Thermal and Mechanical Properties of Ti-Ni-Cu-Sn Amorphous Alloys with a Wide Supercooled Liquid Region before Crystallization

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A wide supercooled liquid region exceeding 50 K before crystallization was observed for melt-spun Ti₃₀Ni₂₂₋ₓCuₓSnₓ (x = 3 and 5 at%) amorphous alloys. The temperature interval of the supercooled liquid region defined by the difference between crystallization temperature (T_c) and glass transition temperature (T_g), ΔT = (T_c - T_g), is 40 K for the 0%Sn alloy and increases to 50 K for the 3% Sn alloy and 60 K for the 5% Sn alloy. With increasing Sn content, the ΔT value decreases significantly. A similar increase in thermal stability of the supercooled liquid was also recognized for the 3 at% Sb-containing alloy in the Ti₃₀Ni₂₂₋ₓCuₓSbx system. The replacement by 3 to 5 at% Sn for Ni also induces an increase of mechanical strength, in addition to the increase in ΔT. The tensile fracture strength (σf), Young’s modulus (E) and Vickers hardness (HV) increase from 1800 MPa, 93 GPa and 530, respectively, for the Ti₃₀Ni₂₂Cu₅ alloy to 2050 MPa, 102 GPa and 650, respectively, for the Ti₃₀Ni₂₂Cu₅Sn₅ alloy. The crystallization takes place through a single exothermic reaction, accompanying the simultaneous precipitation of multiple Cu(Ti + Cu)Ti₃ and Ni(Ti + Cu) phases. The crystallization mode requires long-range atomic rearrangements for precipitation of the crystalline phases, leading to the increase in the stability of supercooled liquid against crystallization. The high thermal stability of the supercooled liquid enabled the production of bulk amorphous alloys in the diameter range up to about 6 mm by copper mold casting. There is no appreciable difference in the stability of the supercooled liquid region between the melt-spun and cast bulk amorphous alloys. The first synthesis of the Ti-based amorphous alloys with high glass-forming ability and good mechanical properties allows us to expect the future development of bulk amorphous alloys as a new type of high specific strength material.

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Keywords: titanium base amorphous alloy, glass transition, wide supercooled liquid region, glass-forming ability, bulk amorphous alloy, high mechanical strength, single-stage crystallization

1. Introduction

Recently, bulk amorphous alloys have gained significant interest in basic science and engineering aspects. One of the reasons is because the bulk alloys have been synthesized in a number of alloy systems such as Ln-Al-TM, Mg-Ln-TM, Zr-Al-TM, Zr-Ti-TM, Zr-Cu-Ni-P, Pd-Cu-Ni-P, Fe-(Al, Ga)-(P, C, B, Si), Pd-Ni-Fe-P, (Fe, Co, Ni)-(Zr, Nb, Ta)-B, Fe-(Zr, Nb, Ta)-(Mo, W)-B and Co-Fe-Zr-B (Ln = lanthanide metal, TM = transition metal). Besides, it has been reported that these bulk amorphous alloys exhibit good engineering properties of high tensile strength, high elastic energy, relatively high impact fracture energy and high corrosion resistance for Zr-based amorphous alloys and good soft magnetic properties, particularly high frequency permeability for Fe-based amorphous alloys and Co-based amorphous alloys. The tensile fracture strength and Vickers hardness of the Zr-based amorphous alloys reach 1600 to 1800 MPa and 480 to 520, respectively, at room temperature and their densities are in the range from 5.9 to 6.7 Mg/m³. If a bulk amorphous alloy with similar high tensile strength is formed in a lower density range, the alloy with higher specific strength is expected to cause a further extension of application fields for bulk amorphous alloys. The success of synthesizing Ti-based bulk amorphous alloy containing more than 50 at% Ti is expected to achieve similar high tensile strength exceeding 1500 MPa combined with lower specific weight.

