Materials Transactions, Vol. 43, No. 8 (2002) pp. 1952 to 1956
Special Issue on Bulk Amorphous, Nano-Crystalline and Nano-Quasicrystalline Alloys IV

Thermal Stability and Mechanical Strength of Bulk Glassy Ni–Nb–Ti–Zr Alloys

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Bulk glassy Ni-based alloys with high fracture strength exceeding 2700 MPa were prepared in $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ system by copper mold casting. The glassy alloys with distinct glass transition were obtained in the wide composition range from 0 to 35%Ti and 0 to 30%Zr and the largest supercooled liquid region before crystallization was 76 K for $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$. The maximum diameter was 2 mm for $Ni_{60}Nb_{20}Ti_{15}Zr_5$ and the glass transition temperature (T_g), crystallization temperature (T_x) and reduced glass transition temperature (T_g/T_l) of the bulk glassy alloy were 841 K, 898 K and 0.61, respectively. The Young's modulus (E), compressive fracture strength ($\sigma_{c,f}$) and compressive fracture elongation ($\varepsilon_{c,f}$) were 156 GPa, 2770 MPa and 2.4%, respectively, for the bulk alloy. There is a tendency for fracture strength to increase with increasing E, T_g and liquidus temperature (T_l). It is therefore interpreted that the high strength is due to strong bonding nature among the constituent elements.

(Received February 20, 2002; Accepted April 17, 2002)

Keywords: *nickel-based alloy, melt spinning, thermal properties, casting, bulk glassy alloy, mechanical properties*

1. Introduction

Recently, the structure, stability and properties of bulk glassy alloys prepared by casting methods have been one of major research subjects in materials science and engineering because all metallic alloys in a bulk form previously reported had been limited to a crystalline structure. The recent success in synthesizing bulk glassy alloys with useful properties has utilized the reduced instability of supercooled liquid in special alloy systems against crystallization found since 1988.[1–4] The bulk glassy alloys have been found in Mg-[5] and lanthanide (Ln)-[6] systems and then widely extended to Zr-,[7,8] Ti-,[9] Fe-,[10] Pd–Cu-,[11] Pd–Fe-,[12] Co-,[13] Ni-[14] and Cu-[15] based alloys. One of advantage points for these bulk glassy alloys is attributed to their unique mechanical properties. The Young's modulus (E) is three times lower than that for the crystalline alloy with the same tensile strength ($\sigma_{t,f}$), while the $\sigma_{t,f}$ is three times higher than that for the corresponding crystalline alloy.[1–3] Although all bulk glassy alloys exhibit high compressive fracture strength ($\sigma_{c,f}$) as well as high Vickers hardness (H_v), the attainment of high $\sigma_{t,f}$ values comparable to the $\sigma_{c,f}$ have been limited to the Mg-, Ln-, Zr, Ti-, Pd–Cu- and Cu-based alloys. The bulk glassy alloys exhibiting the high $\sigma_{t,f}$ values except the Pd–Cu-based alloy are composed of metallic components without metalloid. However, bulk glassy alloys in Fe-, Co- and Ni-based systems always belong to metal-metalloid type as exemplified for Fe–(Al, Ga)–(P, C, B),[10] Fe–(Zr, Hf, Nb)–B,[16] Co–Fe-(Nb, Ta)–B[13] and Ni–(Cr, Mo, Nb)–(P, B)[17] *etc*. There have been no data on the formation of Fe-, Co- and Ni-based bulk glassy alloys exhibiting high $\sigma_{t,f}$. Great efforts have been devoted to synthesize Fe-, Co- and Ni-based bulk glassy alloys consisting only of metallic components. Very recently, we have succeeded in finding Cu-based bulk glassy alloys belonging to metal-metal type by use of the three empirical component rules[1–3] and reported that the new Cu-based bulk glassy alloys exhibit high $\sigma_{t,f}$ of 2000 to 2500 MPa[15,18–20] which can be evaluated as the highest $\sigma_{t,f}$ value among all bulk glassy alloys reported up to date. The success of the new Cu-based bulk glassy alloys allows us to expect that the future search on the basis of the three empirical component rules results in the formation of a new Ni-based bulk glassy alloy belonging to metal-metal type. This paper intends to present the composition dependence of glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region $\Delta T_x (= T_x - T_g)$ and reduced glass transition temperature (T_g/T_l) of the glassy Ni–Nb–Ti–Zr alloys, and the maximum thickness, mechanical properties and fracture behavior of the Ni-based bulk glassy alloys.

