

Icosahedral and Amorphous Phases in Melt-Spun Ti–Zr–Ni–Cu Alloys

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Structure of melt-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 0, 5, 10, 15, 20$ and 25) alloys and crystallization behavior of the amorphous alloys have been studied. The alloys have different structures depending on cooling rate. An icosahedral quasicrystal phase (I-phase) is formed directly upon cooling at a wheel velocity of 20 m/s for $x = 0$ –15, and at wheel velocities of 40 and 60 m/s for $x = 0$. The high cooling rate at 60 m/s for $x = 5$ –25 causes the formation of a single amorphous phase. DSC traces of the amorphous alloys obtained during continuous heating to 1000 K showed distinct exothermic peaks. The first exothermic reaction at low temperatures for $x = 5, 10$ and 15 is due to the precipitation of I-phase, and the following reactions at higher temperatures result from the formation of α -Ti and Ti_2Ni or Ti_2Cu phases. The simultaneous addition of Cu and Ni to Ti–Zr base alloys can enhance the forming ability of I-phase as well as amorphous phase.

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1. Introduction

The formation and crystallization process of Zr- and Hf-based amorphous alloys have been extensively studied^{1–4)} and two kinds of metastable phases have been reported in the initial crystallization process of the amorphous alloys. That is, icosahedral atomic clusters exist in the melt and some of them are retained in a rapidly quenched state. The icosahedral clusters in the melt have been thought to contribute to the high glass-forming ability and the high stability against crystallization. The Ti-based amorphous alloys also exhibit a similar phenomenon, since Ti belongs to the same group as Zr and Hf in the elemental periodic table.

The formation of Ti-based amorphous alloys has been actively tried by rapid solidification for the last three decades, because of engineering importance of Ti-based alloys. It has been previously reported that amorphous alloys containing Ti as a main constituent element are formed in various alloy systems of Ti–Cu–Al,⁵⁾ Ti–Cu–Ni(Co),⁶⁾ Ti–Cu–Zr–Ni,⁷⁾ Ti–Cu–Co–Al–Zr,⁸⁾ Ti–Cu–Ni–Sn(Si),⁹⁾ Ti–Nb–Si,¹⁰⁾ Ti–M–Si ($M = \text{IV–VIII}$ group metals),¹¹⁾ Ti–Nb–Si–B,¹²⁾ and Ti–Zr–Ni–Cu–Al¹³⁾ by melt spinning. It has been pointed out that the alloys with high glass forming ability satisfy the following empirical rules,¹⁴⁾ *i.e.*, (1) multi-component systems consisting of more than three elements, (2) significant difference in atomic size ratios above 12% among the main three elements, and (3) negative heats of mixing among their main elements. Thus, the multi-component amorphous systems like Ti–Zr–Cu–Ni–Al¹³⁾ can exhibit good glass forming ability due to the satisfaction of the above described empirical rules by addition of appropriate elements to binary or ternary systems.

Furthermore, formation of an I-phase in Ti-(Mn, Fe or Co)^{15,16)} binary and Ti–Zr-(Fe, Co or Ni)^{17,18)} ternary alloys by rapid quenching from the melt has been reported. Also, formation of Ti–Zr(Hf)–Ni–Cu amorphous alloys and quasicrystal precipitation upon annealing have been reported in our previous work,¹⁹⁾ where the low temperature annealing reaction corresponds to the precipitation of an icosahedral qua-

sicrystalline phase (I-phase) and further annealing at higher temperatures leads to the decomposition of I-phase to other stable crystalline phases. However, the influence of Cu and Ni concentrations on the formation tendency of I- and amorphous phases in the Ti–Zr–Ni–Cu system remains unknown. The present work is intended to examine the compositional dependence of structure of melt-spun Ti–Zr–Ni–Cu alloys and the crystallization process of the amorphous alloys.

