Ti_{30}Ni_{15}$ alloy at 400 °C. The driving force for hydrogen transport is provided by hydrogen absorption, which varies non-linearly with Ti content, and is dependent on the volume fraction of BCC phase, and levels of Ti and Ni solution in the BCC phase. Diffusion coefficients of atomic H through the bulk alloys alloys are dependent largely on microstructure. Whereas the $V_{85}Ni_{15}$ alloy forms a single phase microstructure, progressive substitution of V with Ti introduced several minor phases; a NiTi-type phase (formed when $x \geq 5$), and a $NiTi_2$-type phase (formed when $x \geq 10$), both as V-containing solid solutions. These minor phases act as barriers to hydrogen diffusion, resulting in a significantly reduced diffusion coefficient compared to single-phase BCC alloys. Importantly, the mechanical stability of these alloys appears to be enhanced by the multi-phase microstructure. These alloys therefore show great promise for meeting future flux, cost and durability targets.

1. Introduction

Gas separation membranes offer several potential advantages over PSA/TSA-type hydrogen purification systems, including continuous separation, higher operating temperatures and the potential for process intensification through integration with gas conversion reactions (*e.g.*, water gas shift and steam methane reforming). Membrane technology still lags behind solvent and sorbent technology for hydrogen-related applications, however, and is currently restricted to niche applications such as bench-top hydrogen purification and several industrial trials. Uptake of membrane technology for H_2/CO_2 separation on a large scale will not occur until significant improvements in hydrogen flux, durability and cost have been achieved.

Of the main classes of hydrogen-selective (alloy, dense ceramic, microporous inorganic, polymer) membranes, alloy membranes offer several favourable characteristics for fossil fuel-based hydrogen production, namely an intrinsically pure hydrogen product, stability in syngas environments and temperatures of operation compatible with hydrocarbon conversion reactions. Aside from palladium alloys, body-centred cubic (BCC) metals are one of the most promising classes of alloy membrane. The hydrogen permeabilities of pure BCC metals such as V, Ta and Nb at 400 °C are all in excess of 1×10^{-7} mol m^{-1} s^{-1} $Pa^{-0.5}$, an order of magnitude greater than Pd [1].

The high permeability of BCC metals can be attributed to high solubility of hydrogen and fast hydrogen diffusion [2]. The high levels of hydrogen absorption, however, can degrade the mechanical properties of these alloys to the point where they suffer from brittle failure under the typical operating conditions (temperatures around 400 °C, hydrogen partial pressures less than 10 bar).

Several groups have attempted to abate the effects of brittle failure of these metals by forming alloys with reduced hydrogen absorption. Vanadium has received most attention because of its ability to maintain the BCC structure over a wider compositional range than Ta or Nb. The best known BCC alloys for membrane applications are vanadium-based solid solutions containing Ni [3–6], and Al, Ag, Pd, Fe, Mn, Co and Cu [7–11].

Multi-phase, BCC-based alloys have also been explored. Formation of NiTi and $NiTi_2$ phases within a BCC matrix has been observed in V–Ni–Ti [12,13], Nb–Ti–Ni [14,15] and Ta–Ti–Ni alloy membranes [13], along with analogous phases in Nb–Ti–Co

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doi:10.1016/j.jallcom.2011.07.020

