Preparation of Ti–Cu–Ni–Si–B Amorphous Alloys with a Large Supercooled Liquid Region

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A large supercooled liquid region exceeding 60 K before crystallization was found in a wide composition range of 15 to 20 at%Cu and 25 to 30 at%Ni for the Ti_{1-x-y}Cu_xNi_ySi_B_y amorphous alloys which satisfy the three criteria of multi-components, significant atomic size ratios and negative heats of mixing. The glass transition temperature (T_g) and the reduced glass transition temperature (T_g/ T_m) of the Ti_{0.5}Cu_{0.25}Ni_{0.4}Si_B alloy are 742 K and 0.63, respectively. The high thermal stability of the supercooled liquid as well as the high reduced glass transition temperature enabled us to produce bulk amorphous alloys with a diameter of 1 mm by copper mold casting. The crystallization of the Ti_{0.5}Cu_{0.25}Ni_{0.4}Si_B amorphous alloy takes place through a single exothermic reaction and the four phases of Cu_{4}Ti_{3}, CuTi, NiTi and TiB precipitate almost simultaneously. The crystallization mode requires the long-range atomic rearrangements of the constituent elements and the necessity seems to cause the increase in thermal stability of the supercooled liquid. The success of forming the bulk amorphous alloys in the Ti–Cu–Ni–Si–B system with lower densities is important for the future development of bulk amorphous materials with a higher specific strength.

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I. Introduction

Exploring amorphous alloys with a large supercooled liquid region before crystallization is of great importance because the appearance of the large supercooled liquid region is expected to cause the production of a bulk amorphous alloy. The large supercooled liquid region with a temperature interval above 60 K had been observed only in Pd- and Pt-based alloy systems(1) among a great number of the amorphous alloys reported before 1988 and hence the production of bulk amorphous alloys with thicknesses of above several millimeters had been limited to the Pd–Ni–P and Pt–Ni–P systems(1)(2)(3). However, the blockade situation was exploded by a series of findings of a number of amorphous alloys with a large supercooled liquid region in Mg–Ln–TM(4), Ln–Al–TM(5), Zr–Al–TM(6), Zr–(Ti, Nb, Pd)–Al–TM(7), Zr–Ti–Be–TM(8), Fe–(Al, Ga)–(P, C, B, Si)(9), Co–Cr–(Al, Ga)–(P, C, B, Si)(10), Pd–Cu–Ni–P(11), Pd–Ni–Fe–P(12), (Fe, Co, Ni)–(Zr, Nb, Ta)–B(11), Fe–Co–(Zr, Nb)–(Mo, W)–B(14) and Co–Fe–(Zr, Nb, Ta)–B(15) (Ln=lanthanide metal, TM=IV to VIII group transition metals) systems. The use of these new multi-component alloy systems has enabled us to produce bulk amorphous alloys by various solidification methods(16)(20) and the largest thickness reaches about 30 mm(21) for the Zr-based alloys and about 75 mm(22) for the Pd-based alloys. The Zr-based bulk amorphous alloys have already gained actual application fields of precision optical materials and sporting goods materials by use of their high glass-forming ability, unique mechanical properties and good viscous flow workability. If the specific strength defined by the ratio of strength to density increases further for bulk amorphous alloys, the application field of the bulk amorphous alloys is expected to be significantly extended. As a candidate alloy system, one can list up Ti- and Al-based alloys with lower densities. When special attention is paid to Ti-based amorphous alloys, it has previously been reported that an amorphous phase in a ribbon form is formed in the Ti–Be–Zr(23), Ti–Si(24), Ti–Ni(24), Ti–Be(25), Ti–TM–Si(24)(26) and Ti–Ni–Cu(27)(28) and Ti–Zr–Ni–Cu(29) systems by melt spinning. Among these alloy systems, the glass transition is observed in the Ti–Ni–Cu(27)(28) and Ti–Zr–Ni–Cu(29) systems, but the supercooled liquid region is below 40 K. Subsequently, we have searched for a new Ti-based amorphous alloy with a larger supercooled liquid region above 60 K, because the bulk amorphous alloys in the Mg–Ln–Zr-based alloy systems have been obtained at the alloy compositions with the supercooled liquid region of over 60 K. More recently, it has been found that a large supercooled liquid region of over 60 K is observed in the Ti–Ni–Cu–Si(30) and Ti–Ni–Cu–Si–B systems. This paper is intended to present alloy compositions at which a large supercooled liquid region above 60 K in the melt-spun Ti_{30–x-y}Cu_xNi_ySi_B alloys is observed before crystallization and the thermal stability and mechanical properties of these Ti-based amorphous alloys, and to investigate the effect of additional Si and B elements on the increase in the thermal stability of the supercooled liquid.