2. Experimental

Alloys ingots with composition of $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 0, 5, 10, 15, 20$ and 25) were prepared by arc-melting the mixtures of pure (> 99.8 mass%) Ti, Zr, Ni and Cu metals in a purified argon atmosphere. From the mother alloy ingot, alloy ribbons with a width of 0.6–1.0 mm and thickness of 15–35 μm were prepared by a single roller melt-spinning technique under an argon atmosphere. The circumferential velocities of the copper wheel were 20, 40 and 60 m/s, respectively. The structure was examined by X-ray diffractometry (XRD). The microstructure was examined by transmission electron microscopy (TEM). The heating treatment of the as-quenched alloys was carried out in a Cu pan at different temperatures under a purified argon atmosphere and measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The melting point of the alloys was measured at a heating rate of 0.17 K/s by differential thermal analysis (DTA).

3. Results and Discussion

XRD patterns of the melt-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ribbons obtained at a circumferential velocity of 20 m/s are shown in Fig. 1. The 0% and 5%Cu alloys contain I-, Ti_2Ni , α -Ti and β -Ti phases and the 10% and 15%Cu alloys consist of amorphous and I-phases. The alloys with high Cu concentrations of 20 at% and 25 at% are mainly composed of α -Ti and Ti_2Cu phases. Figure 2 shows XRD patterns of the as-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ribbons prepared at a circumfer-

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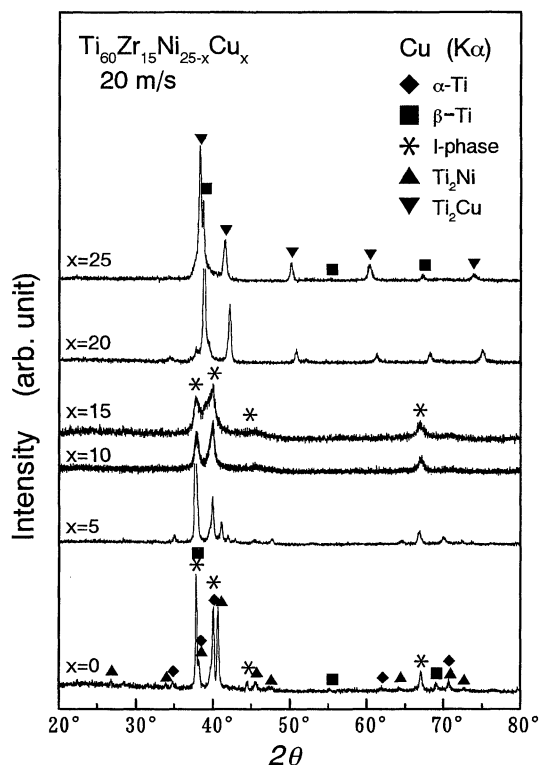


Fig. 1 XRD patterns of melt-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ribbons at a circumferential velocity of 20 m/s.

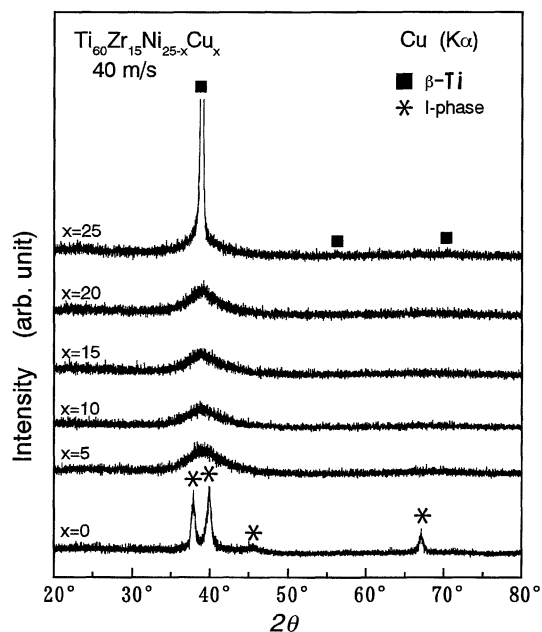


Fig. 2 XRD patterns of melt-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ribbons at a circumferential velocity of 40 m/s.

