Microstructure, Ductility and Hydrogen Permeability of Nb-Ti-Zr-Ni Alloys

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A series of Nb_{40}Ti_{30}Zr_{12}Ni_{48−x} alloys with different Ti/Ni ratios were prepared by arc melting in a purified argon atmosphere. The Ti/Ni ratio affected microstructures, crystal structures, ductility and hydrogen permeability (Φ) of these alloys. The values of hydrogen permeability Φ for the Nb_{40}Ti_{30}Zr_{12}Ni_{48−x} alloys increased with increasing temperature and were higher than those of pure Pd above 573 K. Hydrogen permeation at 673 K, i.e., Φ_{673 K} and the volume fraction of the primary phase in the Nb_{40}Ti_{30}Zr_{12}Ni_{48−x} alloys increased with increasing Ti/Ni ratio. The present work demonstrated that hydrogen permeation properties of the Nb_{40}Ti_{30}Zr_{12}Ni_{48−x} alloy are superior to those of the Nb_{40}Ti_{18}Zr_{12}Ni_{30} one which was reported to be the best one in the Nb_{40}Ti_{30−x}Zr_{12}Ni_{30} alloys. [doi:10.2320/matertrans.MA200808]

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1. Introduction

Hydrogen permeable dense metal membranes on the basis of Pd or Pd-Ag alloys have attracted considerable attention for high purity hydrogen production in recent years due to their high hydrogen permeability (Φ) and high hydrogen selectivity. However, Pd is very expensive and a rare metal, so that the development of new hydrogen permeation alloys other than Pd is urgently required. Generally, metals and alloys showing high Φ suffer from severe hydrogen embrittlement. Some groups have tried to develop new alloys such as V-based alloys, Nb-based alloys, amorphous Zr-Ni alloys, amorphous Zr-Ni-Nb alloys, and so on. However, the overcomin of the hydrogen embrittlement in these alloys is insufficient. Recently, the present authors have developed new non-Pd based hydrogen permeation alloys such as the Nb-TiNi, the Nb-TiCo and the Nb-ZrNi ones. The Nb-TiNi alloys show high Φ and large ductility, while those of the Nb-ZrNi ones do higher Φ and poorer ductility than those of the Nb-TiNi ones, which are attributed to the Ti/Ni phase shows larger ductility than that of the ZrNi one, but the latter does higher Φ than that of the former. In the hydrogen permeation alloys, not only high Φ, but also some ductility is necessary, because the alloy membrane is mechanically sealed with the gaskets. Then, the improvement in Φ keeping ductility is essential. If Ti in the Nb-TiNi alloys is substituted with Zr, the alloys exhibiting higher Φ than that of the Nb-ZrNi ones and larger ductility than that of the Nb-ZrNi ones should be obtained. On the basis of this idea, the present authors investigated microstructures, crystal structures, ductility and Φ of the Nb_{40}Ti_{30−x}Zr_{12}Ni_{30} alloys. The Nb_{40}Ti_{18}Zr_{12}Ni_{30} alloy has been selected to be the best one from the point of view of Φ and ductility. Furthermore, it is expected that ductility, Φ and resistance to the hydrogen embrittlement of the Nb_{40}Ti_{18}Zr_{12}Ni_{30} alloy also depend on the Ti/Ni ratio, because Ti shows rather higher Φ than that of Ni. The purpose of the present work is to select the alloy with higher hydrogen permeability (Φ), some ductility and resistance to the hydrogen embrittlement from the Nb_{40}Ti_{18}Zr_{12}Ni_{48−x} alloys by adjusting the Ti/Ni ratio.

2. Experimental Procedure

Nb_{40}Ti_{12}Zr_{12}Ni_{48−x} alloys (x = 14, 16, 18, 20, 22 and 24) were prepared by arc melting using Nb (99.9 mass% purity), Ti (99.5 mass% purity), Zr (99.7 mass% purity) and Ni (99.9 mass% purity) in a purified argon atmosphere. In this paper, the alloy compositions are expressed by mole%. A scanning electron microscope (SEM, JSM 5300) with an energy dispersive X-ray spectroscopy (EDS) and an X-ray diffractometer (XRD, PANalytical X’Pert PRO) were used to characterize microstructures, alloy compositions and crystal structures of these alloys, respectively. The volume fraction of the primary phase was determined by the SEM observation. Disks 12 mm in diameter and 0.6–0.8 mm in thickness were sectioned from the arc melted ingots by a wire-cutting machine. Both sides of the disks were polished with 0.5 μm alumina particles, and then coated with pure Pd in the thickness of 190 nm by the magnetron sputtering machine to prevent oxidation and to enhance dissociation and recombination of hydrogen. Hydrogen permeability Φ of these alloys were measured through a conventional gas-permeation method at the temperature range of 523–673 K, at the hydrogen pressure up to 0.5 MPa. The experimental procedure has been described in detail elsewhere.

