Thermal Stability and Hydrogen Permeation of Ni$_{42}$Zr$_{30}$Nb$_{28-x}$Ta$_x$ Amorphous Alloys

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The thermal stability and hydrogen permeability of Ni$_{42}$Zr$_{30}$Nb$_{28-x}$Ta$_x$ (x = 0, 7, 14, 21, 28) amorphous alloys have been studied in the present work. The substitution of Nb by Ta was found to be effective in improving the thermal stability of the Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous alloy. The onset crystallization temperature of the Ni$_{42}$Zr$_{30}$Nb$_{28}$Ta$_{14}$ amorphous alloys was increased by 58 K from 807 K for Ta-free composition to 865 K for Ni$_{42}$Zr$_{30}$Nb$_{28}$ due to the Ta addition. The hydrogen permeability of the Pd-coated Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous membrane was measured to be about 0.86 x 10$^{-8}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1/2}$ at 673 K, which is slightly lower than that of the Pd-coated Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous membrane. The hydrogen permeability of the Ni$_{42}$Zr$_{30}$Nb$_{28}$Ta$_{14}$ amorphous membrane revealed to be more temperature dependent in comparison to that of the reference membrane. The higher thermal stability combined with good hydrogen permeability give rise to the possibility of the practical use for Ni$_{42}$Zr$_{30}$Nb$_{28}$Ta$_{14}$ amorphous alloy as a dense metal membrane operating at higher temperatures. [doi:10.2320/matertrans.ME200804]

1. Introduction

The heavy demand of stable hydrogen supply in the hydrogen power society has been urging the development activity of producing gaseous hydrogen and of hydrogen purification. A large portion of the current research has been focused on the hydrogen permeable membrane materials [Ref. 1, 2 and references therein]. Owing to their excellent hydrogen selectivity and high thermal stability, metallic membranes such as Pd-Ag alloys have been used in industries for hydrogen purification for decades. More recently, researchers address themselves to the development of amorphous metal membranes due to the discovery of a wide variety of metallic glasses with large glass-forming ability (GFA) and high thermal stability. Amorphous alloys may have the advantage to tackle the problem of hydrogen embrittlement that occurs with crystalline alloys, while still providing hydrogen permeability comparable to Pd metal. Simultaneously, the time-favored sample preparation procedures and the relative low material costs of these alloys give rise to the possibility of large-scale industrial production.

Amorphous alloys are high strength materials due to the lack of a dislocation mechanism for yielding at room temperatures and a grain boundary gliding mechanism for low applied stress creep at high temperatures as well. Hara et al. studied the hydrogen permeability and embrittlement of Ni-Zr and Ni-Zr-Ti (Ti or Hf) amorphous membranes. The alloys were found to be sufficiently tough to show hardly hydrogen embrittlement, but their hydrogen permeability was much lower than those of Pd-Ag alloys. Inoue et al. reported that Ni-Zr-Ti-Nb metallic glasses exhibited high thermal stability against crystallization to open a wide supercooled liquid regions.8 Subsequently, Yamaura et al. reported that the hydrogen permeability of Ni-Zr-Nb melt-spun alloys was strongly dependent on alloy compositions, particularly on the Zr content of the alloys.9 The Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous alloy was found to show a high hydrogen permeability of 1.3 x 10$^{-8}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1/2}$ at 673 K, which is superior to that of pure Pd metal. A continued research by Yamaura et al. revealed an even better hydrogen permeability of 1.59 x 10$^{-8}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1/2}$ at 673 K for the Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous alloy.10

Amorphous alloys are metastable and, hence the thermal stability is the critical property of metallic glass membranes for hydrogen separation application. For example, high thermal stability of the amorphous membranes can ensure their service durability at the conventional operating temperatures. The onset crystallization temperatures of the above-mentioned Ni-Zr-Nb amorphous alloys with good hydrogen permeability are generally below 800 K,9,10 which to some extent limit their practical application as hydrogen permeation membrane at higher operating temperatures. Noticing that Ta metal has a much higher melting temperature than Nb, and in light of the results of Kim et al. that hydrogen embrittlement of Ni-Nb amorphous alloys can be effectively suppressed by Ta addition,11 in the present work we attempt to investigate the effects of Ta addition on the thermal stability and hydrogen permeability of Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous alloy. The central aim of the work is to develop more stable Ni-Zr-based amorphous alloys with good hydrogen permeability under the condition of Pd surface coating.

