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Development of $Nb_{35}Mo_5Ti_{30}Ni_{30}$ alloy membrane for hydrogen separation applications

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ABSTRACT

Our newly developed $Nb_{35}Mo_5Ti_{30}Ni_{30}$ alloy has been amended and evaluated for hydrogen separation applications in several critical aspects. Firstly, the hydrogen absorption and diffusion energetics in the Nb-Mo system are theoretically studied by density function theory. It is found that the addition of Mo in Nb can reduce the charge acquired by hydrogen and weaken the binding strength between the bcc-Nb lattice and hydrogen, thereby reducing hydrogen solubility. Additionally, optimized minimum energy paths for hydrogen diffusion are generated. These effects clarify the prominent role of Mo in the enhancement of both hydrogen permeability and embrittlement resistance. Secondly, as-cast $Nb_{35}Mo_5Ti_{30}Ni_{30}$ has been cold rolled to a thin membrane with a 0.12 mm thickness and then annealed. A hydrogen flux of ~ 0.21 mol H_2 $m^{-2}s^{-1}$ is obtained for the rolled-annealed membrane at a pure H_2 pressure difference of 0.7 MPa at 400 °C. Thirdly, the membrane is used to separate hydrogen from gas mixtures of H_2/CO_2 and $H_2/(CO_2 + H_2O)$. The hydrogen flux decreases mainly due to the decreasing H_2 partial pressure. The membrane does not suffer any physical damage during the test, and the hydrogen flux is fully recovered afterwards.

1. Introduction

Global H_2 production mainly originates from the conversion of carbon-based fuels (e.g. coal gasification, steam reforming of natural gas etc.), and the co-production of CO_2 necessitates an efficient H_2/CO_2 separation to deliver high purity H_2 to the downstream processes [1–4]. Membrane separation is one of the prominent technologies to separate and purify H_2 from gas mixtures. Pd-based alloys are commonly used membrane materials due to their high hydrogen selectivity and excellent catalytic properties [5–10]. Recently, there has been great interest in research and development of new, less expensive metal membranes owing to the high cost of Pd. Dolan [11] reviewed the development of non-Pd bcc (body centered cubic) alloy membranes for industrial hydrogen separation, which mainly concerns group V metals such as niobium (Nb), vanadium (V) and tantalum (Ta). Promising alloys include solid solution membranes such as Nb-W-Mo [12,13], V-Ni [14–16], Ta-W [17] etc., and eutectic alloy membranes such as Nb-Ti-Ni [18–20], V-Ti-Ni [21–23], Ta-Ti-Ni [24,25] etc. Although, Pd layers of nanoscale thickness are generally deposited on both sides of the non-Pd alloy membrane for dissociation of hydrogen molecules and ionization of hydrogen atoms, i.e. hydrogen uptaken is improved and the material cost is greatly reduced. Besides, the reported hydrogen permeability of these membranes is comparable to or even higher than that of Pd-based ones, while their sensitivity to hydrogen embrittlement (HE) remains the key issue to be solved. Compositional modification is an effective strategy to tailor the hydrogen solubility and diffusivity in the above mentioned bcc alloys, and thus optimizing the combined properties of hydrogen permeability and HE resistance.

Recently, we experimentally [26] found that the pertinent substitution of Nb with Mo in hydrogen permeable $Nb_{40}Ti_{30}Ni_{30}$ can reduce the hydrogen solubility while increase the intrinsic hydrogen diffusivity, thus improving the HE resistance with minimal permeability penalty. This implies that Mo is a desired alloying element in Nb to modulate its hydrogen transport properties, but the physical mechanism has not been clarified up to date. The $Nb_{35}Mo_5Ti_{30}Ni_{30}$ exhibits an attractive hydrogen permeability (nearly twice that of pure Pd at 673 K), and remains robust during pure hydrogen permeation under the operating conditions representative for industrial applications. This

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inspired us to further develop $Nb_{35}Mo_5Ti_{30}Ni_{30}$ alloy membranes with the least possible thickness for enhancement of hydrogen flux. It is also necessary to apply hydrogen permeation tests for thin membranes not only with pure H_2, but also with gas mixtures. The effects of impurity gases (e.g. CO_2, CO, steam etc.) on hydrogen permeability in Pd-based alloys have been widely investigated [27–32], but there is limited information about such effect in bcc alloys.