entail velocity of 40 m/s. The I-phase is formed only in the alloy without Cu element. The bright-field TEM image and selected area electron diffraction pattern of the $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25}$ alloy is shown in Fig. 3. One can see fine and homogenous microstructure of I- and amorphous phases that have been determined by XRD. The X-ray diffraction patterns in Fig. 2 reveal that the addition of 5 to 20 at%Cu causes the formation of an amorphous single phase. The absence of Ni also yields the coexistent structure of amorphous and β -Ti phases. The

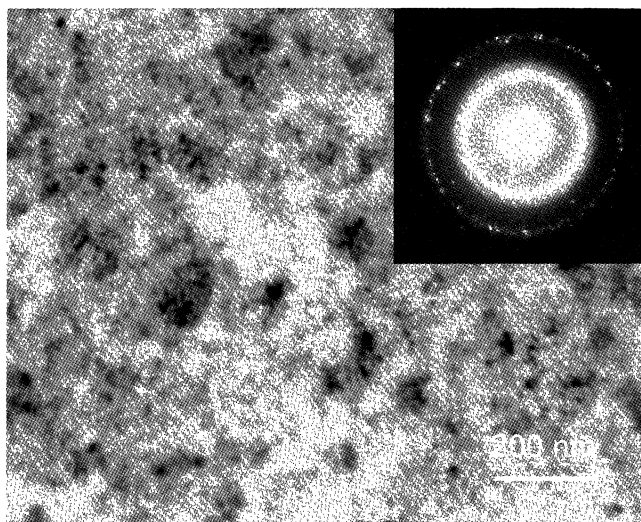


Fig. 3 Bright-field TEM image of a $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25}$ ribbon prepared at a circumferential velocity of 40 m/s.

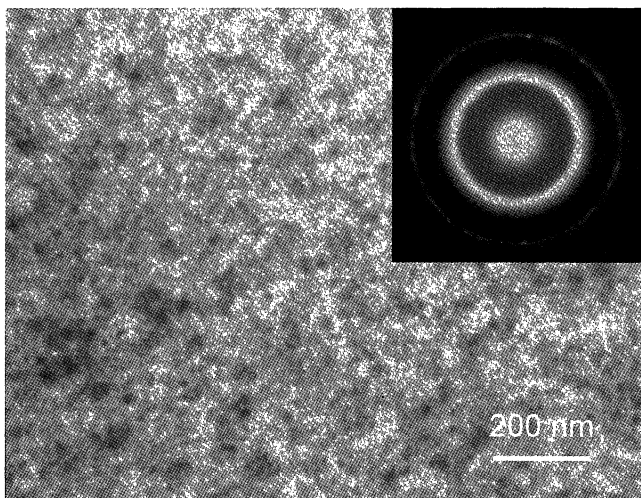


Fig. 4 Bright-field TEM image of a $\text{Ti}_{60}\text{Zr}_{15}\text{Cu}_{25}$ ribbon prepared at a circumferential velocity of 40 m/s.

bright-field TEM image and selected area electron diffraction pattern of the mixed structure of the $\text{Ti}_{60}\text{Zr}_{15}\text{Cu}_{25}$ alloy is shown in Fig. 4. As compared with Fig. 3, the mixed structure of β -Ti and amorphous phases appears to be much finer and more homogenous. Figure 5 shows the XRD patterns of the as-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25}$ and $\text{Ti}_{60}\text{Zr}_{15}\text{Cu}_{25}$ ribbons obtained at a velocity of 60 m/s. By an increase in the circumferential velocity from 40 m/s to 60 m/s, the structure in the $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25}$ alloy change to an amorphous single phase, though the I-phase in the $\text{Ti}_{60}\text{Zr}_{15}\text{Cu}_{25}$ alloy remains unchanged. The present results indicate that the amorphous forming ability is significantly enhanced by the simultaneous addition of Ni and Cu elements.