2. Experimental

Ni$_{42}$Zr$_{30}$Nb$_{28-x}$Ta$_x$ (x = 0, 7, 14, 21, 28) alloy buttons were prepared by arc melting the mixture of constituent metals under a Ti-getter purified argon atmosphere. The purities of metals are 99.5 mass% for Zr and 99.9 mass% for Ni, Nb and Ta, respectively. The button samples were remelted four times for homogeneity. The total weight loss...
of these samples during arc melting process was less than 0.05%. Using these master alloys, ribbon samples were prepared using the single-roller melt-spinning technique. The sample dimension is about 10 mm (width) × 50 μm (thickness). To obtain an active catalytic surface layer for hydrogen dissociation and recombination, Pd thin film was deposited on both sides of the specimens before hydrogen permeation testing by sputtering technique (ULVAC SH-350). The Pd deposition was performed under the condition of radio frequency power source of 100 W for 100 s in a high-purity Ar atmosphere. Membrane specimens with a 5 mm diameter permeation area were mounted in the gas-permeation cell. Hydrogen permeation was measured at 573, 623 and 673 K by a conventional gas-permeation technique using pure hydrogen gas under the hydrogen pressure up to 0.2 MPa. The details on the hydrogen permeation measurement can be referred to our previous studies.9,10)

Amorphous structure identification for ribbon samples before and after hydrogen permeation was carried out using a Rigaku RINT-ultima IIIp X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 0.15406 nm). A TA-DSC Q100 type differential scanning calorimetry (DSC) was employed to examine the thermal stability of the samples under a super-purified argon atmosphere. The constant heating rate for DSC measurement is 40 K/min.

3. Results and Discussion

3.1 Thermal stability

Figure 1 shows the XRD patterns of the melt-spun Ni_{42}Zr_{30}Nb_{28−x}Ta_{x} (x = 0, 7, 14, 21, 28 at%) alloys. The XRD patterns are characterized by a principle diffuse peak centered around 2θ = 38°, and no sharp crystalline peaks are observed within the whole range of 2θ scan. All the melt-spun samples were identified to be amorphous structures. Further, the peak positions and the full widths at half maximum determined from these principle diffraction peaks show little difference at these compositions. In the Periodic Elemental Table, Ta and Nb are neighbored but belong to the same column, having similar outer shell electronic configurations. The two metals share a BCC lattice structure and show complete solubility in their binary phase diagram, indicating their similar chemical properties. In addition, the heats of mixing of Ni-Nb and Zr-Nb are −30 and +4 kJ/mol, respectively, at equi-atomic compositions, and those for Ni-Ta and Zr-Ta are respectively −29 and +3 kJ/mol.12) These thermodynamic data suggest the similar chemical affinities of Nb and Ta with the host elements Ni and Zr. It is also noted that Nb and Ta have the same Goldschmidt atomic radii of 0.147 nm.13) All the above electronic, thermodynamic and geometric parameters assume a random substitution manner of Ta for Nb in these amorphous structures.

The constant heating-rate DSC traces of Ni_{42}Zr_{30}−Nb_{28−x}Ta_{x} amorphous ribbons are shown in Fig. 2, which hardly show any detectable glass transitions below the onset of crystallization. Thus these melt-spun alloys are properly called ‘amorphous alloys’ rather than ‘metallic glasses’. Upon heating, the amorphous samples show three successive exothermic peaks within the temperature range from 800 to 960 K at Ta free, 7 and 14 at% Ta compositions. For samples with higher Ta contents, the crystallization mode is altered to show a single exothermic peak within the temperature range of 800–900 K. The onset crystallization temperature Tx is increased with increasing Ta content. In particular, an overall increase of 58 K from 807 K (x = 0) to 865 K (x = 28) was observed, indicating the significantly enhanced thermal stability of the Ta-bearing alloys. The thermal stabilities of these Ta-bearing Ni_{42}Zr_{30}Nb_{28−x}Ta_{x} amorphous alloys are superior to that of the Ni_{42}Zr_{30}Nb_{28} amorphous alloy, which was found possessing good hydrogen permeability.9)