II. Experimental Procedure

Multi-component alloys with composition Ti_{30–x–y}–
Cu$_{2}$Ni$_{3}$Si$_{5}$B$_{2}$ were examined in the present study. Their alloy ingots were prepared by arc melting pure Ti, Cu and Ni metals and pure Si and B crystals in an argon atmosphere. Rapidly solidified ribbon samples with a cross section of $1 \times 0.02$ mm$^2$ were produced by a melt spinning technique. Bulk cylindrical alloys were also prepared in the diameter range of 0.5 to 3 mm by a copper mold casting method. The amorphous structure was examined by X-ray diffraction and transmission electron microscopy. Thermal stability of supercooled liquid region associated with glass transition and crystallization was measured by differential scanning calorimetry. The melting temperature was also measured by differential thermal analysis. Mechanical properties were measured with an Instron testing machine and a Vickers microhardness tester at room temperature. Fracture surface was examined by scanning electron microscopy.

III. Results

Figure 1 shows the composition range in which an amorphous phase in the Ti$_{44-x}$Cu$_x$Ni$_3$Si$_5$B$_2$ system is formed by melt spinning, together with the data of bending ductility. The amorphous phase is formed in a wide composition range of 0 to 40 at% Cu and 0 to 45 at% Ni. The double open circles represent the formation of ductile amorphous alloys which can be bent through 180 degrees without fracture. All the amorphous alloys in the Ti–Cu–Ni–Si–B system examined in the present study have good bending ductility. Figure 2 shows the DSC curves of the Ti$_{50}$Cu$_{44-x}$Ni$_3$Si$_5$B$_2$ ($x = 4, 14, 19$ and $24$ at%) amorphous alloys. These amorphous alloys exhibit the glass transition, followed by a supercooled liquid region and then crystallization. With increasing Ni content, the $T_g$ increases gradually, leading to an increase in the supercooled liquid region from 788 K for the 4% Ni alloy to 800 K for the 24% Ni alloy. Figures 3(a) and (b) show the compositional dependence of the glass transition temperature ($T_g$) and the temperature interval of the supercooled liquid region defined by the difference between $T_g$ and $T_c$, $\Delta T_c (= T_c - T_g)$, respectively. Although no systematic compositional dependence of $T_g$ is recognized, one can see a distinct change with composition in the $\Delta T_c$ values. A maximum $\Delta T_c$ value of 65 K is obtained for Ti$_{50}$Cu$_{50}$Ni$_3$Si$_5$B$_2$ and the deviation from the alloy composition causes a decrease in $\Delta T_c$. However, it is noticed that the large $\Delta T_c$ values above 50 K are obtained in the wide composition range from 10 to 40% Cu and 10 to 30% Ni.

We further examined the difference in specific heat between the amorphous solid and supercooled liquid, $\Delta C_{p,s-1}$ for the amorphous Ti$_{50}$Cu$_{50}$Ni$_3$Si$_5$B$_2$ alloy. Figure 4 shows the apparent specific heats of the as-quenched and annealed (775 K, 60 s) samples. The $C_{p,s}$ and $C_{p,a}$ represent the specific heats of the as-quenched and annealed samples. As shown in Fig. 4, the $\Delta C_{p,s-1}$ value is measured to be 11.5 J/mol. Besides, the structural relaxation represented by the difference between $C_{p,s}$ and $C_{p,a}$ starts around 560 K, shows a maximum around 625 K and then decreases gradually with increasing temperature. The difference in the specific heats disappears in the supercooled liquid region after the completion of the glass transition stage. The $\Delta C_{p,s-1}$ value is slightly smaller than those (13 to 14 J/mol) for the La–Al–Ni–Cu$^{(1)}$ and Zr–Al–Ni–Cu$^{(2)}$ amorphous alloys. The smaller $\Delta C_{p,s-1}$ value suggests that the present Ti–Cu–Ni–Si–B amorphous alloys belong to a rather strong-type glass.

The melting temperature, $T_m$, was measured by differential thermal analyses. As an example, the DTA curve of the Ti$_{50}$Cu$_{50}$Ni$_3$Si$_5$B$_2$ alloy is shown in Fig. 5. A distinct endothermic reaction due to melting is seen in the temperature range between 1183 and 1214 K and hence the $T_m$ value is determined as 1183 K. Figure 6 shows the
compositional dependence of $T_m$ and $T_e/T_m$ for the Ti$_{54-x}$Cu$_x$Ni$_3$Si$_2$B$_2$ amorphous alloys. The $T_m$ values are in the range from 1140 K to 1320 K and the high $T_e/T_m$ values above 0.6 are obtained in the wide composition range. The highest value of 0.63 is obtained for the Ti$_{64}$Cu$_{30}$Ni$_{2}$Si$_{2}$B$_{2}$ and Ti$_{59}$Cu$_{30}$Ni$_{15}$Si$_{2}$B$_{2}$ alloys. As shown in Fig. 3, the $\Delta T_c$ value of the latter alloy is also as large as 65 K. The high $T_e/T_m$ value of 0.63 as well as the large $\Delta T_c$ value of 65 K indicates the possibility of forming a bulk amorphous alloy by various casting processes.