2. Experimental Procedure

Multi-component Ni-based alloy ingots with composition of $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ were prepared by arc melting the mixtures of pure metals in an argon atmosphere. The alloy composition represents nominal atomic percentage. The glassy alloy rods with diameters up to 3 mm were produced by copper mold casting. The glassy alloy ribbons were also produced by melt spinning. The glassy phase was examined by X-ray diffraction and thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The T_l was measured with a differential thermal analyzer (DTA) at a cooling rate of 0.17 K/s. Mechanical properties under a compressive deformation mode were measured with an Instron testing machine. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height. Fracture surface was examined by SEM.

3. Results

Figure 1 shows DSC curves of the melt-spun $Ni_{60}Nb_{20}Ti_{15}Zr_5$, $Ni_{60}Nb_{20}Ti_{10}Zr_{10}$ and $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$ glassy alloys. It is seen that the phase transition of the Ni-based glassy alloys occurs in the order of glass transition, supercooled liquid region and then crystallization. Among the three glassy alloys, the $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$ alloy exhibits the largest ΔT_x of 76 K.

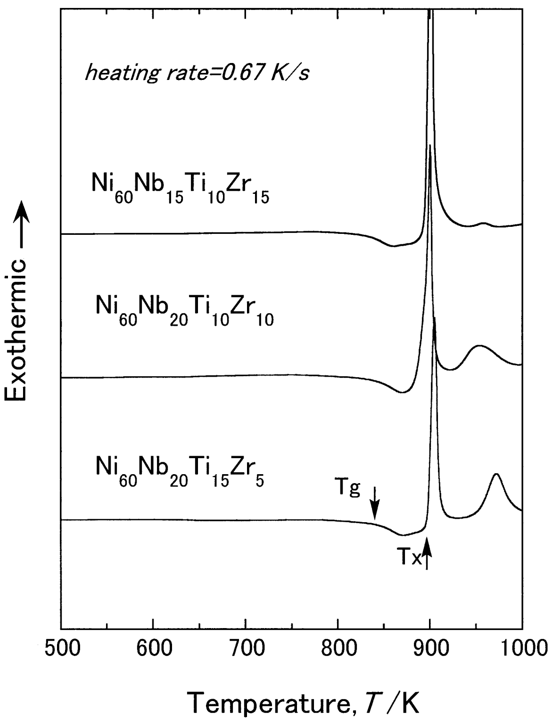

Fig. 1 DSC curves of melt-spun glassy $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$, $Ni_{60}Nb_{20}Ti_{10}Zr_{10}$ and $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloys.

In addition, the glassy alloy with the largest ΔT_x crystallizes through a single exothermic reaction. We have confirmed that the exothermic reaction corresponds to the nearly simultaneous precipitation of NiTi, $NiTi_2$, Ni_4Nb, NiNb and Ni_3Zr phases. Figure 2 shows the compositional dependence of T_g and T_x for the melt-spun $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ glassy alloys. The T_g and T_x increase with increasing Nb content and the increase is more significant for T_x. The difference in the composition dependence between T_g and T_x leads to a maximum ΔT_x of 76 K for $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$ alloy, as shown in Fig. 3. It is also seen in Fig. 3 that the large supercooled liquid region exceeding 50 K is obtained in a rather wide composition range of 5 to 30%Nb, 5 to 10 at%Ti and 0 to 20 at%Zr. The largest ΔT_x value is considerably larger than those (about 50 K) for the other Ni-based glassy alloys such as Ni–Cr–Mo–P–B,[19] Ni–Cr–Nb–P–B[19] and Ni–Zr–Ti-(Si, Sn).[21]

We further measured the T_l by DTA, with the aim of determining the reduced glass transition temperature (T_g/T_l) which can be regarded as one of the most important factors for evaluation of glass-forming ability. It was recognized that the solidification of the $Ni_{60}Zr_{20}Ti_{15}Zr_5$ alloy is practically completed through a single endothermic reaction, leading to a lower liquidus temperature of 1364 K. The DTA curves also suggest that a deep eutectic composition may be located in the vicinity of $Ni_{60}Nb_{20}Ti_{15}Zr_5$. The T_g/T_l values for the present Ni-based glassy alloys were in the range from 0.56 to 0.61 and the highest T_g/T_l was obtained for $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy. The large ΔT_x of 60 K as well as the high T_g/T_l of 0.61 for the $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy indicates that the choice of the alloy composition may lead to the formation of bulk glassy alloys with diameters up to several millimeters by the copper mold casting method.

