A Study on the Development of Ni-Based Alloys with Wide Supercooled Liquid Region

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Ni-based amorphous alloys with wide supercooled liquid region (ΔT_x) have been developed through alloy design based upon the empirical rules for high glass forming alloys. The amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ alloy shows glass transition temperature of 794 K, onset temperature of the first exotherm (T_{x1}) of 808 K and supercooled liquid range ($\Delta T_x = T_{x1} - T_g$) of 14 K, while the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy shows T_g of 830 K, T_{x1} of 876 K and ΔT_x of 46 K. The amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys crystallize through two step reactions. First, primary crystallization of cubic NiTi(Zr) phase occurs from the amorphous matrix and then the NiTi(Zr) and remaining amorphous phases transforms into a mixture of cubic NiTi(Zr) and orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ phase for the ternary alloy and into a mixture of the cubic NiTi(Zr), orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ and an unidentified phase containing Si for the quaternary alloy. Partial replacement of Ti by Si improves glass forming ability. A bulk amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ rod with 2 mm in diameter is fabricated by injection casting.

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1. Introduction

Alloys with large glass forming ability (GFA) have recently been developed in a number of multi-component alloy systems.¹⁻³⁾ The bulk amorphous alloys exhibit many unique properties associated with the atomic structure.⁴⁾ These unique properties that can be rarely found in crystalline materials are attractive for the practical applications as new classes of structural as well as functional materials.

Zr-based alloys have high glass forming ability leading to the development of commercial Zr-based bulk amorphous alloy, Vitaloy TM, for sporting goods. However, due to the limited Zr resources, development of bulk amorphous alloys containing common metals as the major constituent is strongly desired for the extensive practical applications of bulk amorphous alloys. Since the late of 1980s, bulk amorphous alloys of common metals have been developed mainly in the Ni-based,⁵⁾ Ti-based,⁶⁾ and Fe-based⁷⁾ alloy systems. In the Ni-Nb-Cr-Mo-P-B system, bulk amorphous alloy rods with diameter of 1 mm have been fabricated by an injection casting method. The amorphous alloys exhibit high strength (~ 2.6 GPa) and high corrosion resistance.⁵⁾ However, since large amounts of P (~ 15 at%) that has a high vapor pressure should be added to enhance the GFA, fabrication process of the Ni-based bulk amorphous alloys is complicated. Therefore, much effort has been made to develop a new class of Ni-based amorphous alloy having high GFA that can be produced by a conventional casting process.

Recently Ni-Ti-Zr based multi-component alloys containing more than 55%Ni have been developed through a systematic alloy design.⁸⁻¹⁰⁾ Based on the empirical rules for high glass forming alloys,¹¹⁾ the ternary alloys in the Ni-Ti-Zr system are expected to have high GFA since the atomic size difference between Ti (or Zr) and Ni is large ($> 18\%$). In addition, interaction between Ni and Ti (or Zr) is very strong in the liquid state, forming a deep eutectic in the binary phase diagram Ni-Ti (or Ni-Zr).¹²⁾ Indeed, amorphous phase for-

mation during rapid solidification has been reported near eutectic compositions in the binary systems of Ni-Zr and Ni-Ti.^{13,14)} Therefore, the alloy system Ni-Ti-Zr well meets the empirical rules. In order to enhance the GFA, a metalloid Si is selected since the metallic elements Ni, Ti, and Zr have large heats of mixing with Si.¹²⁾

In this study we report the glass forming ability and crystallization behaviors of amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys prepared by melt spinning and injection casting techniques. Crystallization behaviors of the alloys were studied by differential scanning calorimetry (DSC) experiments. Structural change during annealing was characterized by using X-ray diffractometry (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX).

2. Experimental Procedure

Alloys of nominal composition $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ were prepared by arc melting pure metals Ni(99.99%), Zr(99.9%), Ti(99.97%) and Si(99.999%), under an argon atmosphere. Amorphous alloy specimens were produced by melt-spinning and injection casting methods under an Ar atmosphere. For melt-spinning, the alloys were remelted in quartz tubes, followed by ejecting with an over pressure of 35 kPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons exhibit thickness of about 30 μm and width of about 2 mm. Fully amorphous rod specimens of 2 mm in diameter were fabricated by injection casting. The $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy was remelted in quartz tubes, followed by casting into a 2 mm diameter cylindrical cavity of a Cu mold. Heat treatment of the amorphous specimens was performed under an Ar atmosphere at several different conditions depending on alloys. Structural change during the heat treatment was studied by using X-ray diffractometry with monochromatic Cu $K\alpha$ radiation (Rigaku, RINT2200) and transmission electron microscopy (JEOL, 2010F). Thin foil specimens for transmis-

sion electron microscopy were prepared by ion beam milling method. Crystallization behavior of the amorphous alloys was studied by using differential scanning calorimetry (Perkin Elmer, DSC 7). Exotherms and endotherms were monitored in the DSC during isothermal annealing in the temperature range of 840–849 K and during continuous heating up to 983 K at a heating rate of 0.33 K/s.