The formation of Ti-based amorphous alloys have been actively tried by various rapid solidification techniques for the last three decades, because of their engineering importance. It has previously been reported that amorphous alloys containing Ti as a main constituent element are formed in various alloy systems of Ti-Be-Zr, Ti-Ni, Ti-Si, Ti-Ni-Si, Ti-Be, Ti-Nb-Si, Ti-M-Si (M = IV-VIII group metals), Ti-Nb-Si-B, Ti-Ni-Cu, Ti-Ni-Cu-Al and Cu-Ti-Zr-Ni by melt spinning. However, the alloy systems in which a glass transition phenomenon is observed at Ti-rich compositions more than 50 at% Ti have been limited to Ti-Be-Zr, Ti-Ni, Ti-Ni-Cu, Ti-Ni-Cu-Al and Ti-Zr-Ni-Cu-Al. The temperature interval of the supercooled liquid region before crystallization is about 25 K for the former system and about 35 to 40 K for the latter two systems. There have been no Ti-based amorphous alloys which exhibit a wide supercooled liquid region exceeding 50 K as well as a high glass-forming ability of forming a bulk amorphous alloy by casting process. Based on the previous information that the Ti-Ni-Cu amorphous alloys exhibit the glass transition and a supercooled liquid region below 40 K before crystallization, we have examined the possibility that the stability of the supercooled liquid against crystalliza-
tion is enhanced and a bulk amorphous alloy is formed in Ti–Ni–Cu base alloys containing a special additional element. Considering that a binary amorphous alloy has been formed in the Ti–Si system by melt spinning, we paid attention to Sn element because Sn belongs to the same periodic group number (IVB) as that for Si and the heats of mixing against the other constituent elements have large negative values. Besides, the atomic size of the Sn element is different from those of the other constituent elements. In the subsequent research, we have found that the supercooled liquid region before crystallization is significantly extended in Ti–Ni–Cu–Sn system and bulk amorphous alloys are produced in the diameter range up to about 6 mm by the conventional copper mold casting process. After the effectiveness of Sn element was recognized, we further examined the possibility of additional effect of other elements, which are located near Sn in the periodic table, and noticed that Sb element has a similar effectiveness on the extension of the supercooled liquid region before crystallization. The primary aim of this paper is to examine an optimum amount of additional Sn or Sb element for extension of the supercooled liquid region before crystallization for Ti–Ni–Cu–Sn and Ti–Ni–Cu–Sb amorphous alloys and to present the compositional effect on the thermal stability and mechanical properties of the melt-spun Ti-based amorphous alloys. The second is to form a bulk amorphous alloy in the Ti-based alloy systems by the copper mold casting method and to examine a maximum sample thickness and thermal stability of the Ti-based bulk amorphous alloy.

II. Experimental Procedure

Multicomponent alloys with compositions Ti$_{10}$Ni$_{35}$-Cu$_{25}$, Ti$_{10}$Ni$_{35-}$-Cu$_{25}$Sn$_x$, Ti$_{10}$Ni$_{35}$-Cu$_{25}$Sn$_{1+y}$, Ti$_{10}$Ni$_{35}$-Cu$_{25}$Sb, and Ti$_{10}$Ni$_{35}$Cu$_{25}$Sn$_x$Zr$_y$ ($x$ = 1 and 10 at%) were examined in the present study because the Ti$_{10}$Ni$_{35}$Cu$_{25}$ amorphous alloy had been reported to exhibit the distinct glass transition and a narrow supercooled liquid region before crystallization. The prealloyed ingots were prepared by arc melting pure Ti, Ni, Cu, Sn and Sb metals in an argon atmosphere. Amorphous ribbons with a thickness of about 25 μm were prepared by melt spinning. Besides, bulk amorphous alloys were prepared by ejection casting into copper molds and the resulting cylindrical samples have a length of about 50 mm and different diameters up to 10 mm. The amorphous structure was identified by X-ray diffractometry, transmission electron microscopy (TEM) and optical microscopy (OM). The thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Melting temperature was measured by differential thermal analysis (DTA). Tensile strength and Young’s modulus were measured with an Instron testing machine at 298 K and a strain rate of 1.8 × 10$^{-4}$ s$^{-1}$. Vickers hardness was measured with a Vickers hardness indenter with a load of 0.245 N.

III. Results and Discussion

Figure 1 shows X-ray diffraction patterns of the melt-spun Ti$_{10}$Ni$_{35-}$-Cu$_{25}$Sn$_x$ ($x$ = 0, 3 and 5 at%) and Ti$_{10}$Ni$_{35}$Cu$_{25}$Sn$_y$ alloys. The diffraction patterns consist of broad peaks and the main broad peak lies in the vicinity of a wave vector $K = 4\pi \sin \theta / \lambda$ of 29.2 nm$^{-1}$ for the 0%Sn alloy. The peak position of the main broad peak tends to shift to the lower diffraction angle side with increasing Sn content. The continuous change in the peak position indicates the definite dissolution of Sn element with the largest atomic size in the Ti-based amorphous alloys. We could not recognize any harmful influences of the Sn addition on the formation of the amorphous phase in the concentration range up to 7 at% Sn.