We further examined the compositional dependence of the maximum sample thickness ($t_{\text{max}}$) for the formation of an amorphous phase in the Ti$_{54-x}$Cu$_x$Ni$_3$Si$_2$B$_2$ system by use of the copper mold casting method. The $t_{\text{max}}$ value of 1.0 mm is obtained for the Ti$_{55.69}$Cu$_{30.25}$Ni$_{15.24}$Si$_{2}$B$_{2}$ alloys with high $T_e/T_m$ values above 0.60 and large $\Delta T_c$ values above 59 K. Figure 7 shows the outer surface appearance and cross sectional structure of the cast Ti$_{59}$Cu$_{30}$Ni$_{15}$Si$_2$B$_2$ amorphous alloys with a diameter of 1 mm and a length of 30 or 45 mm. The cross sectional structure was taken from the central region at the part of 25 mm from the edge of the cast cylinder with a length of 45 mm. The cast cylinder has a smooth surface and good metallic luster and no distinct contrast of a crystalline phase is seen in the optical micrograph of the cross section. Figure 8 also shows the DSC curve of the cast...
Fig. 6 Compositional dependence of melting temperature \( T_\text{m} \) and reduced glass transition temperature \( T_g / T_\text{m} \) for the amorphous Ti_{84-x}Cu_{x}Ni_{32}Si_{3}B_{2} alloys.

The data of the melt-spun Ti-Cu-Ni-Si-B amorphous ribbon with a thickness of 20 μm are also shown for comparison.

Fig. 7 Outer surface and cross sectional structure of the cast Ti_{80}Cu_{32}Ni_{32}Si_{3}B_{2} amorphous cylinder prepared by copper mold casting.

T_{80}Cu_{32}Ni_{32}Si_{3}B_{2} amorphous alloy with a diameter of 1 mm, together with the data of the melt-spun amorphous ribbon with a thickness of 20 μm. The cast alloy shows a sequent transition of glass transition at \( T_g = 735 \text{ K} \), followed by the supercooled liquid region with a temperature interval of 65 K and then crystallization at \( T_c = 800 \text{ K} \). The feature of the phase transition and the thermal properties of \( T_g, \Delta T_g, \) and \( T_c \) are nearly the same as those for the melt-spun amorphous alloy. The metallographic and thermal analytical data indicate the formation of the bulk amorphous alloys with a diameter of 1 mm in the Ti-based system. According to the previous relation among the \( t_{\text{max}}, T_g / T_\text{m} \) and \( \Delta T_g \) for a number of amorphous alloys in the Mg-, Ln-, Zr-, Fe-, Pd- and Co-based systems\(^{27}(28)\), the \( t_{\text{max}} \) of the alloys with \( T_g / T_\text{m} \) of 0.62 and \( \Delta T_g \) of 60 K is expected to reach about 3 mm which is larger than the present \( t_{\text{max}} \) value of 1.0 mm. The difference is presumably due to a high oxidation tendency for the Ti-based alloys, because the dissolution of oxygen into the Ti-based alloys causes an increase of heterogeneous nucleation frequency through the formation of TiO\(_2\) in the outer surface region of the liquid\(^{33}(34)\).

