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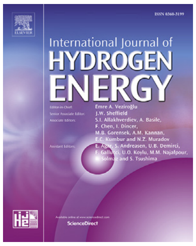

Hydrogen sorption properties of $V_{85}Ni_{15}$

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ABSTRACT

An alloy with nominal composition $V_{85}Ni_{15}$ was prepared in a vacuum induction melting apparatus. The chemical analysis of the sample showed a V (Ni) content of 82.63 (15.68) at% and small contaminations by carbon and aluminum. XRD measurements confirmed that the bcc Ni-V solid solution phase is the main constituent of the sample. However, a minor impurity (approximately 6.5 wt%) due to the precipitation of the sigma NiV_{3-x} phase is present in the sample.

Hydrogen sorption measurements extending from 150 °C up to 400 °C in a wide pressure range (up to 90 bar) were performed. Upon hydrogenation below 250 °C, one observes the subsequent presence of an α phase and of two hydride phases with different values of dehydrogenation enthalpy: $\Delta H_{dehydr} = 21 \pm 1$ kJ/mol for $0.15 \leq H/M \leq 0.30$ and $\Delta H_{dehydr} = 26 \pm 2$ kJ/mol for $0.53 \leq H/M \leq 0.59$. Above 300 °C, there is no evidence of the formation of hydrides and only an α phase is present up to the maximum measured composition, with a hydrogenation enthalpy $\Delta H_{hydr} = 10.0 \pm 0.5$ kJ/mol.

Introduction

An energy economy based on the use of hydrogen as a clean energy vector needs the development of an efficient, reliable and safe technological platform for the hydrogen production, purification and exploitation [1,2]. In particular, PEM (polymer electrolyte membrane) fuel cells use ultra-pure hydrogen for producing electricity through highly efficient energy processes [3,4].

The purification of hydrogen on a small-medium scale up to an ultrapure grade (purity > 99.999%) is industrially achieved by means of the Pd-membrane technology [5]. In general, the lattice of metals is selectively permeable to hydrogen atoms via a mass transfer mechanism (permeation) including several steps. When a dense metal wall is exposed to hydrogen, the hydrogen molecules interact with the high pressure (upstream) metal surface where the adsorption and dissociation into atoms take place. Then the hydrogen atoms diffuse through the metal lattice and on the low pressure (downstream) metal surface they are recombined into molecules and desorbed towards the downstream gas phase. The difference of the hydrogen partial upstream and downstream pressures applied to the membrane and the gradient of hydrogen atoms concentration through the metal lattice drive the hydrogen permeation.

Usually the surface reactions (adsorption, dissociation and the reverse ones) are very fast thus resulting in a low surface

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mass transfer resistance: in these conditions the diffusion through the metal lattice is the controlling mechanism. Accordingly, the hydrogen permeation flux, through a dense metal wall is well described by the equation:

$$J = \frac{Pe}{t}\left(p_{up}^{0.5} - p_{down}^{0.5}\right) \tag{1}$$

where J is the hydrogen permeation flux (mol m^{-2} s^{-1}), p_{up} and p_{down} (Pa) are the hydrogen partial pressures in the upstream and in the downstream side, respectively, t (m) is the membrane thickness and Pe (mol m^{-1}s^{-1}Pa$^{-0.5}$) is the hydrogen permeability.

In particular, the permeability coefficient is given by the product:

$$Pe = D \times S \tag{2}$$

where D is the diffusion coefficient (m^2 s^{-1}) and S the solubility coefficient (mol m^{-3} Pa$^{-0.5}$). Based on the above considerations, the metals suitable for the hydrogen separation have to exhibit high hydrogen permeability (i.e. an optimum combination of hydrogen solubility and diffusivity) and low surface resistance.

Presently, metal membranes made of Pd-alloys are used for pure hydrogen separation [6]. In fact, Pd is characterized by both very high hydrogen permeability and fast kinetic of the surface reactions with hydrogen. However, under thermal and hydrogenation cycling pure Pd can suffer from embrittlement as a consequence of the co-existence of two phases (α and β) characterized by different lattice parameters.

In order to avoid the embrittlement, Pd is alloyed with Ag and the alloy made of Pd-Ag 20–25 wt% is used for hydrogen purification [5,7]. Furthermore, the alloying with Ag increases the hydrogen permeability and mechanical strength of pure Pd thus improving the efficiency and reliability of the membrane modules.

