Thermal Stability and Devitrification Behavior of Ternary Ni-Nb-Ti and Quaternary Glassy Alloys Containing Noble Metals

Takeyuki Shimada^{1,*}, Dmitri V. Louzguine¹, Junji Saida² and Akihisa Inoue¹

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

²Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan

The devitrification of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy has been investigated by X-ray diffraction (XRD), differential scanning and isothermal calorimetry and transmission electron microscopy (TEM). The primarily crystallized phase was a cubic $\text{Ni}(\text{Ti},\text{Nb})$ phase with a lattice parameter of 0.293 nm. A Ni_3Nb phase follows precipitation of the $\text{Ni}(\text{Ti},\text{Nb})$ phase. The cubic $\text{Ni}(\text{Ti},\text{Nb})$ phase undergoes partial transformation to Ni_4Ti_3 phase. These cubic $\text{Ni}(\text{Ti},\text{Nb})$ phases disappear at the equilibrium conditions.

The supercooled liquid region (ΔT_x) of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy was extended to 64 K with the addition of Pt. The $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ glassy alloy rods with diameters up to 2 mm were formed by mold casting. Pt and the other noble metals additions do not alter devitrification of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy.

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1. Introduction

Bulk glassy alloys were obtained by stabilization of the supercooled liquid against crystallization in a various multi-component metallic alloys, at the relatively slow cooling rate of less than 100 K/s from liquid state.¹⁻⁴ The stabilization has enabled the production of bulk glassy alloys in the thickness range of 1–100 mm by using various casting processes. These alloys are promising materials for structural applications as they exhibit high mechanical strength, high fracture toughness and good corrosion resistance.²

Ni-based bulk glassy alloys were obtained in Ni-Zr-Ti-Si,^{5,6} Ni-Zr-Ti-Sn,⁷ Ni-Nb-Ti,⁸ Ni-Nb-Zr-Ti⁹ systems. $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ bulk glassy alloy has an ultimate compressive strength of 3085 MPa and exhibits plastic deformation of about 2%. Bulk glassy alloy with high tensile fracture strength of 2700 MPa a critical diameter of 3 mm has been produced in a multicomponent Ni-Nb-Ti-Zr-Co-Cu system.¹⁰

At the same time, the devitrification process of Ni-based glassy alloys has been poorly studied. The clarification of thermal stability and devitrification processes is of great importance for the glassy alloys which are expected to be used as structural materials. On the other hand, the increase of the thermal stability can be achieved by the proper alloying additions. However, an addition of an ordinary metal or a half-metal has already been performed.

Recently, it has been reported that noble metals (M) addition (Pd, Ag, Pt, Au) have changed thermal stability and altered devitrification pathway of Cu^{11,12} and Zr-based^{13,14} glassy alloys forming an icosahedral quasicrystalline phase.

In this paper, we present the results on the devitrification process of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy (with a supercooled liquid region ΔT_x of 54 K and a reduced glass transition temperature (T_g/T_l) of 0.622), as well as the influence of M (Pd, Ag, Pt, Au) addition on the thermal stability and glass-forming ability of the $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{M}_x$ glassy alloys.

2. Experimental Procedure

The alloy ingots were prepared by arc-melting a mixture of pure metals in an argon atmosphere. From these alloy ingots, ribbon samples with a cross-section of about $0.02 \times 1 \text{ mm}^2$ were prepared by a single roller melt-spinning method in an argon atmosphere. Bulk cylindrical samples of 2 mm or 3 mm in diameter were prepared by copper mold casting in an argon atmosphere. The thermal stability was investigated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and the liquidus temperature (T_l) was measured by differential thermal analysis (DTA) at a cooling rate of 0.067 K/s. Isothermal differential calorimetry tests were also performed. The structure was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mechanical properties were measured with an Instron testing machine at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The gauge dimension for the compressive test was 2 mm in diameter and 5 mm in height.

3. Results

3.1 Devitrification of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy

Figure 1 shows DSC and isothermal calorimetry curves of the melt-spun $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy ribbon samples scanned at 864 K and 874 K. The DSC trace in Fig. 1(a) shows a variation of the baseline at about 864 K related to a glass-transition and two exothermic peaks.

