Microstructural and Mechanical Characterizations of Rapidly Solidified Nb-TiNi Hydrogen Permeation Alloy

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Abstract. The microstructural and mechanical characterizations of the rapidly solidified Nb₂₀Ti₄₀Ni₄₀(at%) hydrogen permeation alloy have been performed. An as-melt spun ribbon consists of an amorphous phase with sound bending ductility. The successive crystallization of B2-TiNi and bcc-Nb solid solution phases takes place during heating. The amorphous phase is stable in the specimens annealed below 773 K. The specimens annealed from 798 to 923 K are quite brittle, although those consist of fine equiaxed grains less than 50 nm. With annealing above 948 K for prolonged periods the grain size is increased to about 150 nm or more and the hardness is decreased about 260 Hv or less. Consequently, the ductility is recovered. The fracture toughness of as-melt spun and annealed ribbons is also investigated by the micromechanical test.

1. Introduction
Pd-Ag alloys have been commercially used as the hydrogen permeation membrane to separate and to purify hydrogen gas. Since Pd is quite expensive and scarce in resources, one of the author groups has recently found out the Nb-Ti-Ni alloy consisting of bcc-Nb and B2-TiNi eutectic microstructures with a sound combination of high hydrogen permeability and excellent hydrogen embrittlement resistance [1,2] as non-Pd-based hydrogen permeation alloys with low cost and high performance. In the present alloy, it is considered that the high hydrogen permeability is attributable to the bcc-Nb solid solution phase, while the excellent hydrogen embrittlement resistance is due to the B2-TiNi phase in the eutectic structure.

It is well-known that the hydrogen permeability increases with decreasing the thickness of the membrane [3]. Therefore, it is advantageous to use the melt spun ribbon of hydrogen permeation alloy in comparison to the bulk alloy. It is apparent that eutectic alloy systems are easily obtained the amorphous state by the rapid solidification. The eutectic quasi-binary Nb-TiNi system mentioned above is suited to the melt spinning technique. Since the melt spun ribbon is usually in nonequilibrium state such as amorphous phase, it is expected that both the mechanical property and the microstructure are drastically changed by heat treatments.

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The purpose of the present paper is to clarify the crystallization behaviours and microstructure changes by heat treatments in the melt spun eutectic Nb-TiNi hydrogen permeation alloy by a conventional transmission electron microscopy and high resolution transmission electron microscopy observations. The relation between microstructures and mechanical properties is also discussed on the basis of micromechanical test.

2. Experimental procedures

Nb\textsubscript{20}Ti\textsubscript{40}Ni\textsubscript{40} eutectic alloy was prepared from 99.9\% Nb, 99.7\% Ti and 99.9\% Ni (% by mass) by arc melting in an argon atmosphere. The melt spun ribbons of 40 µm in thickness were prepared by a single-roller melt spinning method at a circumferential speed of 31.0 m/s. The obtained ribbons were annealed in a vacuum of 0.6 x 10\textsuperscript{-3} Pa at 773 to 973 K for 3.6 to 360 ks. Differential scanning calorimetry (DSC) measurements were performed by using a Shimadzu DSC-50 calorimeter with a heating rate of 10 K/min. The TEM specimens were prepared by the argon ion milling technique. CTEM and HRTEM observations were performed with JEM-2000FX and FEI-Tecnai20F microscopes operated at 200 kV, respectively. TEM-EDX analyses were also carried out with FEI-Tecnai20F. The following lattice parameters were used for the analysis in the B2 TiNi and bcc-Nb solid solution phases; \(a_{\text{B2}} = 0.3022\) nm and \(a_{\text{bcc-Nb}} = 0.3304\) nm, respectively [4].

The hardness was measured using a micro Vickers hardness testing machine. The ductility was estimated by a bending test. The samples that were able to be bent by 180 degrees without fracture were judged to be ductile. The micromechanical test was carried out in the self-assembled equipment [5] and the micro-cantilever specimens with dimensions of 10 x 20 x 50 µm\textsuperscript{3} were prepared by focused ion beam machine as shown in Fig. 1.