In this work, we first investigate hydrogen absorption and diffusion energetics in Nb and Nb-Mo alloys by first principles calculation based on density functional theory (DFT). This contributes to clarify the prominent role of Mo in tailoring hydrogen solubility and diffusivity. Secondly, cold rolling is used to produce thin membranes of $Nb_{35}Mo_5Ti_{30}Ni_{30}$. Considering that rolling induces substantial microstructural changes and defect formation [33–36], a post-annealing process is applied for the rolled membranes. Effects of cold rolling and subsequent annealing on microstructure, hydrogen dissolution, diffusion and permeation in $Nb_{35}Mo_5Ti_{30}Ni_{30}$ membranes are investigated. Thirdly, the rolled-annealed $Nb_{35}Mo_5Ti_{30}Ni_{30}$ membranes are used for hydrogen separation from gas mixtures containing CO_2 and steam impurities. The influence of CO_2 and steam on hydrogen flux are investigated. The operating temperature in both pure H_2 and mixed gas atmosphere is set to 400 °C. These are representative for industrial applications, typically in catalytic membrane reactors when combined with high temperature water gas shift (WGS) reactions [4]. The present work aims to provide important information to evaluate the potential of $Nb_{35}Mo_5Ti_{30}Ni_{30}$ membranes for the use in hydrogen separation and purification.

2. DFT calculations and experiments

2.1. Theoretical method

The electronic structures of pure Nb, binary Nb-Mo alloys, and Nb-H/Nb-Mo-H solid solutions were calculated using DFT as implemented in the open source Quantum Espresso program package. We used the high accuracy pseudo-potentials provided by the Standard Solid State Pseudo-potentials (SSSP) project. The exchange-correlation function was taken within the generalized gradient approximation (GGA) in the parameterization of Perdew-Burke-Ernzerhof (PBE). A plane-wave basis is adopted for the expansion of the valence electron wave functions with kinetic energy cutoffs of 55 Ry.

We used a k-point sampling of 16 × 16 × 16, 8 × 8 × 8, 4 × 4 × 4, and 2 × 2 × 2 for Nb, Nb16, Nb54, and Nb128, respectively, which converged the dissolution energy to within 0.03 eV for each cell. Both the cell shape and atomic positions inside the cells were allowed to relax during the geometry optimization. The Methfessel-Paxton first order spreading method was used for the Fermi surface smearing in order to obtain accurate forces, and a smearing width of 0.01 Ry was chosen such that the error in the extrapolated energy at 0 K is less than 1 meV per atom.

The hydrogen absorption energy, E_{abs}, of hydrogen atoms in bulk metals is given by Eq. (1):

$$E_{abs} = E_{bulk+H} - E_{bulk} - 0.5E_{H_2} - E_{ZPE} \quad (1)$$

Here, E_{bulk+H} is the total energy of the supercell that includes n Nb atoms and 1 H atom, E_{bulk} is the total energy of the supercell that consists of n Nb atoms, E_{H_2} is half the total energy of the hydrogen molecule, which was calculated by setting H_2 in a cubic box with 10 Å sides and carrying out a Γ-point calculation. We obtained a bond length for H_2 of 0.750 Å, a vibrational frequency of 4300 cm^{-1}, and a binding energy of 4.54 eV, which is almost identical to previous GGA results [37]. E_{ZPE} is the zero point energy obtained by summing up the zero point vibrational energies of the H's normal modes. All energies are referenced to gaseous hydrogen molecules and pure Nb.