We have noticed that bulk glassy $Ni_{60}Nb_{20}Ti_{15}Zr_5$ rods are

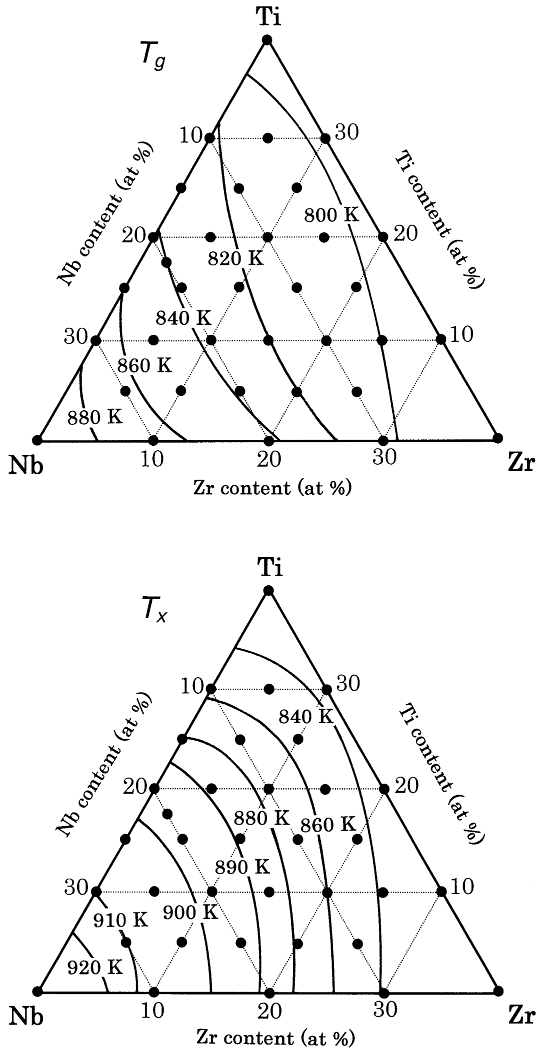

Fig. 2 Composition dependence of glass transition temperature (T_g) and crystallization temperature (T_x) for melt-spun glassy $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ alloys.

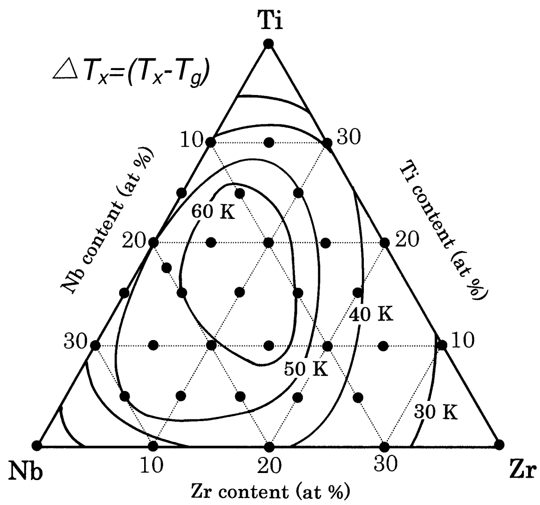

Fig. 3 Composition dependence of supercooled liquid region ΔT_x ($= T_x - T_g$) for melt-spun glassy $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ alloys.

formed in the diameter range up to 2 mm by copper mold casting. The rod samples have a smooth surface with good metallic luster and no distinct ruggedness due to a crystalline phase is seen on the outer surface. The X-ray diffraction patterns of the alloy rods consist only of broad peaks, as exemplified for the alloy rod of 2 mm in diameter in Fig. 4. This diffraction result is also consistent with the absence of a crystalline phase on a micrometer scale by optical microscopy in the etched condition where a crystalline phase is detected. The T_g, T_x and ΔT_x for the 2 mm rod sample were measured as 841 K, 898 K and 57 K, respectively, in agreement with those for the corresponding melt-spun glassy alloy. These results indicate that the glassy alloy rod has the similar disordered structure as that for the glassy alloy ribbon.