3. Results and discussion

3.1. Microstructure and mechanical properties of as-spun material

Figures 2 (a) and (b) show the bright field image and the corresponding electron diffraction pattern of as-melt spun ribbon, respectively. There is no characteristic contrast indicating a crystal phase in Fig. 2 (a). The pattern in Fig. 2 (b) represents the halo ring. These indicate that the microstructure of as-melt spun ribbon consists of the amorphous phase. The DSC measurements are performed to estimate the characteristic temperatures of phase transition such as crystallization. A smooth endothermic peak about 720 K and two sharp exothermic peaks between 850 and 950 K are clearly observed, as indicated by the single and double arrows in Fig. 3. Another exothermic peak about 750 K is probably due to the deflection of base line, since there is no microstructure change in the specimen annealed at 773 K for 3.6 ks as described later. Before the characterization of microstructure changes corresponding to each peak in the DSC curve, Vickers hardness and bending ductility of the ribbons annealed from 773 to 973 K for 3.6 to 360 ks are measured as shown in Fig. 4. There are four regions denoted as I, II, III and IV with respect to the hardness and the ductility. The specimens in the region I have high hardness as well as that of as-melt spun ribbon, while the ductility is diminished. The hardness increases and the ductility further decreases of the specimens in the region II. The hardness decreases with increasing the annealing temperatures and periods, while the ductility is still poor, in the region III. In the region IV the hardness decreases about 260 Hv and the ductility recovers.

![Figure 1. SEM image of the micro-cantilever specimen.](image-url)
To investigate the origin of each DSC peak and change of mechanical properties by annealing, TEM observations for the typical specimens from the four regions are carried out in the next section.

### 3.2. Microstructural changes with heat treatment

Figures 5 (a) and (b) show the bright field image and the corresponding electron diffraction pattern of the ribbon annealed at 773 K for 3.6 ks, that is, the specimen in the region I. Although some fine contrasts probably due to the formation of nanocrystalline clusters are observed in Fig. 5 (a), the halo ring of Fig. 5 (b) indicates that the microstructure mainly consists of the amorphous phase with fine crystalline cluster like contrast. Therefore, it is concluded that an endothermic peak about 720 K in the Fig. 3 is considered to be a glass transition and no obvious crystallization occurs in the region I. However, the ductility decreases remarkably, which is probably attributable to the reduction of free volume in the amorphous matrix by the nanocrystalline clusters.

Figure 6 (a) shows the typical bright field image of the ribbon annealed at 823 K for 36 ks, which corresponds to the specimen in the region II. There are two kinds of microstructures typically denoted

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**Figure 2.** (a) Bright field image and (b) corresponding electron diffraction pattern of as-melt spun Nb$_{20}$Ti$_{40}$Ni$_{40}$ ribbon.

**Figure 3.** DSC heating curve of as-melt spun Nb$_{20}$Ti$_{40}$Ni$_{40}$ ribbon.

**Figure 4.** Hardness and ductility of Nb$_{20}$Ti$_{40}$Ni$_{40}$ melt spun ribbon annealed at various conditions.

**Figure 5.** (a) Bright field image and (b) corresponding electron diffraction pattern of Nb$_{20}$Ti$_{40}$Ni$_{40}$ melt spun ribbon annealed at 773 K for 3.6 ks.
by B and C in the micrograph. The electron diffraction pattern in Fig. 6 (b) taken from the area B in (a) consists of halo ring and two sets of Debye rings. The outer ring corresponds to the interplanar spacing of \{110\}_{B2} of TiNi phase. The inner ring is identified to be the interplanar spacing of \{110\}_{bcc} of Nb solid solution phase, although the intensity is very low and its distribution is not uniform in comparison to the outer ring. Therefore, the area B consists of mainly nanocrystalline TiNi phase with random orientation and small amount of Nb phase in the amorphous matrix. The pattern in Fig. 6 (c) taken from colony-like morphology in the area C in (a) consists of two sets of reflections of the [001] \textit{B2} and [001] \textit{bcc} zone axes of the TiNi and Nb solid solution phases, respectively. This indicates that these two phases are in the cube-on-cube orientation relationship as reported previously [4]. Although we do not reproduce the micrograph, the dark field image taken by using 010 \textit{B2} reflection reveals that the colony-like region consists of fine grains of TiNi and Nb solid solution phases about 50 nm or less in diameter. Therefore, the colony-like morphology is expressed as the duplex structure hereinafter. In order to clarify the detailed microstructures of the area B in Fig. 6 (a) on the atomic level, HRTEM observations and EDX analyses are performed. The two-dimensional lattice image is presented in Fig. 6 (d). We can observe the crystallite of several tens nm in diameter as bounded by the dotted line in the amorphous matrix. Although we do not reproduce the corresponding FFT image, the foil normal of the crystallite is confirmed to be [111] \textit{B2} of TiNi phase. The estimated interplanar spacing of \{110\}_{B2} from the micrograph is consistent with the calculated one from the lattice constant described above. The results of TEM-EDX analyses reveal that the chemical compositions of the TiNi crystallite and the amorphous matrix in Fig. 6 (d) are estimated to be 43.0 at% Ti-51.4 at% Ni-5.6 at% Nb and 33.8 at% Ti-47.9 at% Ni-18.3 at% Nb, respectively. The composition of the TiNi phase agrees essentially with that of the bulk alloy [4]. In the amorphous matrix the concentration of the Ti is lower than that of the nominal eutectic composition. Since it is reported that the Ti segregates in the bcc-Nb solid solution, the Ti is probably consumed by the formation of the duplex structure.