Two overlapped peaks are observed in the isothermal calorimetry curves (Fig. 1(b)) corresponding to the first DSC peak (Fig. 1(a)). This indicates that two phase transitions might have happened simultaneously. We applied the heat treatment regime 1 (HT1) (see Fig. 1(b)) to the sample. It was subjected to argon-flow cooling after the achieving of the top of the first exothermic peak of the isothermal calorimetry curve (see Fig. 1(b)).

Figure 2 shows the XRD data of the glassy alloy heat-treated at some temperatures. Cubic $\text{Ni}(\text{Ti},\text{Nb})$ phase with a lattice parameter of $a = 0.293 \text{ nm}$ and orthorhombic Ni_3Nb phase with the lattice parameter of $a = 0.511 \text{ nm}$, $b =$

*Graduate Student, Tohoku University,
E-mail: takeyuki@imr.tohoku.ac.jp

Fig. 1 (a) DSC curve of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy and (b) isothermal calorimetry curves of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy at 874 K and 864 K.

Fig. 2 XRD patterns of $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy heat-treated at some temperatures. “as-q” means as-quenched, HT1 is heat treatment regime 1.

Fig. 3 Bright-field TEM image of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ alloy, annealed by at HT1 regime (a) and annealed at 918 K for 15 min (b).

0.424 and $c = 0.454$ nm are observed in the sample heat treated in the HT1 regime. These phases also exist after the completion of the first exothermic peak. However, these phases disappeared after heating for 30 min at 1173 K and one can observe two equilibrium phases, *i.e.*, hexagonal Ni_6Nb_7 phase with lattice parameters of $a = 0.489$ and $c = 2.66$ and hexagonal Ni_9NbTi_2 phase with lattice parameters of $a = 0.513$ nm and $c = 0.421$ nm. The Ni_9NbTi_2 phase appears to precipitate prior to Ni_6Nb_7 one. Moreover, the equilibrium orthorhombic $\text{Ni}_{11}\text{Nb}_3\text{Ti}_6$ phase with the lattice parameters of $a = 0.879$ nm, $b = 1.187$ nm and $c = 0.881$ nm also precipitates at 1173 K.

Figure 3 shows the TEM structures of the HT1 sample and the sample annealed at 918 K for 15 min. The cubic $\text{Ni}(\text{Ti},\text{Nb})$ particles have an equiaxed morphology with a diameter of about 100 nm while the Ni_3Nb particles have a rod-shaped morphology with a diameter of about 30 nm and a length of about 100 nm. The energy-dispersive X-ray (EDX) analysis of these particles gave a composition of $\text{Ni}_{64}\text{Nb}_{19}\text{Ti}_{16}$ which can be regarded as a solid solution of Nb in the NiTi phase substituting Ti.

Figure 4 shows the selected-area electron diffraction patterns (SAEDP)s of the equiaxed phase. The equiaxed phase is partially transformed to $\text{R}\bar{3}$ Ni_4Ti_3 phase. SAEDPs of the Ni_3Nb rod-shaped phase is shown in Fig. 5. Formation of R-phase is also possible.

3.2 Change of the thermal stability by the addition of noble-metals

Figure 6 shows the DSC curves of the amorphous Ni-based alloys containing 5 at% of Pd, Ag, Pt or Au. The glass transition temperature (T_g), crystallization temperature (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) are shown in Fig. 7. The ΔT_x increased to 64 K when the sample contains 5 at% Pt. In order to investigate the effect of Pt on ΔT_x , the Pt content was changed. Figure 8 shows DSC curves of the melt-spun $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_x$ ($x = 0 \sim 7.5$) glassy alloys. The T_g , T_x and ΔT_x as a function of Pt content are shown in Fig. 9. It is seen that the rise in T_g and T_x is proportional to Pt content but the maximum of ΔT_x of 64 K is attained at 5 at% Pt. This alloy has slightly lower T_g and higher T_x (see Fig. 9).

Fig. 4 Selected-area electron diffraction patterns of Ni (Ti,Nb) phase (a) [111], (b) [100], and Ni_4Ti_3 phase (c) [001].

3.3 Formation of bulk glassy alloys

Figure 10 shows XRD patterns of $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_x$ ($x = 2.5 \sim 7.5$) bulk samples with a diameter of 2 mm produced by copper mold casting. The XRD pattern of the sample containing 5 at%Pt consists only of a broad diffrac-

Fig. 5 Selected-area electron diffraction pattern of Ni_3Nb phase. Zone axes (a) [010] and (b) [112].

tion peaks indicating the formation of an amorphous single phase. The peaks of Ni(Ti,Nb) phase are observed in the as-solidified rods containing 2.5 at%Pt and 4 at%Pt. A $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ bulk alloy rod of 3 mm in diameter was also produced but the structure was crystalline.

