Effect of Ni Addition on the Glass Forming Ability and Mechanical Properties in Cu$_{60}$Zr$_{22}$Ti$_{18}$ Metallic Glass Alloy

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This paper investigates the effects of Ni addition on the glass forming ability (GFA) and mechanical properties in Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ ($x = 0$–15) metallic glass alloys. Partial substitution of Cu by Ni in the alloys improved the GFA. By increasing Ni content $x$ from 0 to 6, the supercooled liquid region ($\Delta T_g$) and crystallization temperature ($T_c$) were increased, whereas the liquidus temperature decreased to reach the lowest value at $x = 6$. The compressive strength and micro-hardness of the alloys were raised by increasing Ni content, and the Ni containing alloy showed some macroscopic plasticity after yielding. [doi:10.2320/matertrans.MRA2008041]

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1. Introduction

Since the first report of a metallic glass, a number of glass forming alloys have been reported. Because of their specific properties such as high strength, high corrosion resistance and electromagnetic properties, the metallic glass alloys have been considered a potential engineering material. However, because a high cooling rate is required for the formation of amorphous phase from a liquid state, metallic glass has generally been produced in the form of ribbon or powders. Since the late 1980s, bulk metallic glasses (BMGs) in the form of rod more than 1 mm in diameter have been developed in the Pd-, Zr-, Cu-, Ti-, Fe- and Ni-based alloy systems.$^{2-7}$

Recently, BMGs such as Cu-, Ti-, Fe-, and Ni-based alloys have been attracting much attention because the base materials are commercial elements. Among these alloy systems, Cu-based BMGs, in particular, have been constantly reported in Cu-Zr, Cu-(Zr,Hf)-Ti, Cu-Zr-Ti-Ni, Cu-Zr-Ti-(Y,Be), Cu-Zr-Al, Cu-Zr-Al-(Ag, Y) systems, with their GFA being enhanced from 1 mm to 10 mm diameter.$^{8-14}$

Making the alloy systems more complex through partial substitution of elements has been used to increase the GFA of the alloys. Using this alloying method of adding elements, the alloy systems can have a low melting temperature (near the alloys. Using this alloying method of adding elements, the alloy systems can have a low melting temperature (near

2. Experimental Procedures

Alloys of nominal composition (at%) Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ ($x = 0, 3, 6, 9, 12, 15$) were prepared by arc melting under an argon atmosphere with the mixtures of pure Cu (99.9%), Ni (99.9%), Zr (99.2%) and Ti (99.9%) metals. The alloyed powders were remelted in quartz tubes and ejected with an over pressure of 35 kPa through a nozzle onto a Cu wheel surface rotating at a surface velocity of 40 m/s under an argon atmosphere. BMGs in a rod form were prepared by the suction casting method using copper molds with cylindrical cavities of varying diameters from 1 to 6 mm and a height of around 30 mm.

Thermal properties of the samples were measured by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The glass transition and crystallization of the glassy alloys (bulk and ribbon) were examined by the DSC at a heating rate of 0.67 K/s in a copper pan. The melting temperatures of alloys were measured using the DTA at a heating rate of 0.67 K/s under a flowing 99.999% Ar atmosphere. Equilibrium crystalline samples were used to measure the melting temperatures. In order to prepare samples near equilibrium state,$^{16}$ glassy rods showing a nominal composition at any part of rods were chipped for proper amount, and the glass chips weighing 30–40 mg were melted at 1373 K on the cold compacted Y$_2$O$_3$ powder and solidified at a cooling rate of 1 K/min. The Y$_2$O$_3$ powders were used because there was no reaction with the molten alloys. The samples obtained from the glass chips were placed in alumina crucibles whose insides were also covered with Y$_2$O$_3$ powders to prevent a reaction between the crucibles and the samples, then the melting points of the samples were measured.