Figure 2 shows DSC curves of the four Ti-based amorphous alloys. It is to be noticed that all the alloys exhibit a distinct glass transition. The glass transition temperature ($T_g$) decreases in the Sn content up to 5 at% and then increases with further increasing Sn content, while the onset temperature of crystallization ($T_c$) remains almost constant in the Sn content up to 3 at% and then increases in the higher Sn content range. The resulting temperature interval of the supercooled liquid region before crystallization defined by the difference between $T_c$ and $T_g$, $\Delta T_c (= T_c - T_g)$ is measured to be 40 K for the 0%Sn alloy, 50 K for the 3%Sn alloy, 60 K for the 5%Sn alloy and 49 K for the 7%Sn alloy. Thus, the $\Delta T_c$ shows a maximum at 5%Sn and then decreases with a further increase.
in Sn content. The addition of a small amount of Sn element is concluded to be very effective for the increase of the stability of the supercooled liquid against crystallization. This is believed to be the first evidence for the appearance of the wide supercooled liquid region of over 50 K for Ti-based alloys containing more than 50 at.%Ti. Furthermore, it is seen that the crystallization of the 3% Sn and 5%Sn alloys takes place through a single exothermic reaction in spite of the multicomponent alloy compositions. The crystalline phase of the 5%Sn-containing alloy annealed for 600 s at 850 K was identified to consist of CuTi, Cu$_3$Ti and NiTi phases. Based on the data for the structural analyses and density measurements, it has been pointed out that the supercooled liquid in the multicomponent amorphous alloys has a higher dense random packed structure and a new local atomic configuration which is different from those for the corresponding equilibrium compounds. Consequently, the simultaneous precipitation of the multiple crystallized phases implies that the crystallization requires long-range atomic rearrangements for the precipitation of each crystalline phase with significantly different components. The crystallization mode is consistent with that for other amorphous alloys in Ln$_{1-x}$Mg$_x$, Ln$_{1-x}$Zr$_x$, and Fe$_{70}$ based systems having a wide supercooled liquid region of over 50 K before crystallization. The melting temperature ($T_m$) of the Ti$_{50}$Ni$_{30}$Cu$_{20}$Sn$_5$ alloy was measured to be 1229 K. The reduced glass transition temperature ($T_g / T_m$) is evaluated to be 0.58, indicating that the Ti–Ni–Cu–Sn alloy has a rather high glass-forming ability.

Subsequently, we measured the difference in the specific heats between amorphous solid ($C_{p,a}$) and supercooled liquid ($C_{p,l}$), $\Delta C_{p,a,l}$ for the Sn-containing alloys. Figure 3 shows the temperature dependence of the apparent specific heat of the Ti$_{50}$Ni$_{30}$Cu$_{20}$Sn$_5$ alloy. The $C_{p,a}$ and $C_{p,l}$ represent the $C_p(T)$ of the as-quenched sample and the sample heated for 60 s at 745 K between $T_s$ and $T_r$, respectively. The difference between the $C_{p,a}$ and $C_{p,l}$ values is due to the structural relaxation caused by continuous heating at 0.67 K/s. The heat of structural relaxation defined by $\Delta H_r = \int C_p(T) dT$ ($\Delta C_{p,a,l} \neq 0$) is measured to be 870 J/mol. The temperature dependence of the apparent specific heats of the amorphous solid and supercooled liquid is expressed by the following relations:

For the amorphous solid,

$$C_{p,a}(T) = 24.3 + 2.8 \times 10^{-2}(T - 430) \quad (430 \leq T \leq 600 \text{ K}) \quad (1)$$

for the supercooled liquid,

$$C_{p,l}(T) = 40.1 + 3.7 \times 10^{-2}(760 - T) \quad (730 \leq T \leq 760 \text{ K}) \quad (2)$$

The difference in specific heat between amorphous solid and supercooled liquid, $\Delta C_{p,a,l}$, is evaluated to be 15.8 J/mol·K. The $\Delta C_{p,a,l}$ value has been reported to be 14.0 J/mol·K for the La$_{53}$Al$_{25}$Ni$_{22}$ amorphous alloy$^{(30)}$, 17.4 J/mol·K for the Mg$_{68}$Ni$_{20}$La$_{12}$ amorphous alloy$^{(31)}$, 14.5 J/mol·K for the Zr$_{60}$Al$_{10}$Ni$_{10}$Cu$_{20}$ amorphous alloy$^{(32)}$ and 17.2 J/mol·K for the Pd$_{46}$Cu$_{20}$Ni$_{10}$P$_{24}$ amorphous alloy$^{(33)}$. It is therefore said that the new Ti-based amorphous alloy seems to have nearly the same magni-

![Fig. 2](image-url) Differential scanning calorimetric (DSC) curves of the melt-spun Ti$_{50}$Ni$_{30}$Cu$_{20}$Sn$_5$ (x=0, 3 and 5 at%) and Ti$_{50}$Ni$_{30}$Cu$_{20}$Sn$_5$ amorphous alloys.