The Climbing Image Nudged Elastic Band (CI-NEB) method is used to locate the minimum energy paths (MEPs) and the transition states for diffusion of hydrogen in pure Nb and Nb-Mo alloys. An interpolated chain of configurations (images) between the initial and final positions is connected by springs and relaxed simultaneously to the MEP. We used 5 images in the current calculation to discretize the diffusion path. A quasi-Newton Broyden's second method was used for the optimization scheme. With the climbing image scheme, the image highest in energy does not feel the effect of springs and is allowed to climb along the path. When we use the CI-NEB method in this study, all the images are relaxed until the maximum force acting on an atom is less than 0.01 eV/Å.

2.2. Experimental procedures

2.2.1. Samples

About 40 g ingots of as-cast $Nb_{35}Mo_5Ti_{30}Ni_{30}$ alloy were prepared by arc melting in an Ar atmosphere using Nb, Mo, Ti and Ni (99.99 mass % purity for all). Rectangular samples (10 × 10 × 2 mm^3) were cut from the as-cast ingots using a spark erosion wire-cutting machine. The samples were cold rolled into thin sheets at room temperature by successive thickness reduction until a crack was first observed with the bare eye on the surfaces of the samples. More details of the rolling procedure can be found in Ref. [36]. The minimum thickness of the cold rolled sheets was 0.12 mm after grinding and polishing of the surfaces. Disk samples of 12 mm in diameter were cut from the thin sheet and then annealed at 1273 K for one week under high purity Ar. The cold rolled samples are termed as “cold rolled” and the subsequently annealed samples are termed as “rolled-annealed”. Characterization of constituent phases and crystallographic structure using X-ray diffraction (XRD) analysis was performed. Microstructural observations were carried out using scanning electron microscopy (SEM-Quanta200FEG) in backscattered electron (BSE) mode combined with energy diffraction X-ray analysis (EDX).

2.2.2. Hydrogen absorption and permeation

Disk samples of 12 mm in diameter were cut from the as-cast ingots and the cold rolled sheets using a spark erosion wire-cutting machine. Both surfaces of the as-cast, cold rolled and rolled-annealed samples were ground and polished. The final thickness (d) of the as-cast samples was 0.6 mm, and the thickness of the cold rolled and rolled-annealed samples was 0.12 mm. For avoiding oxidation and promoting hydrogen uptake into the material, a ~ 190 nm layer of pure Pd was then coated on both sides of each sample by a radio frequency magnetron sputtering machine (ZC-1000). The sputtering process was carried out at 300 °C under a sputtering distance of 60 mm, a back pressure of 8×10^{-6} Pa, a working pressure of 1.6 Pa, a working power of 400 W, and a sputtering duration of 200 s.

For characterizing hydrogen solubility in the as-cast, cold rolled and rolled-annealed $Nb_{35}Mo_5Ti_{30}Ni_{30}$ samples, the pressure-composition isotherms (*PCT*s) were measured using a Sieverts-type apparatus (PCTPro-2000) which can operate over a wide range of temperature, room temperature to 1000 °C, and H_2 pressure, 0.01–1 MPa. The *PCT* curves were measured at pressures in the range of 0.01–1.0 MPa at 400 °C and 350 °C, respectively. The amount of absorbed hydrogen was calculated from the pressure drop in the constant inner volume chamber. More details about the experimental procedure can be found in Refs. [38–40].

Hydrogen permeation tests were performed in an in-house built gas permeation apparatus which is identical as that described Ref. [41,42]. Disk samples were sandwiched by two copper gaskets and sealed in the apparatus. Both sides of the sample were evacuated, heated to 400 °C in vacuum and kept for 20 min. Pure H_2 was introduced at pressures from 0.2 to 0.8 MPa to the upstream step and step and 0.1 MPa to downstream sides of the sample, respectively. The hydrogen permeation flux through the sample was measured using a mass flow meter. After finishing characterization of hydrogen permeation with an upstream H_2 pressure of 0.8 MPa at 400 °C, the sample was cooled at a fixed rate of