Figure 11 shows DSC curves of the $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ alloy rod with a diameter of 2 mm. The T_g , T_x and ΔT_x are 875 K, 925 K and 50 K, respectively, and the total heat release upon devitrification of -55 J/g is close to that of the ribbon sample.

3.4 Devitrification of Ni-Nb-Ti-M alloys

The $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{M}_5$ glassy alloys showed essentially the same devitrification behavior as that of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ alloy, *i.e.* primary formation of the Ni(Ti,Nb) and Ni_3Nb phases (Fig. 12).

Thus, contrary to Cu-based alloys the addition of noble metals does not alter the devitrification behavior of the Ni-based alloys.

Fig. 6 DSC curves of $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{M}_5$ (M=Pt, Ag, Pd, Au) glassy alloys.

Fig. 8 DSC curves of $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_x$ ($x = 0$ to 7.5 at%) glassy alloys.

Fig. 7 Glass transition temperature (T_g), crystallization temperature (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) of $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{M}_5$ (M=Pt, Ag, Pd, Au) glassy alloys.

4. Discussions

Both Ni(Ti,Nb) phase and Ni_3Nb phase are observed in the sample heat treated by HT1 regime (Fig. 2). These phases also exist after the completion of the first exothermic peak. It follows that the competitive nucleation and growth of these

two phases takes place from the supercooled liquid at the first exothermic reaction and the Ni(Ti,Nb) phase precipitates first.

Here one should notice that the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy in as-solidified state does not have pre-existing nuclei (Fig. 13) Ni(Ti,Nb) and Ni_3Nb phases transform to the equilibrium Ni_6Nb_7 , Ni_9NbTi_2 and $\text{Ni}_{11}\text{Nb}_3\text{Ti}_6$ phases on further heating. Cubic Ni(Ti,Nb) phase completely disappeared upon heating for 30 min at 1173 K.

The Pt addition improves glass-forming ability (GFA) of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ alloy. The bulk glassy samples obtained for $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ alloy have a critical diameter of about 2.5 mm. This result is in good correlation with the largest ΔT_x which is obtained for the sample with the highest GFA among the studied alloys. The reason may be connected with highly negative mixing enthalpy in liquid in Ti-Pt and Nb-Pt atomic pairs of -74 and -67 kJ/mol, respectively. Ni-Pt atomic pair also has a negative mixing enthalpy of -5 kJ/mol. Moreover, Pt has an atomic size (0.137 nm) larger than that of Ni (0.125 nm). All these factors are favorable for improving glass-forming ability. Surprisingly $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ alloy has slightly lower T_g/T_l ratio (Fig. 9) compared to some other Ni-Nb-Ti-Pt alloys. It indicates that for these alloys ΔT_x is a better index of glass-forming ability than T_g/T_l ratio.

Contrary to the Cu-based alloys studied earlier^{15,16,18,19} the addition of noble metals does not alter devitrification behavior of Ni-Nb-Ti alloys. Moreover, the addition of Ni to Cu-Zr-Ti system causes precipitation of the equilibrium (Ni,Cu)₁₀Zr₇ phase directly from the supercooled liquid at more than 5 at% of Ni content^{17,18} ($\text{Ni}_{10}\text{Zr}_7$ phase forms primarily in the Ni-Zr-Ti alloy on devitrification)¹⁹ and no

Fig. 9 (a) T_g , T_x , (b) ΔT_x and (c) T_g/T_l as a function of Pt content for the $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_x$ ($x = 0$ to 7.5) glassy alloys.

formation of the icosahedral phase is observed in the Ni-Zr-Ti-Pd alloy.²⁰⁾ This is in consistent with the previous data that the icosahedral phase is formed more readily in Zr-Cu alloys than in Zr-Ni ones.^{20,21)}

5. Conclusions

(1) In the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ alloy, Ni(Ti,Nb) and Ni_3Nb phases precipitate primarily from the supercooled liquid by the competitive nucleation and growth. The former phase has a primitive cubic lattice with a lattice parameter of $a = 0.293$ nm. It is a solid solution of Nb in a cubic NiTi phase.