![Fig. 3](image-url) Thermograms of the melt-spun Ti$_{50}$Ni$_{30}$Cu$_{20}$Sn$_5$ amorphous alloy. The $C_{p,a}$ and $C_{p,l}$ represent the apparent specific heats of the as-spun sample and the sample heated once for 60 s at 745 K in the supercooled liquid region between $T_s$ and $T_r$, respectively.
tude of $\Delta T_{c}$, as those for the typical amorphous alloys with a wide supercooled liquid region before crystallization.

With the aim of investigating the reason for the remarkable effect of Sn on the appearance of the supercooled liquid region, the crystallized structure of the Ti-based alloy was examined. Figure 4 shows X-ray diffraction patterns of the fully crystallized Ti$_{50}$Ni$_{35}$Cu$_{25}$ and Ti$_{50}$Ni$_{25}$Cu$_{25}$Sn$_{5}$ alloys by annealing for 600 s at 990 K. The diffraction peaks are identified to consist of Cu$_{4}$Ti$_{3}$ + NiTi + CuTi for the Ti–Ni–Cu alloy and CuTi + Cu$_{2}$Ti$_{3}$ + NiTi for the Ti–Ni–Cu–Sn alloy. Furthermore, the peak intensity suggests that the main crystalline phases are composed of Cu$_{4}$Ti$_{3}$ and NiTi for the ternary alloy and CuTi, Cu$_{2}$Ti$_{3}$ and NiTi phases for the quaternary alloys and their grain sizes are considerably smaller for the Sn-containing alloy. However, we could not observe any diffraction peaks of Sn-containing compounds. Considering the similarity in the atomic sizes between Ti and Sn elements, the Sn element is thought to be dissolved by replacing the Ti sites in their compounds. The change in the X-ray diffraction pattern also indicates that the simultaneous precipitation of the three phases becomes significant for the Sn-containing alloy. Consequently, the crystallization mode for the Sn-containing alloy plays an important role in the increase in stability of the supercooled liquid against crystallization.

We have also searched for other useful additional elements to increase the thermal stability of the supercooled liquid region and noticed that the addition of 3 at% Sn is also effective for the increase in $\Delta T_{c}$ for the Ti-based amorphous alloys. Figure 5 shows a DSC curve of the melt-spun Ti$_{50}$Ni$_{25}$Cu$_{25}$Sb$_{5}$ amorphous alloy. The Sb-containing amorphous alloy also exhibits the sequential phase transition of amorphous solid, glass transition, supercooled liquid and crystallization, and the $\Delta T_{c}$ is measured to be 45 K. However, with further increasing Sb content to 5 at% Sn, the $\Delta T_{c}$ decreases significantly to 28 K.

Table 1 summarizes the Vickers hardness ($H_{v}$), tensile fracture strength ($\sigma_{f}$) and Young's modulus ($E$) of the melt-spun Ti$_{50}$Ni$_{25}$Cu$_{25}$, Ti$_{50}$Ni$_{25}$–xCu$_{25}$Sn$_{x}$ ($x$ = 3 and 5 at%), Ti$_{50}$Ni$_{25}$Cu$_{25}$Sn$_{5}$ and Ti$_{50}$Ni$_{25}$–xCu$_{25}$Sb$_{x}$ ($x$ = 1 and 3 at%) amorphous alloys, together with the data of thermal stability. The best mechanical properties of 2050 MPa for $\sigma_{f}$, 102 GPa for $E$ and 650 for $H_{v}$, were obtained for the Ti$_{50}$Ni$_{25}$Cu$_{25}$Sn$_{5}$ alloy with the largest $\Delta T_{c}$. Here, it is important to point out that the $\sigma_{f}$, $E$ and $H_{v}$ values are considerably higher than those for Zr–Al–Ni–Cu$^{(12)}$ and Zr–Ti–Al–Ni–Cu$^{(17)}$ amorphous alloys. The finding
Table 1 Thermal stability and mechanical properties of the melt-spun Ti$_{60}$Ni$_{35}$Cu$_{5}$Sn$_{5}$ (x=0, 3 and 5 at%), Ti$_{60}$Ni$_{35}$Cu$_{25}$Sn$_{5}$, and Ti$_{60}$Ni$_{35}$Cu$_{25}$Sb$_{5}$ (x=1 and 3 at%) amorphous alloys. $T_g$: glass transition temperature, $T_{ud}$: onset temperature of crystallization, $H$: Vickers hardness, $\sigma$: tensile fracture strength, $E$: Young's modulus.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$(K)</th>
<th>$T_{ud}$(K)</th>
<th>$T_u-T_{ud}$(K)</th>
<th>$H$ (GPa)</th>
<th>$\sigma$ (MPa)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
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<tr>
<td>Ti$<em>{60}$Cu$</em>{25}$Ni$_{35}$</td>
<td>713</td>
<td>753</td>
<td>40</td>
<td>620</td>
<td>1800</td>
<td>93</td>
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<td>765</td>
<td>50</td>
<td>640</td>
<td>2050</td>
<td>98</td>
</tr>
<tr>
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<td>770</td>
<td>60</td>
<td>650</td>
<td>2050</td>
<td>102</td>
</tr>
<tr>
<td>Ti$<em>{60}$Ni$</em>{35}$Cu$<em>{25}$Sn$</em>{5}$</td>
<td>710</td>
<td>759</td>
<td>49</td>
<td>670</td>
<td>2200</td>
<td>105</td>
</tr>
<tr>
<td>Ti$<em>{60}$Ni$</em>{35}$Cu$<em>{25}$Sb$</em>{5}$</td>
<td>707</td>
<td>740</td>
<td>33</td>
<td>610</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ti$<em>{60}$Ni$</em>{35}$Cu$<em>{25}$Sb$</em>{5}$</td>
<td>763</td>
<td>718</td>
<td>45</td>
<td>615</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