3. Results and Discussion

Figure 1 shows the temperature dependence of hydrogen permeability Φ for the as-cast Nb_{40}Ti_{12}Zr_{12}Ni_{48−x} alloys (x = 14, 18, 20, 22 and 24) in the form of an Arrhenius plot. The values of Φ for pure Pd are also plotted for reference, while those of Φ for the alloy for x = 16 is omitted because of overlapping with the others. The values of Φ for all these alloys increase with increasing temperature, and are higher than those of pure Pd above 573 K. The value of Φ is measurable for all samples between 523 K and 673 K, so that we can say that these alloys have resistance to the hydrogen embrittlement. From the slope of these Arrhenius plots, activation energy E_a for hydrogen permeation can be calculated and are tabulated in Table 1. There is no clear difference in activation energy between them except for that of Nb_{40}Ti_{22}Zr_{12}Ni_{26} alloy. Hydrogen permeability at 673 K, i.e., Φ_{673 K} for the Nb_{40}Ti_{12}Zr_{12}Ni_{48−x} alloys is plotted against

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the Ti/Ni ratio (or the Ti content) in Fig. 2. It is clearly seen that $\Phi_{673K}$ for these alloys increases with Ti/Ni ratio. We investigate microstructures and crystal structures of these alloys in order to make clear the reasons for this increment of $\Phi_{673K}$.

Figure 3 shows SEM images of the as-cast Nb$_{40}$Ti$_{x}$Zr$_{12}$Ni$_{48-x}$ alloys ($x = 14, 16, 18, 20, 22$ and 24). These SEM images indicate that these alloys consist of the primary (white) and another phases. Fine lamellar microstructures of the eutectic phases, which are typical ones in the Nb$_{40}$Ti$_{30}$Ni$_{30}$ and Nb$_{40}$Ti$_{40}$Ni$_{10}$ alloys, are not observed in these alloys.

Figure 4 shows the relationship between the volume fraction of the primary phase $V_i$ and the Ti/Ni ratio (or the Ti content) in the as-cast Nb$_{40}$Ti$_{x}$Zr$_{12}$Ni$_{48-x}$ alloys. We can see that their volume fraction increase with TiNi ratio. On the other hand, it has been reported that hydrogen permeation in the Nb-TiNi alloys is mainly determined by the primary phase. Then, the main reason for the increment of $\Phi$ with increasing Ti/Ni ratio is considered to be the increase of the volume fraction of the primary phase. Chemical compositions of the primary phases vary widely and complicatedly as shown in Table 1, but we can notice the following tendency. As the Ti/Ni ratio increases, the concentrations of both Ti and Zr in the primary phases are increased, but that of Nb is decreased. On the other hand, the concentration of Ni is almost constant independent of the Ti/Ni ratio. It has been reported that $\Phi$ of Zr is rather higher than that of Nb. Then, the increment of $\Phi$ with increasing Ti/Ni ratio may be enhanced by the increase of the Zr content in the primary phase.

Figure 5 shows XRD patterns of the as-cast Nb$_{40}$Ti$_{x}$Zr$_{12}$Ni$_{48-x}$ alloys ($x = 14, 16, 18, 20, 22$ and 24). From these XRD patterns, we can see that the alloys ($x = 14, 16$ and 18) consist of the bcc-(Nb,Ti,Zr) and B2-(Ti,Zr)Ni phases, while the alloys ($x = 20, 22$ and 24) consist of the bcc-(Nb,Ti,Zr) and the orthorhombic (Zr,Ti)Ni ones. Here, the B2-(Ti,Zr)Ni phase means that Zr dissolves in the B2-TiNi phase. The crystal structures of these alloys change from the bcc-(Nb,Ti,Zr) + B2-(Ti,Zr)Ni phases to the bcc-(Nb,Ti,Zr) + the orthorhombic (Zr,Ti)Ni when the Ti/Ni ratio is higher than 0.71, but which does not give rise to change of the lattice parameters in the primary phases. We can notice that $\Phi_{673K}$ of the alloys with the structure of bcc-(Nb,Ti,Zr) + B2-(Ti,Zr)Ni phases is lower than that of those alloys with the bcc-(Nb,Ti,Zr) and the orthorhombic (Zr,Ti)Ni ones as seen in Fig. 2.