Figure 6 shows the DSC curves of the as-quenched ribbons including an amorphous phase in the $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ system. The DSC traces were obtained with a heating rate of 0.67 K/s from room temperature to 1000 K. The crystallization took place through multiple exothermic reactions for these amorphous alloys. The tardy peak of the first exothermic reaction is due to the precipitation of I-phase from the amorphous phase for the 5%, 10% and 15%Cu alloys and

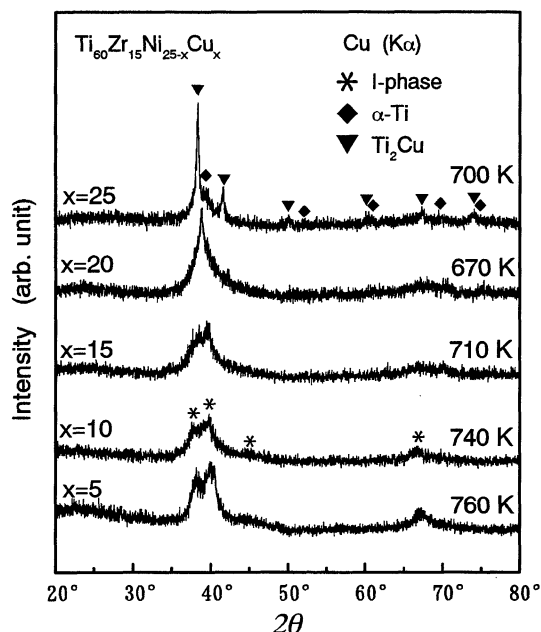


Fig. 7 XRD patterns of the $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25}$ I-phase plus amorphous and $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 5-25$) amorphous alloys heated to different temperatures at a rate of 0.67 K/s.

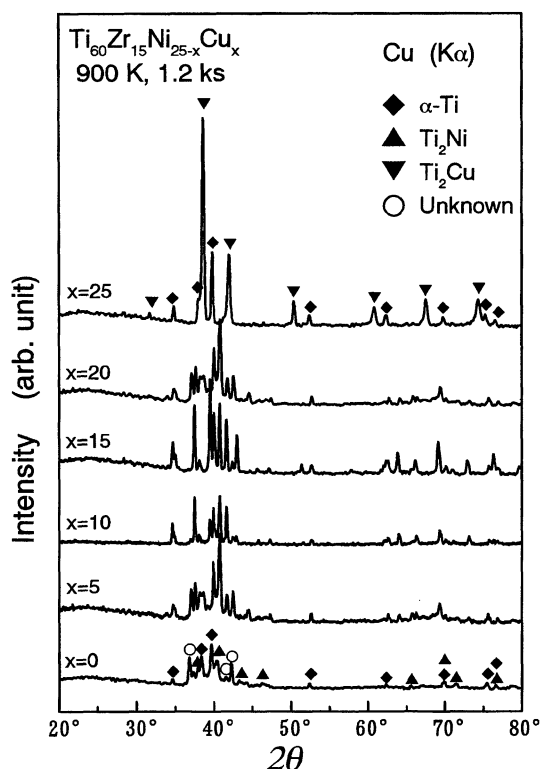


Fig. 8 XRD patterns of the melt-spun $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 0-25$) alloys annealed at 900 K for 1.2 ks.

1.2 ks, as shown in Fig. 8. It is identified that the I-phase is in a metastable state and the α -Ti, Ti₂Ni or Ti₂Cu phases coexist after annealing at higher temperatures. The initial precipitation phase is in these alloys completely different, implying that Ni and Cu were redistributed to different compounds in the phase transformation from the as-quenched phase.