IV. Discussion

It has previously been reported\(^{(27)(28)}\) that an amorphous phase in the Ti–Cu–Ni ternary system is formed in a wide composition range of 10 to 40% Cu and 0 to 30% Ni and the amorphous alloys with compositions of 10 to 40% Cu and 0 to 30% Ni exhibit the glass transition and supercooled liquid region before crystallization. The largest \( \Delta T_g \) value is 40 K for Ti_{80}Cu_{32}Ni_{32}. However, there have been no data on the formation of a bulk amorphous alloy. The appearance of the larger \( \Delta T_g \) value of 65 K and the formation of the bulk amorphous alloy with a diameter of 1 mm by copper mold casting indicate clearly that the addition of Si and B elements causes a significant increase in the glass-forming ability. It has
been pointed out\((16)-(20)\) that the alloys with high glass-forming ability satisfy the following three empirical rules, \textit{i.e.}, (1) multi-component systems consisting of more than three elements, (2) significant difference in atomic size ratios above about 12\% among the main three elements, and (3) negative heats of mixing among their main elements. Furthermore, the feature of the main three components has been divided into four groups\((16)\), as summarized in Fig. 9. Here, ETM and LTM represent the IV to VI group early transition metals and the VIII group late transition metals including Cu, respectively, in the periodic table. The first group consists of ETM, Al and LTM elements as exemplified for Zr–Al–Ni and Ln–Al–Ni systems. The second group is composed of LTM, ETM and metalloid as exemplified for Fe–Zr–B and Fe–Nb–B systems. The third group is exemplified for Fe–(Al, Ga)–(P, C, B, Si). The fourth group consists of Mg–Ln–LTM(Ni, Cu) and ETM(Zr, Ti)–Be–LTM(Ni, Cu) systems. All the alloy systems belonging to the groups 1 to 4 satisfy the above-described three empirical rules. When the Ti–Cu–Ni and Ti–Cu–Ni–Si–B alloys are compared with the four group components in Fig. 9, one can notice that the Ti–Cu–Ni–Si–B alloy belongs to the II group consisting of ETM (Ti), LTM (Cu and Ni) and metalloid (Si and B) elements. However, the Ti–Cu–Ni alloy cannot join into any groups. Thus, the high glass-forming ability of the Ti–Cu–Ni–Si–B amorphous alloys is due to the satisfaction of the three empirical rules for stabilization of supercooled liquid. The increase in the stability of the supercooled liquid region for the alloys with the three empirical rules has been reported\((16)-(20)\) to be attributable to the formation of a new type of liquid with a highly dense random packed atomic configuration, homogeneous atomic configuration on a long-range scale and new local atomic configuration which is different from those for the corresponding crystalline phases.

In addition, it is known that the alloys with the three empirical rules crystallize through a single exothermic reaction accompanying the simultaneous precipitation of more than two kinds of crystalline phases\((16)-(20)\). In order to confirm the appropriateness of the concept about the crystallization behavior, the X-ray diffraction patterns of the \(\text{Ti}_{60}\text{Cu}_{30}\text{Ni}_{30}\text{Si}_{30}\text{B}_{2}\) and \(\text{Ti}_{50}\text{Cu}_{30}\text{Ni}_{30}\) amorphous alloys annealed for 600 s at 850 K. The data of an amorphous \(\text{Ti}_{60}\text{Cu}_{30}\text{Ni}_{30}\) alloy are also shown for comparison.
The diffraction peaks are identified to be a metastable CuTi phase for the Ti-Cu-Ni alloy and Cu₅Ti₃, CuTi, NiTi and TiB phases for the Ti-Cu-Ni-Si-B alloy. The simultaneous precipitation of the four phases implies the necessity of rearrangements of the constituent elements on a long-range scale for the progress of crystallization. The necessity causes the retardation of the nucleation and growth reactions of their crystalline phases, leading to the increase in the thermal stability of the supercooled liquid.

V. Conclusions

With the aim of searching for a new bulk amorphous alloy in Ti-based system, we examined the thermal stability of the supercooled liquid region and the reduced glass transition temperature of the Ti₅₄₋ₓ₋ₓCuₓNiₓSiₓBₓ amorphous alloys. The results obtained are summarized as follows.

1. An amorphous phase was formed in a wide composition range of 10 to 40%Cu and 0 to 30%Ni and the distinct glass transition phenomenon was observed over the whole composition range. The $T_g$ and $T_x$ are in the range of 730 to 740 K and 780 to 810 K, respectively. The resulting temperature interval of the supercooled liquid region exceeds 60 K in the composition range of 25 to 30%Ni and 15 to 20%Cu and the largest $\Delta T_x$ reaches 65 K for Ti₅₀Cu₃₀NiₓSiₓBₓ. The difference in specific heat between amorphous solid and supercooled liquid was measured to be 11.5 kJ/mol which is judged to be a strong-type amorphous alloy.

2. The crystallization of the Ti₅₀Cu₃₀NiₓSiₓBₓ amorphous alloy with the largest $\Delta T_x$ value takes place through a single stage of Cu₅Ti₃ + CuTi + NiTi+ TiB. The crystallization mode indicates the necessity of long-range atomic rearrangements of the constituent elements for the progress of crystallization.

3. The bulk amorphous alloys with a diameter of 1 mm were produced in the composition range of 20 to 25%Cu and 20 to 25%Ni by copper mold casting. The $T_g$, $T_x$, and $\Delta T_x$ values of the bulk amorphous Ti₅₀Cu₃₀NiₓSiₓBₓ alloy are 735, 800 and 65 K, respectively, which are nearly the same as those for the melt-spun amorphous alloy ribbon.

The finding of the new Ti-Cu-Ni-Si-B amorphous alloys with high glass-forming ability is promising the future development of a new bulk amorphous alloy with higher specific strength.

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