Figure 5 shows a stress-elongation curve under a compressive applied load for the glassy $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy rod of 2 mm in diameter. It is seen that the alloy exhibits distinct plastic elongation after yielding. From the stress-elongation curve, its mechanical properties were determined as follows, *i.e.*, 156 GPa for E, 2770 MPa for $\sigma_{c,f}$ and 2.4% for compressive fracture elongation including elastic elongation ($\varepsilon_{c,f}$). It is noticed that the fracture strength level is much higher than those for the other bulk glassy alloys, *e.g.*, about 1800 MPa for Zr-based bulk glassy alloys,[1–3] about 2000 MPa for Cu–Zr–Ti based bulk glassy alloys[12] and 2500 MPa for Cu–Zr–Ti–Be bulk glassy alloys.[20] We have also noticed that the tensile fracture strength and compressive fracture strength increase to 2750 MPa and 3010 MPa, respectively, by the simultaneous addition of Co and/or Cu elements to Ni–Nb–Ti–Zr alloys, in addition to an increase in the maximum rod diameter to 4 mm for glass formation.[22] The additional element effect on the glass-forming ability and mechanical properties of the Ni–Nb–Ti–Zr glassy alloys will be presented elsewhere. This attainment of high $\sigma_{t,f}$ comparable to the $\sigma_{c,f}$ for the present Ni–Nb–Ti–Zr base series is significantly different from the previously reported result that Ni-based bulk glassy alloys in Ni–Cr–(Nb or Mo)–P–B[19] and Ni–Zr–Ti–(Si, Sn)[21] systems are too brittle to measure the tensile fracture strength. The fracture behavior and fracture surface appearance under the compressive deformation mode are shown in Fig. 6. The fracture takes place along the maximum shear plane which is declined by about 45 degrees to the direction of applied load and the fracture surface consists mainly of well developed vein pattern. The feature of the fracture morphology is the same as that for the other bulk glassy alloys with much lower fracture strength.

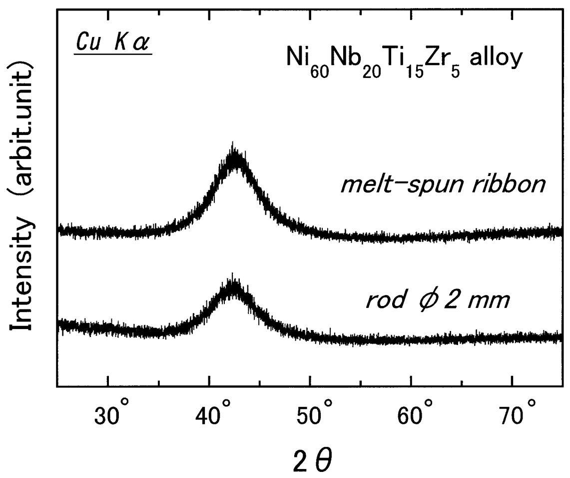

Fig. 4 X-ray diffraction pattern of the cast $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy rod with a diameter of 2 mm. The data of the corresponding melt-spun alloy ribbon are also shown for comparison.

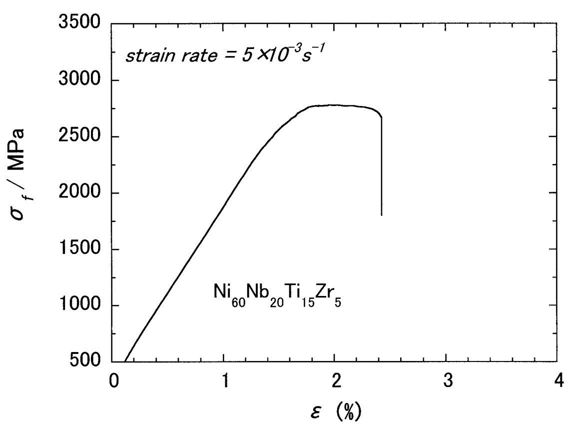

Fig. 5 Stress and elongation curve in compressive deformation mode for the cast bulk glassy $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy.