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The structure of the amorphous specimens was characterized by X-ray diffractometry (XRD). The mechanical properties of the samples were measured at room temperature under compressive mode with a strain rate of $5 \times 10^{-4} \text{s}^{-1}$. Cylindrical specimens with dimension of $\phi 2 \times 4 \text{ mm}$ were prepared for compression tests. The hardness of the samples was measured on a micro Vickers hardness tester. The microstructures of the tested specimens were observed using scanning electron microscopy (SEM).

3. Results

The GFA of the Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys is given in Fig. 1. As the Ni content, $x$, increased, the maximum diameter increased up to 6 mm at $x = 6$, and then decreased to 2 mm with further increment of Ni content to $x = 15$. The maximum diameter reveals a direct parameter that shows the GFA of an alloy. The results clearly demonstrated that partial substitution of Cu by Ni improved the GFA in the Cu-Zr-Ti alloy. The formation of a fully amorphous structure of the Cu$_{54-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys was confirmed by XRD analysis as shown in Fig. 2. The XRD patterns of the suction cast BMGs show only a broad halo diffraction peak in the $2\theta$ range of $34^\circ$–$46^\circ$, which is characteristic of the amorphous structure.

Figure 3 shows the typical DSC traces obtained from the melt-spun Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ ribbon at a heating rate of 40 K/s. The DSC traces exhibit an endothermic event corresponding to glass transition to supercooled liquid, and the overlapped exothermic peaks corresponding to the crystallization process. $T_g$ and $T_x$ (onset temperature of first exothermic peak) are marked by arrows on the DSC traces. As Ni content $x$ increases from 0 to 15, the $T_g$ slightly rose from 711 K to 725 K, and the $T_x$ noticeably increased from 745 K to 793 K, resulting in an increase of the supercooled liquid region, $\Delta T_x$. The addition of Ni leads to an increase in $\Delta T_x$ as well as $T_g$ and $T_x$, changing the crystallization mode from two stages to a single stage.

Figure 4 shows the DTA traces of the Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys at a heating rate of 0.67 K/s. The solidus temperature ($T_{\text{sol}}$) and liquidus temperature ($T_{\text{liq}}$) were taken from the onset and the end temperature, respectively, of the melting endotherm. The solidus temperature of the Cu$_{60}$Zr$_{22}$Ti$_{18}$ alloy was 1110 K, and that of the other alloys was all near 1096 K while the $T_{\text{liq}}$ of the alloys were strongly dependent on Ni content $x$. The alloy at $x = 6$ shows the minimum $T_{\text{sol}}$ and $T_{\text{liq}}$ of 1096 K and 1207 K, respectively. The difference between $T_{\text{liq}}$ and $T_g$ can be presented by using a $T_{\text{rg}} = T_g/T_{\text{liq}}$, which showed the minimum value at $x = 6$. 

![Fig. 1 Glass forming ability of amorphous Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys.](image1)

![Fig. 2 XRD patterns and GFA of amorphous Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys.](image2)

![Fig. 3 DSC traces obtained from the ribbon amorphous Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ alloys.](image3)
The parameter $\gamma = T_s/(T_g + T_{liq})$ increased from 0.364 at $x = 0$ to 0.401 at $x = 6$, and then slightly decreased with further increase of $x$, reaching 0.400 at $x = 15$. $T_g$, $T_s$, $\Delta T_s$, $T_{liq}$, $T_{rg}$ and $\gamma$ of the alloys are summarized in Table 1.