(2) Ni(Ti,Nb) and Ni_3Nb phases are transform upon further heating to the Ni_6Nb_7 , Ni_9NbTi_2 and $\text{Ni}_{11}\text{Nb}_3\text{Ti}_6$ phases. Ni_4Ti_3 phase was also formed as a result of transformation of the Ni(Ti,Nb) cubic phase.

(3) The Pt addition improves glass-forming ability (GFA) of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ alloy. The $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ amorphous alloy with the largest ΔT_x has a critical diameter of about 2.5 mm. The reason may be connected with the highly negative mixing enthalpy in Ti-Pt and Nb-Pt atomic pairs. ΔT_x is better index of the glass-forming ability of the Ni-Nb-Ti-Pt alloys than T_g/T_l ratio.

Fig. 10 X-ray diffraction patterns of $\text{Ni}_{60-x}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_x$ ($x = 2.5$ to 7.5) bulk samples with a diameters of 2 mm (a), and $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ alloy rod with a diameter of 3 mm (b).

Fig. 11 DSC curves for $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{Pt}_5$ bulk alloy with a diameter of 2 mm. The data of the melt-spun ribbon are also shown for comparison.

Fig. 12 XRD results of $\text{Ni}_{55}\text{Nb}_{25}\text{Ti}_{15}\text{M}_5$ ($\text{M}=\text{Pt}, \text{Ag}, \text{Pd}, \text{Au}$) alloy annealed at the first peak temperature (T_p) for 300 ks.

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REFERENCES

- 1) A. Inoue: *Mater. Trans.*, JIM **36** (1995) 866.
- 2) A. Inoue: *Acta Mater.* **48** (2000) 279–306.
- 3) W. L. Johnson: *MRS Bull* **24** (1999) 42.
- 4) Y. C. Kim, W. T. Kim and D. H. Kim: *Mater. Sci. Eng. A* **375–377** (2004) 127.
- 5) S. Yi, T. G. Park and D. H. Kim: *J. Mater. Res.* **15** (2000) 2425–2430.
- 6) J. K. Lee, S. H. Kim, S. Yi, W. T. Kim and D. H. Kim: *J Non-Cryst Solids* **291** (2001) 132–136.
- 7) H. Choi-Yim, D. Xu and W. L. Johnson: *Appl. Phys. Lett.* **82** (2003) 1030.
- 8) T. Zhang and A. Inoue: *Mater. Trans.* **43** (2002) 708.
- 9) A. Inoue, W. Zhang and T. Zhang: *Mater. Trans.* **43** (2002) 1952.
- 10) W. Zhang and A. Inoue: *Mater. Trans.* **43** (2002) 2342–2345.
- 11) D. V. Louzguine and A. Inoue: *Scr. Mater.* **48** (2003) 1325.
- 12) D. V. Louzguine and A. Inoue: *J. Alloys Compd.* **361** (2003) 153.
- 13) A. Inoue, J. Saida, M. Matsushita and T. Sakurai: *Mater. Trans.* **41** (2000) 362–365.
- 14) A. Inoue, T. Zhang, M. Matsushita, M. W. Chen and T. Sakurai: *Mater. Trans.*, JIM **40** (1999) 1137–1143.
- 15) A. Inoue, T. Zhang, M. Matsushita, M. W. Chen and T. Sakurai: *Mater. Trans.*, JIM **40** (1999) 1181–1184.
- 16) T. Zhang, T. Yamamoto and A. Inoue: *Mater. Trans.* **43** (2002) 3222.
- 17) D. V. Louzguine and A. Inoue: *Mater. Sci. Forum/Journal of Metastable & Nanocrystalline Materials*, **31** (2003) 15–16.
- 18) D. V. Louzguine and A. Inoue: *J. Non-Cryst. Solids* **325** (2003) 187.
- 19) D. V. Louzguine and A. Inoue: *J. Non-Cryst. Solids*, in Press.
- 20) J. Saida, M. Matsushita and A. Inoue: *Intermetallics* **10** (2002) 1089–1098.
- 21) M. Leonhardt, W. Löser and H.-G. Lindenkreuz: *Acta Mater.* **47** (1999) 2961–2968.

Fig. 13 High-resolution TEM image of the $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$ glassy alloy in as-solidified state.