4. Discussion

We investigated the E and $\sigma_{c,f}$ relationship for the $Ni_{60}Nb_{20}Ti_{15}Zr_5$ bulk glassy alloy, in comparison with the previous data for the other typical bulk glassy alloys. Although the $\sigma_{c,f}$ of the Ni-based glassy alloy lied at the slightly lower side, a rather good linear relation between E and $\sigma_{t,f}$ was recognized. We also examined the $\sigma_{c,f}$ and T_g or T_l relationships for typical bulk glassy alloys including the present Ni-based glassy alloys, the relations between $\sigma_{c,f}$ and T_g or T_l for the bulk glassy alloys are shown in Fig. 7. One can see a clear tendency for $\sigma_{c,f}$ to increase with increasing T_g or T_l. Considering the previous concept that the T_g and T_l of the glassy alloys reflect the bonding force among the constituent elements,[23] it is concluded that the high $\sigma_{c,f}$ values of the present Ni-based bulk glassy alloys originate from the strong bonding nature among the constituent elements.

In addition, we discuss the reason why the present Ni-based bulk glassy alloy exhibited high fracture strength accompanying the distinct plastic elongation of 2.4%, though no distinct plastic elongation was observed even in the compressive deformation mode for all other Ni-based bulk glassy alloys. The Ni-based bulk glassy alloys reported up to date are classified into two groups; (1) metal-metalloid type such as Ni–Cr–Mo–P–B,[17] Ni–Cr–Nb–P–B[17] and Ni–Zr–Ti–(Si, Sn)[21] systems, and (2) metal-metal type as exemplified for Ni–Nb–Ti–Zr and Ni–Nb–Ti–Zr–(Co, Cu)[22] systems. It is recognized that all these Ni-based bulk glassy alloys satisfy the three empirical component rules for the formation of bulk glassy alloys and the stabilization of supercooled liquid;[1–3] (1) multicomponent consisting of more than three elements, (2) significant atomic size mismatches among the main constituent elements, and (3) suitable negative heats of mixing among their elements. However, the ductile nature as demonstrated by the distinct plastic elongation was obtained only for the Ni–Nb–Ti–Zr and Ni–Nb–Ti–Zr–(Co, Cu)[22] alloys. In comparison with the alloy components of the other Ni-based bulk glassy

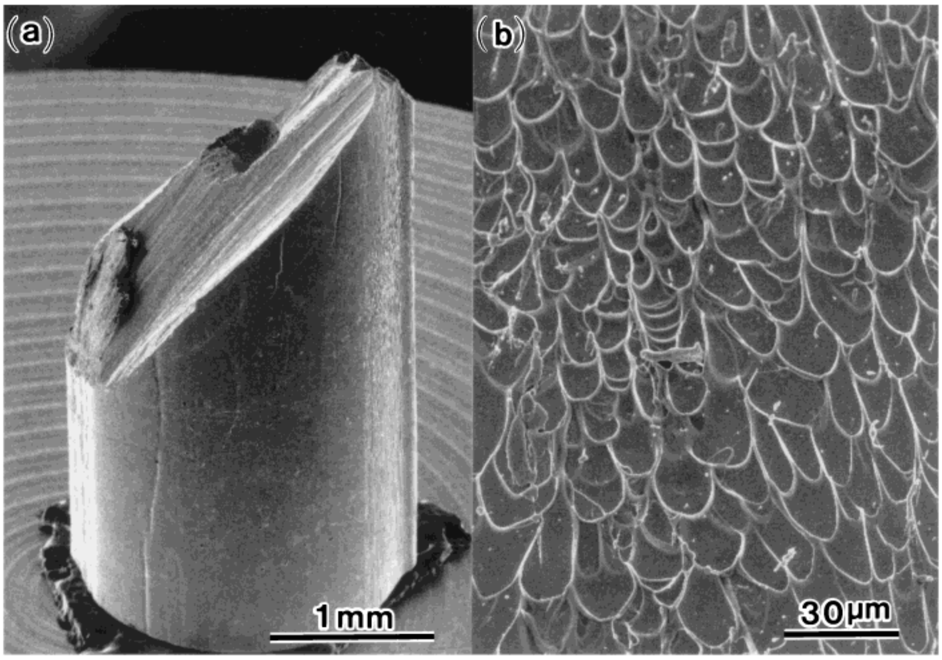

Fig. 6 Fracture surface appearance of the cast bulk glassy $Ni_{60}Nb_{20}Ti_{15}Zr_5$ alloy.

