Thermal Stability and Mechanical Properties of Glassy and Amorphous Ni–Nb–Zr Alloys Produced by Rapid Solidification

Hisamichi Kimura¹, Akihisa Inoue¹, Shin-ichi Yamaura¹, Kenichiro Sasamori¹,
Motonori Nishida², Yoichiro Shinpo² and Hitoshi Okouchi

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Fukuda Metal Foil & Powder Co., LTD, Kyoto 607-8305, Japan

Rapidly solidified Ni–Nb–Zr alloys in a ribbon form with a thickness of about 20 μm were prepared by a single roller melt-spinning technique. Amorphous alloys were formed in the composition range of 20 to 75 at%Ni, 0 to 60 at%Nb and 0 to 80 at%Zr. Furthermore, glassy alloys were also synthesized in the range of 50 to 70 at%Ni, 5 to 35 at%Nb and 5 to 45 at%Zr. The maximum temperature interval of the supercooled liquid region was 51 K for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy. The tensile fracture strength and Vickers hardness of the glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy are 2160 MPa and 700, respectively. Wide ribbons with a width of 50 mm of amorphous $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30}$ and glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloys were produced at a circumferential velocity of the copper roller of 20 m/s.

(Received February 20, 2003; Accepted April 17, 2003)

Keywords: glassy, amorphous, Ni–Nb–Zr alloy, mechanical property

1. Introduction

Rapidly solidified Nb–Ni¹⁾ and Ni–Zr^{2,3)} alloys are known to have an amorphous phase in their wide composition ranges. Aoki *et al.* have examined hydrogen absorption properties of rapidly solidified Ni–Zr alloys, in addition to the formation range of an amorphous phase.³⁾ It has also been reported that the amorphous Ni–Zr alloys exhibit useful properties such as high efficient catalytic characteristics for hydrogenation of carbon monoxide^{4,5)} and hydrogenation of benzene,⁶⁾ and hydrogen permeable membrane.⁷⁾ Recently, Inoue *et al.* have found that Ni-based bulk glassy alloys with a large supercooled liquid region before crystallization are formed in the Ni–Nb–Ti–Zr system.⁸⁾ It is well known that Nb and Zr metals exhibit high hydrogen permeability.⁹⁾ It is therefore expected that Ni–Nb–Zr alloys with glassy or amorphous phase are formed in a wide composition range by rapid solidification and exhibit high hydrogen permeability. In this paper we have investigated the formation ranges of glassy and amorphous phases in the rapidly solidified Ni–Nb–Zr alloys and their thermal stability and mechanical properties.

2. Experimental Procedure

Ternary Ni–Nb–Zr alloy ingots were prepared by arc melting mixtures of pure Ni, Nb and Zr metals with desired compositions in a purified argon atmosphere. Ribbons of about 20, 25 and 40 μm in thickness and about 1.5 and 50 mm in width were prepared by a single roller melt-spinning technique in an argon atmosphere. The structure of the melt-spun ribbons was examined by X-ray diffractometry (Cu-K α , 35 kV, 15 mA). Thermal stability such as glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region ($\Delta T_x = T_x - T_g$) and the crystallization process was examined by at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). The tensile fracture strength was measured at a strain rate of $8 \times 10^{-4} \text{ s}^{-1}$ with an Instron-type testing machine. The hardness was also measured by a Vickers microhardness tester with a load of 25 g.

3. Results

We examined the formation tendency of an amorphous phase in rapidly solidified Ni–Nb–Zr alloys where Zr was added to the well-known amorphous $\text{Ni}_{50}\text{Nb}_{50}$ alloy. Figure 1 shows X-ray diffraction patterns of the rapidly solidified $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30$, and 40 at%) alloys. Only broad diffraction peaks are seen for all the alloys, indicating the formation of a single amorphous phase. It is recognized that the diffraction angle (2θ) of the main broad peak shifts to a lower angle side with an increase of Zr concentration because of the larger atomic size of Zr. Figure 2 shows the composition range in which amorphous Ni–Nb–Zr alloys are formed by rapid solidification, together with the previous data of Ni–Zr binary alloys.³⁾ The amorphous phase is formed in a wide composition range of 20 to 75 at%Ni, 0 to 60 at%Nb and 0 to 80 at%Zr. Figure 3 shows differential scanning calorimetric (DSC) curves of the amorphous $\text{Ni}_{60}\text{Nb}_{40-x}\text{Zr}_x$ ($x = 10, 20$, and 30 at%) alloys. Here T_g and T_x denote the glass transition temperature and crystallization temperature, respectively. The DSC data indicate clearly that

Fig. 1 X-ray diffraction patterns of rapidly solidified $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30, 40$ at%) alloys.

Fig. 2 Composition dependence of structure in rapidly solidified Ni-Nb-Zr alloys.: (○) amorphous; (◐) amorphous and crystalline; (●) crystalline. The single open circles represent the formation of amorphous alloys with good bending ductility.