The melt-spun structure of Ti–Zr–Ni and Ti–Zr–Ni (Co, Fe) alloys was previously reported.^{20,21} No amorphous single

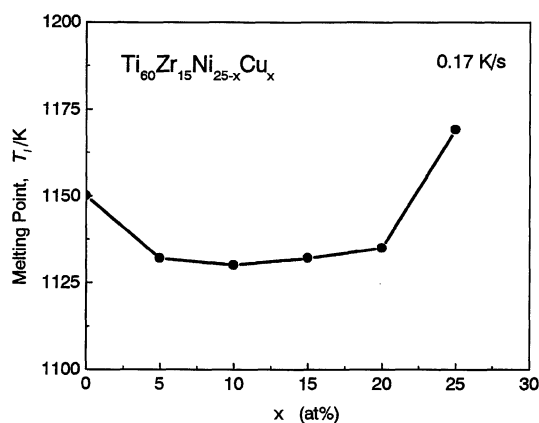


Fig. 9 Melting points (T_l) as a function of Cu concentration for $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 0-25$) alloys.

phase has been reported probably because of low amorphous forming ability in their ternary systems with high Ti concentrations. In contrast, a single amorphous state was prepared successfully in the present work, indicating that the addition of Cu to the Ti–Zr–Ni system is effective in increasing amorphous forming ability. The atomic radii and the chemical affinities of the constituent elements usually affect the atomic configuration of an amorphous alloy. Cu (0.128 nm) has the similar atomic radius as compared to Ni (0.125 nm). Cu also has different chemical affinity with Ti and Zr. The Ti–Zr–Ni–Cu amorphous structure can be considered to be composed mainly of Ti–Zr–Ni atomic configurations with some Ni sites occupied by Cu. The atomic radii lie in the order of $\text{Ni} < \text{Cu} < \text{Ti} < \text{Zr}$. The difference seems to increase the atomic packing density. Furthermore, Fig. 9 shows the change in the melting points (T_l) with Cu concentration (x), T_l of the 5%, 10%, 15% and 20% Cu alloys decreases with Ni and Cu concentrations. These factors are considered to be effective for the increase in amorphous forming ability.

However, the behaviors of Ni and Cu are different in the initial crystallization process of these melt-spun alloys. During the crystallization process shown in Fig. 7, the stable compounds in the Ti–Zr–Ni–Cu alloys consist of Ti_2Ni and Ti_2Cu . The structure of Ti_2Ni (cubic, $Fd\bar{3}m$, $a = 1.13$ nm) is completely different from Ti_2Cu (tetragonal, $I4/mmm$, $a = 0.294$ nm and $c = 1.08$ nm). This implies that Cu and Ni are redistributed to different compounds in the phase transformation from the melt, which contributes to the high amorphous forming ability of the Ti–Zr–Ni–Cu alloys as compared with those of Ti–Zr–Ni or Ti–Zr–Cu alloys.

The stability of the I-phase is also thought to correlate to the amorphous forming ability of Ti-based alloys. Zhang *et al.* reported the formation of a metastable I-phase in Ti–Ni alloys.²² Kelton *et al.* reported the formation of a stable I-phase in Ti–Zr–Ni alloys.²³ It is speculated that icosahedral atomic clusters are formed in the melt of Ti–Zr–Ni alloys and these clusters can grow even during rapid quenching. It is presumed that the icosahedral atomic clusters with high stability in the Ti–Zr–Ni–Cu amorphous alloy causes high nucleation rate of the I-phase as compared with that of the stable crys-

talline phases for the alloys with low Cu concentrations of 5%, 10% and 15%. This can explain the present experimental results that an I-phase precipitates in the initial crystallization process and transfers to other crystalline phases upon annealing to high temperatures.

4. Summary

(1) The amorphous forming ability in the $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 0, 5, 10, 15, 20$ and 25) alloys depended on Cu concentration. The optimum Cu concentration for the formation of the amorphous alloys was 5 to 25%. By comparing with the crystalline counterpart, it is recognized that the addition of Cu to the Ti–Zr–Ni system leads to a significant improvement in amorphous forming ability.