of the Ti-based amorphous alloy having good mechanical properties and high stability of the supercooled liquid against crystallization is important for future development of a new type of bulk amorphous alloy with lower specific weight.

The high thermal stability of the supercooled liquid evidenced by the large $\Delta T_g$ values exceeding 50 K indicates the possibility of forming a bulk amorphous alloy by various solidification techniques. By using an amorphous Ti$_{50}$Ni$_{35}$Cu$_{25}$Sn$_{5}$Zr$_{5}$ alloy which has a lower melting temperature as compared with Ti$_{60}$Ni$_{30}$Cu$_{25}$Sn$_{5}$ alloy, we tried to produce bulk amorphous alloys by the copper mold casting method. Figure 6 shows the outer shape and surface appearance of the cast cylinders with diameters of 3 and 5 mm and a length of about 50 to 55 mm. The cast cylinders have smooth outer surface and metallic luster. No distinct contrast due to the precipitation of a crystalline phase is seen on the outer surface of both samples. No appreciable crystalline peaks were seen in the X-ray diffraction patterns of the cast cylinders with diameters of 3 and 5 mm and the cast cylinders was identified to be composed of an amorphous phase. The DSC curves of the cast cylinders with diameters of 3 and 5 mm are shown in Fig. 7, where the data of the melt-spun amorphous alloy ribbon are also shown for comparison. There is no appreciable difference in $T_g$, $T_{ud}$, $\Delta T_g$ and crystallization peak between the cast cylinders and the melt-spun ribbon. The similarity suggests that the cast bulk cylinders have nearly the same amorphous structure as that for the melt-spun ribbon.

We further examined the critical sample thickness for glass formation. The cast cylinder with a diameter of 7 mm consists of an amorphous phase containing a small amount of crystalline phase and the further increase in diameter to 10 mm induces the formation of a mostly crystalline phase. The change in the structure with sample diameter allows us to conclude that the critical diameter for glass formation is about 6 mm. Mechanical properties of the cast bulk amorphous cylinders will be presented elsewhere.

IV. Summary

New Ti-based amorphous alloys in Ti–Ni–Cu–Sn system were found to exhibit a wide supercooled liquid region exceeding 50 K before crystallization. The largest $\Delta T_g$ reaches as large as 60 K for the Ti$_{60}$Ni$_{30}$Cu$_{25}$Sn$_{5}$ alloy. The $\Delta T_g$ value is much larger than the largest value (40 K) for the Ti–Ni–Cu ternary system and the addition of a small amount of Sn is effective for the increase of the stability of the supercooled liquid against crystallization. The 5 at%Sn-containing alloy also exhibits good mechanical properties, i.e., high $\sigma$ of 2050 MPa, high $H$ of 102 GPa and high $H_s$ of 650 which are superior to those for previously reported Zr–Al–Ni–Cu amorphous alloys. Besides, the high stability of the supercooled liquid against crystallization resulted in the formation of bulk amorphous alloys with diameters up to about 6 mm by the copper mold casting method. The good combination of high
glass-forming ability and high mechanical strength for the Ti-based alloys is promising for future development as a high specific strength bulk amorphous material.

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