Fig. 4 Composition ranges of amorphous and glassy phases in rapidly solidified Ni-Nb-Zr alloys.: (○) amorphous; (◐) glassy; (◐) amorphous and crystalline; (●) crystalline. The double open circles represent the formation of glassy alloys.

Fig. 3 Differential scanning calorimetric (DSC) curves of rapidly solidified $\text{Ni}_{60}\text{Nb}_{40-x}\text{Zr}_x$ ($x = 10, 20, 30$ at%) alloys.

these Ni-based alloys have a glassy structure. The supercooled liquid region ($\Delta T_x = T_x - T_g$) is measured as 40 K at $x = 10$, 51 K at $x = 20$ and 24 K at $x = 30$. Figure 4 summarizes the composition range of the glassy-type alloys. The glassy alloys are formed in the composition range of 50 to 70 at%Ni, 5 to 35 at%Nb and 5 to 45 at%Zr. Figure 5 shows the composition dependence of T_x and ΔT_x of the glassy Ni-Nb-Zr alloys. T_x and ΔT_x are in the ranges from

Fig. 5 Composition dependence of crystallization temperature (T_x) and supercooled liquid region $\Delta T_x (= T_x - T_g)$ of glassy Ni-Nb-Zr alloys.

Fig. 6 Crystallization temperature (T_x), Vickers hardness (H_v) and fracture strength (σ_f) as a function of Zr content for amorphous $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30, 40$ at%) alloys.

800 to 910 K and 20 to 55 K, respectively. The highest T_x is 910 K for the $\text{Ni}_{60}\text{Nb}_{30}\text{Zr}_{10}$ alloy while the largest ΔT_x is 51 K for the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy. Figure 6 shows the crystallization temperature (T_x), Vickers hardness (H_v), and tensile fracture strength (σ_f) as a function of Zr content for the amorphous $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30$, and 40 at%) alloys. The T_x , H_v and σ_f increase almost linearly with decreasing Zr content and the highest values of 856 K for T_x , 760 for H_v and 2300 MPa for σ_f are obtained for the 10%Zr-containing alloy. Figure 7 shows the composition dependence of H_v and σ_f of the glassy Ni–Nb–Zr alloys. The σ_f is in the range from 1900 to 2400 MPa and H_v lies in the range from 600 to 800. There is a tendency for H_v and σ_f to increase with increasing Nb content. The highest values of H_v and σ_f are 760 for $\text{Ni}_{60}\text{Nb}_{30}\text{Zr}_{10}$ and $\text{Ni}_{50}\text{Nb}_{20}\text{Zr}_{30}$ alloys and 2340 MPa for $\text{Ni}_{60}\text{Nb}_{30}\text{Zr}_{10}$ alloy, respectively.

4. Discussion

Inoue *et al.* have produced a great number of bulk glassy alloys and found that the bulk glassy alloys have the following three component rules:¹⁰⁾ 1) multi-component system consisting of more than three elements, 2) significantly different atomic size ratios above about 12% among the main constituent elements, and 3) negative mixing enthalpy among their elements. Table 1 summarizes atomic size ratios¹¹⁾ and mixing enthalpies¹²⁾ of the constituent elements in Ni–Nb–Zr system. The glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy exhibits the largest supercooled liquid region of 51 K.

Fig. 7 Vickers hardness (H_v) and fracture strength (σ_f) of glassy Ni–Nb–Zr alloys.

Table 1 Atomic size ratios [small atomic radius (r)/large atomic radius (R)] and mixing enthalpy (ΔH) among the constituent elements in Ni–Nb–Zr system.

Atomic pair	Atomic size ratio r/R	Mixing enthalpy $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$
Ni–Nb	0.87 ($r_{\text{Ni}}/R_{\text{Nb}}$)	–30
Ni–Zr	0.77 ($r_{\text{Ni}}/R_{\text{Zr}}$)	–49
Nb–Zr	0.88 ($r_{\text{Nb}}/R_{\text{Zr}}$)	4

Atomic radius, Ni: 0.125 nm, Nb: 0.143 nm, Zr: 0.162 nm

As seen in Table 1, the above second rule is satisfied between the elements in the Ni–Nb–Zr alloys. On the other hand, mixing enthalpy between the pairs of Ni–Nb and Ni–Zr is negative, but that between Nb–Zr is positive. Recently, Takeuchi and Inoue¹³⁾ have carried out the thermodynamical calculations of the mixing enthalpy for 6450 alloys in 351 ternary amorphous systems on the basis of the extended

Fig. 8 X-ray diffraction patterns of rapidly solidified $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30, 40$ at%) alloys produced at a circumferential velocity of 20 m/s.

regular solution model.¹⁴⁾ Their results show that the chemical mixing enthalpies of most of them are able to be negative, even in the alloys in which mixing enthalpies between two pairs of constituent elements are negative and that between one pair is positive. According to their model, the chemical mixing enthalpy is estimated to be $-37.3 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy, supporting the above third rule.