(2) The $\text{Ti}_{60}\text{Zr}_{15}\text{Ni}_{25-x}\text{Cu}_x$ ($x = 5-15$) amorphous alloys crystallize through multiple exothermic reactions, of which the low temperature one corresponds to the precipitation of a metastable I-phase.

REFERENCES

- 1) M. W. Chen, T. Zhang, A. Inoue, A. Sakai and A. Sakurai: *Appl. Phys. Lett.* **75** (1999) 1697–1699.
- 2) A. Inoue, J. Saida, M. Matsushita and T. Sakurai: *Mater. Trans., JIM* **41** (2000) 362–365.
- 3) C. Li, M. Matsushita, J. Saida and A. Inoue: *Appl. Phys. Lett.* **77** (2000) 528–530.
- 4) J. Saida, M. Matsushita, C. Li and A. Inoue: *Philos. Mag. Lett.* **80** (2000) 737–743.
- 5) A. Inoue, N. Nishiyama, K. Amiya, T. Zhang and T. Masumoto: *Mater. Lett.* **19** (1994) 131–135.
- 6) T. Zhang, A. Inoue and T. Masumoto: *Mater. Sci. and Eng.* **A181/A182** (1994) 1423–1426.
- 7) X. D. Liu, M. Nagumo and M. Umemoto: *Mater. Trans., JIM* **39** (1998) 343–350.
- 8) L. Battezzati, M. Baricco, P. Fortina and W. N. Myung: *Mater. Sci. Eng.* **A226–228** (1997) 503–506.
- 9) T. Zhang and A. Inoue: *Mater. Trans., JIM* **39** (1998) 1001–1006.
- 10) A. Inoue, H. M. Kimura and T. Masumoto: *J. Appl. Phys.* **51** (1980) 5475–5482.
- 11) A. Inoue, H. M. Kimura, S. Sakai and T. Masumoto: *Proc. 4th Intern. Conf. On Titanium*, ed. by K. Kimura and O. Izumi (Japan Inst. Metals, Sendai, 1980) pp. 1137–1140.
- 12) A. Inoue, T. Masumoto, C. Suryanarayana and A. Hoshi: *J. Physique* **41** (1980) C8-758–C8-761.
- 13) K. Amiya, N. Nishiyama, A. Inoue and T. Masumoto: *Mater. Sci. Eng.* **A179/A180** (1994) 692–696.
- 14) A. Inoue, T. Zhang and T. Masumoto: *J. Non-Cryst. Solids*, **156–158** (1993) 473–480.
- 15) K. F. Kelton, P. C. Gibbons and P. N. Sabes: *Phys. Rev. B* **38** (1988) 7810–7813.
- 16) X. Zhang and K. F. Kelton: *Scr. Metall. Mater.* **26** (1992) 393–398.
- 17) W. J. Kim and K. F. Kelton: *Philos. Mag. Lett.* **74** (1996) 439–447.
- 18) B. S. Murty, W. T. Kim, D. H. Kim and K. Hono: *Mater. Trans.* **42** (2001) 372–375.
- 19) L. Wang, C. Li and A. Inoue: *Mater. Trans.*, **42** (2001) 528–531.
- 20) V. V. Molokanov and V. N. Chebotnikov: *J. Non-Cryst. Solids*, **117/118** (1990) 789–792.
- 21) W. J. Kim, P. C. Gibbons and K. F. Kelton: *Philos. Mag. A* **78** (1998) 1111–1124.
- 22) Z. Zhang and K. H. Kuo: *Philos. Mag. Lett.* **54** (1986) 83–87.
- 23) K. F. Kelton, W. J. Kim and R. M. Stroud: *Appl. Phys. Lett.* **70** (1995) 3230–3232.