3. Results

Figure 1 shows typical DSC spectra obtained during continuous heating at a heating rate of 0.33 K/s for the melt-spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys and for the injection cast $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy. Also DSC trace of the annealed $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys at 843 K for 1.8 ks is included for comparison. The DSC trace from the melt-spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ alloy exhibits an endothermic event corresponding to glass transition to supercooled liquid, and two overlapped exothermic peaks corresponding to crystallization of the supercooled liquid. The alloy shows glass transition temperature (T_g) of 794 K, onset temperature of the first exotherm (T_{x1}) of 808 K and integrated heat of crystallization of 65.3 J/g. The supercooled liquid range, defined as $\Delta T_x = T_{x1} - T_g$, is about 14 K for the alloy. Amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy exhibits significantly different thermal behavior from the ternary $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ alloy. The DSC trace for the melt spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy exhibits a glass transition at 830 K, followed by two exothermic peaks with onset temperatures and exothermic heats of 876 K and 35.1 J/g for the first strong exotherm and 927 K and 10.6 J/g for the second weak exotherm, respectively. Injection cast $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy shows almost same crystallization behavior as the ribbon specimen with glass transition temperature of 831 K and two crystallization peak temperatures of 876 and 941 K. The integrated heat of the exotherms for the bulk specimen is almost same as that in the melt-spun specimen, indicating fully amorphous structure was obtained in the injection cast specimen. ΔT_x of the $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy is about 46 K, which is significantly larger than that of the ternary $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ al-

loy. The DSC trace for the $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy, annealed for 1800 s at 843 K, shows only one weak exothermic peak with peak temperature of 941 K due to the occurrence of partial crystallization of the amorphous phase during the annealing treatment. The peak position and integrated heat of the exotherm are almost identical to those corresponding to the second exotherm of the melt-spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy. The results clearly indicate that phase transformation corresponding to the first exothermic reaction took place during the annealing treatment.

In order to identify the crystallization products for each exothermic reaction, annealing treatments were performed under two conditions: i) to complete the first exothermic reaction; and ii) to complete the final exothermic reaction. Figure 2 shows typical XRD traces obtained from the melt-spun and annealed $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimens. The as-spun ribbon specimen shows a broad halo pattern, with $\Delta 2\theta$ range of 17° , characteristic of the amorphous structure. The specimen annealed for 3.6 ks at 843 K, corresponding to the first exothermic reaction, shows sharp diffraction peaks superimposed on a weak halo pattern, indicating partial crystallization occurs. The diffraction peaks could be analyzed into an ordered bcc structure with a lattice constant of $a = 0.301$ nm, which is larger than that of NiTi ($a = 0.299$ nm) due to the replacement of Ti by Zr. Therefore it can be concluded that the first crystallization exotherm of $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy corresponds to primary crystallization of amorphous phase into a cubic NiTi(Zr) phase. The XRD trace from the specimen annealed for 300 s at 983 K, shows several sharp diffraction peaks. All the diffraction peaks could be analyzed into a mixture of orthorhombic $\text{Ni}_{10}\text{Zr}_7$ with lattice constants $a = 0.921$ nm, $b = 0.916$ nm, $c = 1.239$ nm and the cubic NiTi(Zr) phases. The diffraction peaks corresponding to $\text{Ni}_{10}\text{Zr}_7$ are in good agreement with the calculated diffraction pattern by Rietveld method with crystallographic data of $\text{Ni}_{10}\text{Zr}_7$.

Figures 3(a)–(c) show, respectively, a typical bright field TEM image, a corresponding selected area diffraction pattern (SADP) and a dark field image taken from the strong ring reflection of the $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimen annealed for

Fig. 1 Typical DSC spectra obtained during continuous heating at a heating rate of 0.33 K/s: (a) as-spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$; (b) as-spun $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$; (c) injection cast $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy and (d) annealed $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys at 843 K for 1.8 ks.