Figure 7 (a) shows the TEM micrographs of the melt spun ribbon annealed at 923 K for 36 ks, that is, the specimen in the region III. From the corresponding electron diffraction pattern in Fig. 7 (b) the amorphous phase completely disappears and the duplex structure with the cube-on-cube relationship is developed in the whole area. The dark field image in Fig. 7 (c) taken by using (010) \textit{TiNi} reflections in (b) suggests that the fine grains of the TiNi and the Nb solid solution phases align alternately. It is quite interesting that the specimens in the regions II and III is quite brittle albeit those have nanocrystalline structure. The origin of the brittleness is not clarified at present.
Figure 8 shows the TEM micrographs of the melt spun ribbon annealed at 973 K for 360 ks, which corresponds to the region IV in Fig. 4. Although the coarsening of both phases in the duplex structure occurs, these are still in the cube-on-cube relationship. The average grain size is about 150 nm in diameter for both phases. The recovery of the ductility is attributable to this coarsening.

On the basis of these observations, it is considered the crystallization and microstructure changes in the melt spun ribbon as follows. There are two exothermic peaks after the glass transition in the DSC heating curve in Fig. 3. From the microstructures presented in Figs. 6 and 7, the TiNi phase initially crystallize and then the duplex structure develops with the cube-on-cube orientation in places. The former phenomenon corresponds to the first exothermic peak in the DSC curve. The volume fraction of the duplex structure increases as increasing the annealing periods in the region II. This fact supports that the initial crystallized product is the TiNi phase. Subsequently, bcc-(Nb, Ti) solid solution neighbouring at the TiNi phase crystallizes with the cube-on-cube orientation relationship and then the duplex structure forms. Therefore, the second exothermic peak in the DSC curve corresponds to the crystallization of the bcc-Nb solid solution phase.

3.3. Micromechanical characterizations

The micromechanical test is carried out for the four specimens as presented in Figs. 9 and 10. The load-displacement curve of as-melt spun ribbon increases lineally up to 3 mN and shows slight
ductility. The fracture load is about 4 mN. Vein pattern is observed in the fracture surface as shown in Fig. 10 (a). The melt spun ribbon annealed at 773 K for 3.6 ks has no ductility and its fracture load is about 2 mN. The fracture surface is flat and smooth without Vein pattern as recognized in Fig. 10 (b). There are serrations in the load-displacement curve of the ribbon annealed at 823 K for 36 ks. The flat fracture surface is mainly observed and the irregular one is also seen in places as presented in Fig. 10 (c). The latter is probably responsible for the serrations. The specimen annealed at 973 K for 360 ks has sound ductility and no fracture occurs within the present experimental condition as shown in Figs. 9 and 10 (d). The estimated fracture toughness value ($K_Q$) of each specimen is listed in Table 1. The $K_Q$ of as-melt spun ribbon is 5.30 MPam$^{1/2}$. In contrast, the $K_Q$ of the ribbons annealed at 773 K for 3.6 ks and 823 K for 36 ks decreases to 2.84 and 2.36 MPam$^{1/2}$, respectively. With annealing above 973 K fracture toughness increases again. Further details of the relation between microstructures and mechanical properties are described elsewhere [6].

4. Conclusions

The microstructural and mechanical characterizations of the rapidly solidified Nb$_{20}$Ti$_{40}$Ni$_{40}$ (at%) hydrogen permeation alloy have been performed. There are two exothermic peaks about 875 and 915 K in DSC heating curve, which corresponds to the crystallization of B2-TiNi and bcc-Nb solid solution phases, respectively. The specimens annealed from 798 to 923 K are quite brittle, although those consist of fine equiaxed grains less than 50 nm. With annealing above 948 K for prolonged periods the grain size is increased to about over 150 nm and the hardness is decreased about 260 Hv or less. Consequently, the ductility and the fracture toughness are recovered. These results suggest that the high temperature annealing is required for the application to the hydrogen permeation membrane.

| Heat-treatment condition | Fracture toughness $K_Q$ (MPam$^{1/2}$) | Vickers hardness (Hv) |
|--------------------------|----------------------------------------|-----------------------|
| As-spun                  | 5.30                                   | 740                   |
| 773 K for 3.6 ks         | 2.84                                   | 740                   |
| 823 K for 36 ks          | 2.36                                   | 760                   |
| 973 K for 360 ks         | No fracture                            | 261                   |

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