When the glassy Ni–Nb–Zr alloys with high hydrogen permeability are used as a hydrogen permeable membrane, the glassy alloys must have a wide ribbon form. It is known that the wide ribbons can be prepared at lower cooling rate (low circumferential velocity of the copper roller) in a single roller melt-spinning technique. Figure 8 shows the X-ray diffraction patterns of the melt-spun $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ alloy ribbons with a width of about 1.5 mm and a thickness of about $40 \mu\text{m}$ which were prepared at the circumferential velocity of 20 m/s. When the Zr content exceeds 20 at%, broad diffraction peaks due to an amorphous phase are seen. We further prepared amorphous $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30}$ (a) and glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ (b) alloy ribbons of 50 mm in width and $25 \mu\text{m}$ in thickness as shown in Fig. 9. Figure 10 shows X-ray diffraction patterns of both the wide ribbons. It is seen that they have amorphous and glassy phases. The 50 mm for the ribbons is the maximum value which can be produced by using the present single roller equipment in our laboratory. The formation of wide amorphous and glassy alloy ribbons also indicates that the Ni–Nb–Zr alloys liquids have good cast ability in the melt-spinning process.

5. Summary

We examined the structure, thermal stability and mechanical properties of the rapidly solidified Ni–Nb–Zr alloys. The results obtained are summarized as follows:

- (1) Amorphous alloys in Ni–Nb–Zr system were formed in a wide composition range of 20 to 75 at%Ni, 0 to 60 at%Nb and 0 to 80 at%Zr.
- (2) The T_x , H_v and σ_f of the amorphous $(\text{Ni}_{0.5}\text{Nb}_{0.5})_{100-x}\text{Zr}_x$ ($x = 10, 20, 30$, and 40 at%) alloys are in the range from 770 to 870 K, 540 to 760 and 1530

Fig. 9 Outer shape and surface morphology of amorphous $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30}$ (a) and glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ (b) alloy ribbons with a width of 50 mm and a thickness of $25 \mu\text{m}$.

Fig. 10 X-ray diffraction patterns of amorphous $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30}$ (a) and glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ (b) alloy ribbons with a width of 50 mm and a thickness of about $25 \mu\text{m}$.

to 2300 MPa, respectively. There is a tendency for T_x , H_v and σ_f to increase with increasing Nb content.

- (3) Glassy alloys in Ni–Nb–Zr system were also formed in the composition range of 50 to 70 at%Ni, 5 to 35 at%Nb and 5 to 45 at%Zr. The largest value of the supercooled liquid region was 51 K for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$.
- (4) The σ_f and H_v of the glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy with the largest supercooled liquid region are 2160 MPa and 700, respectively.
- (5) Wide ribbons of 50 mm in width were prepared for the amorphous $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30}$ and glassy $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloys at the circumferential velocity of 20 m/s.

Acknowledgements

The authors wish to express their sincere thanks to Dr. A. Takeuchi, Institute for Materials Research, Tohoku University for his useful discussions.

REFERENCES

- 1) R. C. Rhul, B. C. Giessen, M. Cohen and N. J. Grant: *Acta Metall.* **15** (1967) 1693.
- 2) K. H. J. Buschow and N. M. Beekmans: *Phys. Rev. B* **19** (1979) 3843.
- 3) K. Aoki, A. Horata and T. Masumoto: *Proc. 4th Int. Conf. on Rapidly Quenched Metals* (1981) 1649.
- 4) Y. Shimogaki, H. Komiyama, H. Inoue, T. Masumoto and H. Kimura: *J. of Chem. Soc. Jap.* **58** (1985) 661.
- 5) Y. Shimogaki, H. Komiyama, H. Inoue, T. Masumoto and H. Kimura: *J. of Chem. Eng. Jap.* **21** (1988) 293.
- 6) T. Takahashi, S. Higashi, T. Kai, H. Kimura and T. Masumoto: *Catalysis Letters* **26** (1994) 401.
- 7) S. Hara, K. Sasaki, N. Itoh, H. M. Kimura, K. Asami and A. Inoue: *J. Membrane Sci.* **164** (2000) 289.
- 8) A. Inoue, W. Zhang and T. Zhang: *Mater. Trans.* **43** (2002) 1952.
- 9) T. Seki and I. Yasuda: *Distributed Energy Systems & Fuel Cell Technologies*, ed. by K. Hirata, (CMC Publishing Co., Ltd., Tokyo, 2001) p. 168.
- 10) A. Inoue: *Mater. Trans., JIM* **36** (1995) 866.
- 11) *Metals Databook*, ed. by Japan Inst. Metals, (Maruzen, Tokyo, 1984) p. 8.
- 12) F. R. Niessen: *Cohesion in Metals*, (Elsevier Science Publishers, B. V., Amsterdam, 1988).
- 13) A. Takeuchi and A. Inoue: *Mater. Trans., JIM* **41** (2000) 1372.
- 14) F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen: *Cohesion in Metals (Cohesion and Structure, Vol. 1*, ed. By F. R. de Boer and D. G. Pettifor), Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1988).