So far, the high cost of Pd has limited its use to niche applications such as small laboratory devices (i.e. hydrogen generators) and membrane modules for the recovery of hydrogen isotopes in the fusion fuel cycle [8]. To reduce the costs, composite membranes made of porous supports covered with thin Pd-layers have been developed: these membranes exhibit high hydrogen permeability and reduced cost, while their selectivity and durability need to be further increased. As an alternative for reducing the costs, metal membranes with different chemical composition are highly desired. Indeed, some metals show a hydrogen permeability comparable or higher than that of Pd [9]. Among them, Ni, Co, Nb, Zr, V are less expensive and, therefore, are considered as possible alternatives to palladium. Also some combinations of these metals in an amorphous state has been considered as an alternative to Pd membranes [10]. Particularly, pure V has a permeability higher than that of Pd [9] but, similarly to palladium, it can suffer of embrittlement. Therefore, alloying with different metals, such as Pd, Cu, Ni, Ti, Al, W, Mo, or combinations of these ones, has been proposed as a tool to mitigate such inconvenience [11–16].

The hydrogen diffusion and solubility coefficients of some $V_{100-x}Ni_x$ alloys (x = 5, 10, 15) were investigated by Dolan et al. [17] in the temperature range between 300 and 400 °C. The permeability of such membranes have been calculated to be of the order of 10^{-8}–10^{-7} mol m^{-1}s^{-1}Pa$^{-0.5}$ [17], values comparable to that of Pd. More recent measurements of hydrogen solubility in $V_{85}Ni_{15}$ extended the temperature range from 150 up to 400 °C in the pressure range below 1000 Torr (about 1.33 bar) [18]. The study of the hydrogen adsorption properties of a material candidate as purification membrane is important for two reasons. The first is strictly related to the hydrogen solubility coefficient and thus to the hydrogen permeation coefficient of the material itself (see Eq. (2)). The second reason is linked to the knowledge of the mechanical properties, which are required for addressing the manufacturability and the stability of the membranes. In fact, the study of the solubility by means of pressure-composition isotherms gives useful information about the occurrence of different crystalline phases, such as solid solutions or hydrides that in general display different resistance to embrittlement.

In this paper, we synthesize a $V_{85}Ni_{15}$ sample by means of a vacuum induction technique and we investigate the sorption properties in a wide temperature (150 °C ≤ T ≤ 400 °C) and pressure range (up to 90 bar). The particular composition was chosen as a compromise between expected solubility, permeability and mechanical strength.

Materials and methods

The $V_{85}Ni_{15}$ alloy was prepared in a vacuum induction melting (VIM) apparatus at the Centro Sperimentale Materiali (CSM) Institute. The CSM plant has a capacity in the range of 5–80 kg and allows to take liquid specimen during melting to check and eventually correct the composition of the melt. The V-Ni alloy was melt in an isostatic graphite crucible by using loading elements having a purity higher than 99.9%. The fabrication process was carried out in several steps. At first, a $V_{65}Ni_{35}$ was placed inside the crucible, washed with argon several times and then evacuated at 1 Pa. In these vacuum conditions, the furnace temperature was increased up to 1380 °C to melt the charged materials. The melt was maintained for about 30 min and strongly mixed by electromagnetic force. Then the furnace temperature was raised up to 1800 °C and the required amount of pure V was added to reach the desired composition: $V_{85}Ni_{15}$. The so-formed alloy was poured inside a ceramic shell having dimension of 100 × 50 × 5 mm, which was removed after cooling. Small parts of this ingot were cut and used for characterization measurements.

X-ray diffraction analysis has been carried out at the Italian Synchrotron Facility in the ELETTRA laboratories in Trieste (MCX beamline) in reflection mode on a planar ingot of the sample: an energy of 12 keV (wavelength 1.03 Å) has been adopted. The diffraction pattern has been collected with a step size of 0.015° and a time/step of 6 s. The diffraction pattern has been fitted by using the Rietveld Refinement method [19] and the GSAS code [20] starting from the bcc (body centered cubic) lattice of the Ni-V alloy [21] and considering also the possible presence of the so-called σ-phase [22,23].

Sorption measurements were performed by means of a home-made Sieverts apparatus described in Refs. [24,25]. The measurements were conducted on a sample with a mass of ~2.3 g. The specimen had the shape of an irregular

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