Mechanical properties of the Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ glassy rods were investigated by means of the compressive and micro hardness test. Uniaxial compression tests were conducted on the BMG cylinders with a diameter of 2 mm and height of 4 mm, and each alloy sample was tested five times. The stress-strain curves which are the closest results to the mean value of the Cu$_{60-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ ($x = 0, 6, 12$) alloys are shown in Fig. 5. The alloy at $x = 0$ exhibits a fracture strength of about 2020 MPa, however, no plastic deformation region was observed. In contrast, the alloys containing Ni element ($x = 6, 12$) showed some macroscopic plasticity after yielding. The compressive fracture strength and plastic strain were 2034 MPa and 0.7%, respectively, at $x = 6$, and 2190 MPa and 0.6%, respectively, at $x = 12$. Micro hardness of the alloys was increased as in the result of the compressive strength as the Ni was substituted for Cu. The mechanical properties of the alloys are listed in Table 1. The secondary electron images in Figs. 6(a) and (b) were obtained from the specimen surface near the failed area and fracture surface. Shear bands are seen at the region near the fracture, and vein patterns, a typical fracture characteristic of metallic glass alloys, are observed on the fracture surface.

### 4. Discussion

The existence of large $\Delta T_s$ in the BMGs is of technological and scientific interest. By using the viscous flow and superplastic behavior in the $\Delta T_s$, it is possible to consolidate metallic glass powder for large scale fabrication of BMG and also to deform a BMG for application of engineering parts. In the Cu-Ni-Zr-Ti system studied, the $\Delta T_s$ was significantly increased by the addition of Ni, which is similar to the references. According to the studies, the Ni addition suppresses the crystallization of CsCl-type Cu(Zr,Ti) phase from the Cu$_{60}$Zr$_{22}$Ti$_{18}$ alloy melt and enables the direct precipitation of (Cu,Ni)$_{10}$(Zr,Ti)$_7$ phase. i.e. Ni stabilizes the (Cu,Ni)$_{10}$(Zr,Ti)$_7$ phase in Cu-Ni-Zr-Ti, and this results in the significant extension of the $\Delta T_s$. Although the composition of the Cu$_{60}$Zr$_{22}$Ti$_{18}$ alloy studied in this paper is different from that of the Cu$_{60}$Zr$_{22}$Ti$_{18}$ alloy, it is assumed that the Ni plays a similar role to increase the $\Delta T_s$ of Cu-Ni-Zr-Ti alloys. In addition, the increased $\Delta T_s$ can be explained by the large difference in atomic size between Ni and other constituent elements and also by the large interaction energy of Zr-Ni and Ti-Ni. A large atomic size difference between Ni and other constituent elements is favorable to increasing an atomic packing density of the liquid structure, leading to an increase in viscosity in the supercooled liquid region. The heats of the mixing of Zr-Ni and Ti-Ni are $-49$ and $-35$ kJ/mol, respectively. These large negative values of heat of
mixing enhance the interactions among the constituent elements, which can stabilize the supercooled liquid. Owing to the strong interaction of atomic pairs, the long range diffusion of atoms for nucleation and growth of the crystalline phase in the supercooled liquid phase is kinetically restrained, which results in enlarging the $\Delta T_c$. Besides, we need to consider that the high atomic packing density and the interactions among constituent elements contribute to the slight increment of the compressive strength and micro hardness like the widened $\Delta T_c$.

In particular, the Ni containing alloys ($x = 6, 12$) showed some macroscopic plasticity after yielding. The nature of the plasticity in the Cu-Zr bearing monolithic alloys has been studied by Lee et al. They have suggested that the plasticity of metallic glasses is related to the activation energy of the overall crystallization process, and that the metallic glasses with low activation energy for crystallization tend to form nanocrystals during deformation, which would act as initiation sites to form multiple shear bands, leading to enhanced plasticity. In this study, we confirmed the activation energies for overall crystallization by using the Kissinger method. The activation energies for crystallization are about 360, 332 and 324 kJ/mol for the Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ ($x = 0, 6, 12$) alloys, respectively. The alloy at $x = 6, 12$ exhibiting some plasticity showed a lower activation energy for crystallization than the alloy at $x = 0$.