3.2 Hydrogen permeability

The hydrogen permeability of Ni_{42}Zr_{30}Nb_{28} melt-spun samples prepared at identical melt-spinning parameters has been thoroughly studied by Yamaura et al.9) In this work the sample was taken as the reference one for a comparative study. Hydrogen permeation of these amorphous alloys was measured at the same operating temperature of 673 K. The obtained hydrogen permeation coefficient (P_H) as a function of Ta content is shown in Fig. 3. The permeation coefficient of the reference sample was well reproduced to be about 1.25 × 10^{−8} mol·m^{-1}·s^{-1}·Pa^{-1/2} at 673 K in our measurements. The samples containing 14 and 28 at% Ta...
exhibited slightly lower $P_H$ of $0.88 \times 10^{-8}$ and $0.86 \times 10^{-8}$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-1/2}$ at 673 K, respectively. The measured hydrogen permeation coefficient data indicate that the hydrogen permeability was not significantly deteriorated in these Ta-bearing amorphous samples. As mentioned above, Nb and Ta share similar properties, and the Ta substitution for Nb may be in a random manner in these amorphous alloys. Therefore, their close hydrogen permeation coefficients seem to be a reasonable consequence.

Figure 4 shows the XRD patterns of the Pd-coated Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane before (a) and after (b) permeation testing at 673 K for 3 h.

Fig. 3 The hydrogen permeability of Ni$_{42}$Zr$_{30}$Nb$_{28-x}$Ta$_x$ ($x = 0, 14, 28$ at%) amorphous membranes at 673 K.

Fig. 4 XRD patterns of the Pd-coated Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane samples before and after hydrogen permeation for 3 h at 673 K. The sharp diffraction peaks come from the Pd-coatings with FCC crystalline structure. The profiles of the two XRD patterns are almost reproducible, indicating the membrane sample persist in its initial amorphous structure even after the hydrogen permeation test at high temperature and high hydrogen pressure. The good service stability of the amorphous membrane is evidently revealed. Figure 5(a) shows the Arrhenius plots of the hydrogen permeability of the reference membrane (Ni$_{42}$Zr$_{30}$Nb$_{28}$) and the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous alloy. Plots of Pd-23 mass%Ag and pure Pd metal are also included in the figure for comparison. It is seen that the hydrogen permeability of the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane is comparable to pure Pd metal at 673 K. At lower temperatures, however, the permeability of the membrane exhibited a more declined slope as compared to that of the reference amorphous membrane and those of crystalline Pd metal and Pd-Ag alloy.

As the slope of an Arrhenius plot approximates to the apparent activation energy for hydrogen permeation,$^{10}$ the permeability data of Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane imply a larger energy barrier for hydrogen diffusion than those in the reference samples. The hydrogen permeability of Ni$_{42}$Zr$_{30}$Nb$_{28}$ and Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane was further plotted as the function of the reduced temperature ($T/T_x$). As shown in Fig. 5(b), the Ni$_{42}$Zr$_{30}$Nb$_{28}$ membrane showed a more stable permeability than Ni$_{42}$Zr$_{30}$Ta$_{28}$ in a wide temperature span. However, considering the much higher crystallization temperature of the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous alloy than Ni$_{42}$Zr$_{30}$Nb$_{28}$, for the former membrane, the rapid increase of the permeability with increasing temperature suggests that higher hydrogen permeability can be safely extended to higher operating temperatures. These results indicate that the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous alloy is another possible candidate for future practical use as dense metal hydrogen membrane materials at higher temperatures.
4. Conclusions

A series of Ni$_{42}$Zr$_{30}$Nb$_{28-x}$Ta$_x$ (x = 0, 7, 14, 21, 28) amorphous alloys were prepared in this study. The substitution of Ta for Nb has been proven effective in improving the thermal stability of the previously reported Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous alloy with good hydrogen permeability. The complete substitution of Nb by Ta results in an increase of 58 K in the crystallization temperature. The hydrogen permeability of the Pd-coated Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane was measured to be about $0.86 \times 10^{-8}$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-1/2}$ at 673 K, which is nearly the same as that of pure Pd metal, but is slightly lower than that of the Pd-coated Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous membrane. The hydrogen permeability of the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous membrane is more temperature dependent in comparison to those for crystalline Pd metal/alloy and the Ni$_{42}$Zr$_{30}$Nb$_{28}$ amorphous membrane. The higher crystallization temperature of the Ni$_{42}$Zr$_{30}$Ta$_{28}$ amorphous alloy ensures a safe extension of the hydrogen permeability at elevated permeation temperatures.

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