The hydrogen permeation alloy membrane is mechanically sealed with the copper gaskets and is applied by the
Fig. 3 SEM images of as-cast (a) Nb$_{40}$Ti$_{14}$Zr$_{12}$Ni$_{34}$, (b) Nb$_{40}$Ti$_{16}$Zr$_{12}$Ni$_{32}$, (c) Nb$_{40}$Ti$_{18}$Zr$_{12}$Ni$_{30}$, (d) Nb$_{40}$Ti$_{20}$Zr$_{12}$Ni$_{28}$, (e) Nb$_{40}$Ti$_{22}$Zr$_{12}$Ni$_{26}$, and (f) Nb$_{40}$Ti$_{24}$Zr$_{12}$Ni$_{24}$ alloys.

Fig. 4 The relation between the volume fraction of the primary phase $V_f$ and the Ti/Ni ratio (or the Ti content) in the as-cast Nb$_{40}$Ti$_x$Zr$_{12}$Ni$_{48-x}$/C$_0$ alloys.

Fig. 5 XRD patterns of Nb$_{40}$Ti$_x$Zr$_{12}$Ni$_{48-x}$/C$_0$ alloys with different compositions ($x = 14, 16, 18, 20, 22$ and $24$).
pressure difference in both sides of it. Then, these alloys must have at least some ductility. Either ductile or brittle as-cast Nb_{40}Ti_{x}Zr_{12}Ni_{48–x} alloys (x = 14, 16, 18, 20, 22 and 24) is tabulated in Table 1. In this paper, the alloy broken easily by hammering is defined as brittle, while the one not broken by it is defined as ductile. As well known, the bcc-(Nb,Ti,Zr) and the B2-(Ti,Zr)Ni phases are ductile, but the orthorhombic (Zr,Ti)Ni one is brittle. The alloys for x = 22 and 24 are brittle due to the presence of the brittle orthorhombic (Zr,Ti)Ni phase, while those for x = 14 and 16 are brittle in spite of the absence of the brittle phase. On the other hand, it is interesting that the Nb_{40}Ti_{20}Zr_{12}Ni_{28} alloy is ductile even though it contains a small amount of the brittle (Zr,Ti)Ni phase.

Finally, we discuss which alloys in the as-cast Nb_{40}Ti_{x}Zr_{12}Ni_{48–x} alloys (x = 14, 16, 18, 20, 22 and 24) show good hydrogen permeation properties combing ductility and resistance to the hydrogen embrittlement with high hydrogen permeability. All these alloys are resistant to the hydrogen embrittlement by hammering. All these alloys are resistant to the hydrogen embrittlement with high hydrogen permeability. The Nb_{40}Ti_{20}Zr_{12}Ni_{28} alloy is the best one in the Nb_{40}Ti_{12}Ni_{48–x} alloys showing some ductility, good resistance to hydrogen embrittlement and higher Phi.

### 4. Conclusion

Microstructures, crystal structures, ductility and hydrogen permeability (Phi) of Nb_{40}Ti_{x}Zr_{12}Ni_{48–x} alloys are investigated to select the alloy with higher hydrogen permeability, some ductility and resistance to the hydrogen embrittlement from these alloys. Their microstructures are quite different from each other with different Ti/Ni ratio. The high Ti/Ni ratios result in larger volume fraction of the primary phases thereby improving Phi, but decreasing resistance to the hydrogen embrittlement. The crystal structures of the alloys with the Ti/Ni ratios higher than 0.71 are changed into the orthorhombic ZrNi from the B2-TiNi phase, which increases Phi of the alloys and decreases ductility of the alloys. In a word, the Nb_{40}Ti_{20}Zr_{12}Ni_{28} alloy shows the best hydrogen permeation properties in the Nb_{40}Ti_{x}Zr_{12}Ni_{48–x} alloys.

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