As shown in Fig. 4, the Ni content also affected the melting behavior, especially $T_{liq}$. The alloy ($x = 0$) without Ni content has a relatively high $T_{liq}$ as compared with the alloy with Ni content, showing the two endothermic events during the melting process, which indicate that the composition of alloy is away from a ternary eutectic composition. When the Ni content was increased up to $x = 6$, the alloy showed a lower $T_{liq}$ of about 1207 K, and the melting process exhibited two overlapped endothermic reactions, indicating that composition of the alloy ($x = 6$) was close to a quaternary eutectic point. As the Ni content was further increased, the $T_{liq}$ became higher, reaching 1256 K at $x = 15$.

Many alloy systems with deep eutectic compositions have been reported to have a higher value of $T_{eg}$ and exhibit better GFA. A deep eutectic indicates that the liquid phase is stabilized in a wide temperature range above and below the eutectic point, and the driving force for nucleation and growth of the crystalline phase is relatively small compared with the case of non-eutectic. Accordingly, the amorphous phase upon solidifying liquid is easily formed, avoiding the crystallization.

The amorphous phase is formed by continuous cooling from the liquid state at a rate high enough to avoid the nucleation and growth of a competing crystalline phase in the temperature range between $T_g$ and $T_{liq}$ which can be presented by $T_{eg} = T_g/T_{liq}$. The alloy at $x = 6$ exhibits the minimum temperature range between $T_g$ and $T_{liq}$ and the maximum GFA as shown in Table 1. Therefore, the value of $T_{eg}$ was a good indicator of GFA in the present alloy systems. The $\gamma$ parameter has been used as a parameter for GFA in terms of the crystallization process during cooling and reheating of the supercooled liquid. The relationship between $\gamma$ parameter and maximum diameter of the alloys indicates that the $\gamma$ parameter is also an effective GFA indicator in the alloys investigated.

The solidus temperature of the Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ alloy shown in Fig. 4 was slightly decreased from 1110 K to 1096 K by the substitution of Cu for Ni. The solidus temperature of the Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ alloys, except for the Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ alloy, seems to share the solidus temperature of 1096 K. In addition, the liquidus temperature of Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ alloy was lowered by the Ni addition to 6 at.%, and the maximum GFA was obtained at $x = 6$. Similar to this Cu$_6$Ni$_{1-x}$Zr$_{22}$Ti$_{18}$ BMG development, many BMGs were found to be showing enhanced GFA by the decrease in their melting temperature. For example, BMGs such as Cu-Zr-Ti, Cu-Zr-Al, Cu-Zr-Al-Ag, Cu-Zr-Al-Y, Pt-Cu-P, Pd-Cu-Ni-P developed by small substitution of elements showed a decrease not only in liquids temperature but also in solidus temperature. The decrease in solidus temperature by an element addition indicates that the alloy is laid on another multi component eutectic system consisting of more complicated phases, and this resulted in a remarkable increase of GFA.

There are many eutectic compositions in Cu-Ni-Zr-Ti alloy system owing to the complicated phase diagrams of Cu-Zr, Cu-Ti, Ni-Zr, and Ni-Ti alloys. These alloy systems consist of various binary eutectic compositions surrounded by intermetallic compounds. Therefore, if an alloy having a eutectic temperature below 1096 K were developed in the Cu-Ni-Zr-Ti alloy system, or elements stabilizing the liquid
phase like Ni in Cu-Zr-Ti alloys were found, this could give us a chance to find a new BMG with GFA exceeding a 6 mm-diameter.

5. Conclusion

The glass forming ability and mechanical properties of the Cu$_{54-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ (x = 0, 3, 6, 9, 12, 15) alloys were investigated. The Cu$_{54-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ (x = 6) alloy exhibited the highest GFA. The improved GFA of the Cu$_{54-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ (x = 6) alloy can be explained on the basis of its lowered solidus and liquidus temperature. The Cu$_{54-x}$Ni$_x$Zr$_{22}$Ti$_{18}$ (x = 6, 12) alloys show some macroscopic plasticity after yielding, which can be interpreted in terms of the activation energy for crystallization.

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REFERENCES

16) Clear melting curves from the alloys would not be obtained when using amorphous samples. However, slowly solidified ones showed clear melting curves.