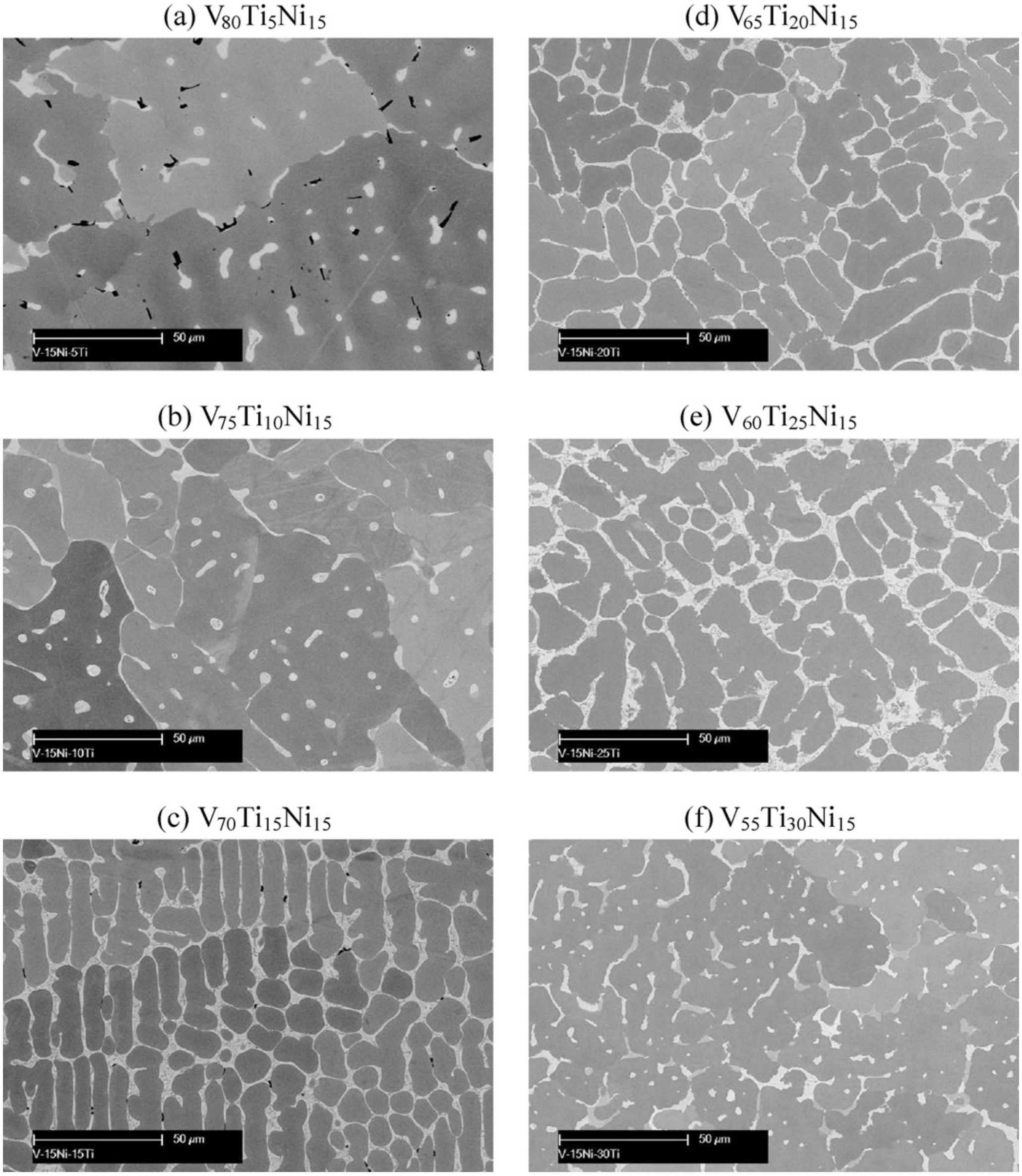
(a) $V_{80}Ti_5Ni_{15}$
(d) $V_{65}Ti_{20}Ni_{15}$
(b) $V_{75}Ti_{10}Ni_{15}$
(e) $V_{60}Ti_{25}Ni_{15}$
(c) $V_{70}Ti_{15}Ni_{15}$
(f) $V_{55}Ti_{30}Ni_{15}$

Fig. 1. Electron micrographs (BSE mode) of (a) $V_{80}Ti_5Ni_{15}$, (b) $V_{75}Ti_{10}Ni_{15}$, (c) $V_{70}Ti_{15}Ni_{15}$, (d) $V_{65}Ti_{20}Ni_{15}$, (e) $V_{60}Ti_{25}Ni_{15}$ and (f) $V_{55}Ti_{30}Ni_{15}$. Each image shows an area of 190 μm × 140 μm. The black features are pores.

[16] and Nb–Zr–Ni alloys [17]. In each case, the Ni-based compounds are purported to stabilise the alloy membranes against embrittlement. Of these examples, the $Nb_{40}Zr_{30}Ni_{30}$ alloy with 40% of the BCC solid solution exhibited the highest permeability (4.6×10^{-8} mol m^{-1} s^{-1} Pa$^{-0.5}$ at 400 °C), however significant increases in permeability are required to meet future performance targets. NiTi is best known as a shape-memory alloy with high mechanical strength and high ductility [18,19], but is also of interest for hydrogen storage applications. When hydrided, NiTi forms an interstitial solid solution [20] with H preferentially occupying the octahedral interstice. According to Schmidt et al. [21] and Wipf [22], the diffusion coefficient of hydrogen in α-NiTi hydride at 400 °C ($\sim 2 \times 10^{-10}$ m^2 s^{-1}) is around two orders of magnitude lower than in V ($\sim 2 \times 10^{-8}$ m^2 s^{-1}). Similarly, the hydrogen absorption of NiTi is significantly less than V. Using the numerical expression presented by Schmidt et al., the H/M ratio of NiTi at 400 °C and 6 bar is ~0.06, compared to ~0.58 for V [2]. This reduced diffusion coefficient and driving force suggest that formation of NiTi within a V-based BCC alloy would decrease the hydrogen permeation rate significantly. This was confirmed by Hashi et al. [14], who measured the permeability of NiTi to be 3 orders of magnitude lower than V.

The $V_{85}Ni_{10}Ti_5$ alloy reported by the present authors [8] demonstrated the positive effect that Ti can have on hydrogen permeability when added in certain proportions, with the permeability of $V_{85}Ni_{10}Ti_5$ being ~4 times greater than $V_{85}Ni_{15}$ at 400 °C, and up to 8 times greater than V–Ni–Ti alloys reported previously. The main reason for this high permeability was found to be due to a large increase in hydrogen absorption, which was countered slightly by a small decrease in the hydrogen diffusion coefficient. This observed behaviour may be due to elemental partitioning within the multi-phase microstructure: the addition of Ti to the V–Ni solid solution precipitates several NiTi-rich compounds, thereby depleting Ni from the solid solution and enriching the V content of the primary BCC phase. This in