Fig. 2 Typical XRD traces obtained from the as-spun and annealed $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimens: (a) as-spun; (b) annealed for 3.6 ks at 843 K; and (c) annealed 300 s at 983 K.

Fig. 3 Transmission electron micrographs taken from $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimen annealed for 3.6 ks at 843 K: (a) bright field TEM image; (b) corresponding SADP and (c) dark field image taken from the strong ring reflection.

3.6 ks at 843 K. The SADP consists of several ring patterns superimposed on a diffuse halo patterns, indicating a mixture of crystalline and residual amorphous phases. All the ring patterns could be analyzed into the ordered bcc structure, which is in agreement with the XRD results shown in Fig. 2. The annealed alloy exhibits a homogeneous distribution of the cubic $\text{NiTi}(\text{Zr})$ phase with a typical size of about 40 nm and amorphous phase locating at grain boundary region, which can be inferred from the network image in the dark field image due to the illumination from amorphous phase at grain boundary region.

Figures 4(a)–(c) show, respectively, typical bright field TEM images with two different magnifications and an SADP with schematic analysis obtained from the $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimen annealed for 3.6 ks at 873 K. The microstructure consisted of equiaxed grains with typical size of about 80 nm and fine particles with typical size of about 10 nm at grain boundaries. Electron diffraction works confirm that the equiaxed grains are mostly orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ phase. Occasionally orientation relationship between the orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ phase and the cubic $\text{NiTi}(\text{Zr})$ phase are observed as shown in Fig. 4(c). The particles at grain boundaries were too small to be identified by TEM analysis. However nanoprobe EDX experiments show that the solubilities of Si in the $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ and $\text{NiTi}(\text{Zr})$ phases are small, while the small particles at boundaries contain high Si content, even though quantitative analysis of the composition is

difficult due to the effect of surrounding region. Also it can be noticed that the small particles are pinning grain boundaries preventing grain growth as can be seen clearly in Fig. 4(b).

From the DSC, XRD and TEM experiments, it can be summarized that the first crystallization exotherm of $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy corresponds to the primary crystallization of amorphous phase into a cubic $\text{NiTi}(\text{Zr})$ phase and the second exothermic reaction corresponds to the formation of orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ and unidentified Si containing phase from the $\text{NiTi}(\text{Zr})$ and residual amorphous phases. Also it should be noted that the temperature difference between two peaks is about 65 K for the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys, which is indicating that the thermal stability of the residual amorphous phase is high.

4. Discussion

The DSC and XRD results indicate that the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys crystallize through two reactions. First, primary crystallization of cubic $\text{NiTi}(\text{Zr})$ phase occurs from the amorphous matrix and then the $\text{NiTi}(\text{Zr})$ and remaining amorphous phases transforms into a mixture of cubic $\text{NiTi}(\text{Zr})$ and orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ phase for the ternary alloy and into a mixture of the cubic $\text{NiTi}(\text{Zr})$, orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ and an unidentified phase containing Si for the quaternary alloy.

Even though the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and

Fig. 4 Transmission electron micrographs taken from $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ ribbon specimen annealed for 3.6 ks at 873 K: (a) bright field TEM image at low magnification; (b) bright field TEM image at high magnification and (c) an SADP with schematic analysis.

$\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ phases show basically same crystallization sequences, the quaternary alloy exhibits much better thermal stability than the ternary alloy as shown in Fig. 1. The amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy exhibits higher T_g , T_{x1} and larger ΔT_{x1} than corresponding values of the $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ alloy by 36, 68 and 32 K, respectively. The increase in glass transition and crystallization temperatures by the partial replacement of Ti by Si can be understood by large interaction energy between Ti-Si and Zr-Si.¹²⁾ The atomic size of Si is not much different from that of the main constituent Ni. Therefore atomic size effect on the glass forming ability is not expected to be high. The mixing enthalpies of Ni-Si, Ti-Si and Zr-Si atomic pairs are estimated to be -23, -59 and -67 kJ/mol, respectively.¹²⁾ The strong interaction Ti-Si and Zr-Si atomic pairs may contribute to stabilize the amorphous phase. Due to the formation of the strong atomic pairs, atomic rearrangement for glass transition and for nucleation and growth of crystalline phase in the supercooled liquid phase is kinetically retarded and thus, the ΔT_x is enlarged. The more significant increase of crystallization temperature than the glass transition temperature with Si content is partially attributed to small solubility of Si in the cubic NiTi(Zr) phase. For the nucleation and growth of the cubic phase partitioning of Si at interface is necessary.

The formation of homogeneous nanocrystalline cubic

NiTi(Zr) particles with amorphous phase at grain boundary region in annealed $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy may be explained by nanocrystalline phase formation mechanism in Al-Ni-Y alloys.¹⁵⁾ *i.e.*, (1) primary crystallization involving solute partitioning during crystallization; (2) a high thermal stability of the remaining amorphous phase; and (3) suppression of subsequent growth reaction. As mentioned in previous section, the thermal stability of the residual amorphous phase remaining after the first exothermic reaction is high, which can be inferred from the large temperature difference between two exotherms shown in Fig. 1.

Development of the Ni-based bulk amorphous alloys having a large supercooled liquid region is of scientific and technological importance. Since the alloys do not contain any high vapor pressure element such as P, melting process can be simplified using the mixture of pure metals and Si. The maximum diameter of the fully amorphous rod that can be prepared directly from liquid state is extended up to 2 mm. Moreover, by heating the amorphous alloy to a temperature within the large supercooled liquid region in which the amorphous alloy behaves as a viscous fluid, the material can be shaped by injection molding just as in the case of plastics. Also, through warm processing in the temperature range of the supercooled liquid region, amorphous materials of a large scale can be effectively produced, leading to high potentials

for a large variety of practical applications.

5. Conclusion

The amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ alloy shows glass transition temperature of 794 K, onset temperature of the first exotherm (T_{x1}) of 808 K and supercooled liquid range ($\Delta T_x = T_{x1} - T_g$) of 14 K, while the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloy shows T_g of 830 K, T_{x1} of 876 K and ΔT_x of 46 K. The amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{21}$ and $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ alloys crystallize through two step reactions. First, primary crystallization of cubic $\text{NiTi}(\text{Zr})$ phase occurs from the amorphous matrix and then the $\text{NiTi}(\text{Zr})$ and remaining amorphous phases transforms into a mixture of cubic $\text{NiTi}(\text{Zr})$ and orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ phase for the ternary alloy and into a mixture of the cubic $\text{NiTi}(\text{Zr})$, orthorhombic $\text{Ni}_{10}(\text{Zr}, \text{Ti})_7$ and an unidentified phase containing Si for the quaternary alloy. Partial replacement of Ti by Si improves the glass forming ability. Bulk amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_5$ rod with 2 mm in diameter was fabricated by injection casting.

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REFERENCES

- 1) A. Peker and W. L. Johnson: Appl. Phys. Lett. **63** (1993) 2342–2344.
- 2) Y. He, R. B. Schwarz and J.I. Archuleta: Appl. Phys. Lett. **69** (1996) 1861–1863.
- 3) A. Inoue, T. Nakamura, N. Nishiyama and T. Masumoto: Mater. Trans., JIM **33** (1992) 937–945.
- 4) A. Inoue: Acta Metall. Mater. **48** (2000) 279–306.
- 5) X. Wang, I. Yoshii, A. Inoue, Y. H. Kim and I. B. Kim: Mater. Trans., JIM **40** (1999) 1130–1136.
- 6) T. Zhang and A. Inoue: Mater. Trans., JIM **40** (1999) 301–306.
- 7) A. Inoue, T. Zhang, T. Itoi and A. Takeuchi: Mater. Trans., JIM **38** (1997) 359–362.
- 8) T. G. Park, S. Yi and D. H. Kim: Scripta. Mater. **43** (2000) 109–114.
- 9) S. Yi, T. G. Park and D. H. Kim: J. Mater. Res. **15** (2000) 2425–2430.
- 10) S. Yi, J. K. Lee, W. T. Kim and D. H. Kim: J. Non-Cryst. Solids. submitted (2000).
- 11) A. Inoue: Mater. Trans., JIM **36** (1995) 866–875.
- 12) F. R. Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen: *Cohesion in Metals*, (North-Holland, Amsterdam, 1989) pp. 291–336.
- 13) M. G. Scott, G. Gregan and Y. D. Dong: *Proc. 4th Int. Conf. on Rapidly Quenched Metals*, ed. by T. Masumoto and K. Suzuki, (The Japan Inst. Metals, 1982) pp. 671–674.
- 14) D. E. Polk, A. Calka and B. C. Giessen: Acta. Metall. **26** (1978) 1097–1103.
- 15) A. Inoue: Nanostruct. Mater. **6** (1995) 53–64.