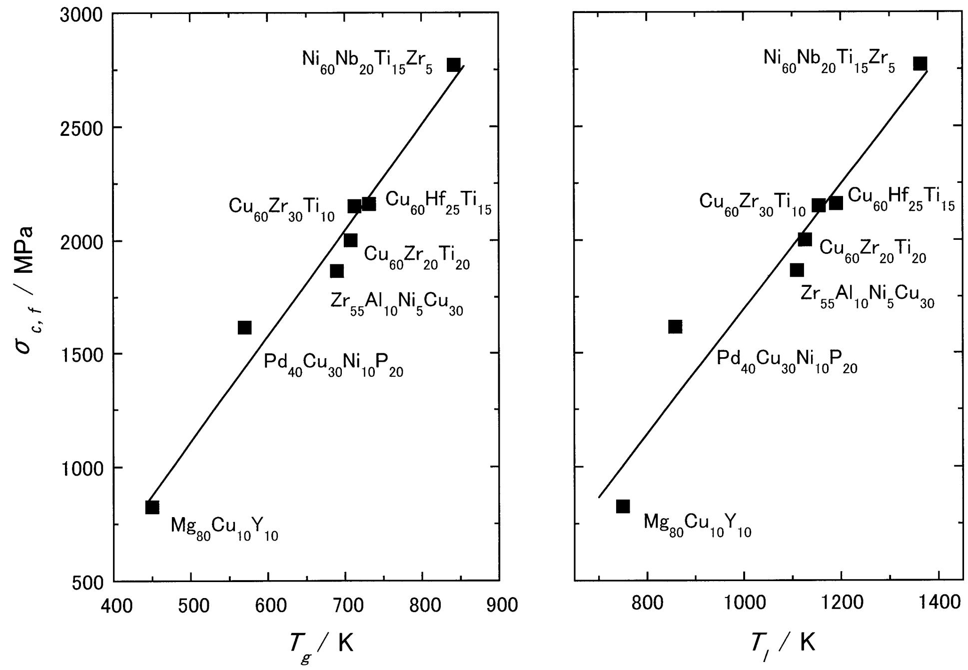

Fig. 7 Relation between compressive fracture strength ($\sigma_{c,f}$) and glass transition temperature (T_g) or liquidus temperature (T_l) for Ni–Nb–Zr–Ti glassy alloys. The data of other bulk glassy alloys are also shown for comparison.

alloys, it is pointed that the Nb addition to the metal-metal type Ni-based alloys is effective for enhancement of ductility. This result suggests that the addition of an element which has a nearly zero heat of mixing against a part of the constituent elements is necessary for the formation of a glassy alloy with good ductility leading to high fracture strength. This concept is also supported from the previous result[23] that the plastic elongation before fracture in a compressive deformation mode increases from nearly zero % for $Cu_{60}Zr_{30}Ti_{10}$ consisting only of the elements with negative heats of mixing to about 2.5% for $(Cu_{0.6}Zr_{0.3}Ti_{0.1})_{95}Nb_5$ and about 4.5% for $(Cu_{0.6}Zr_{0.3}Ti_{0.1})_{95}Ta_5$ containing Cu–Nb or Cu–Ta atomic pairs with positive heats of mixing.

5. Conclusions

In the $Ni_{60}Nb_{40-x-y}Ti_xZr_y$ glassy alloys, the glass transition followed by a supercooled liquid region was observed in a wide composition range of 0 to 35%Ti and 0 to 30%Zr. The T_g and T_x increase from 793 to 895 K and 782 to 929 K, respectively, with increasing Nb content and the largest $\Delta T_x (= T_x - T_g)$ was 76 K for $Ni_{60}Nb_{15}Ti_{10}Zr_{15}$. The use of the alloy component enabled us to form bulk glassy alloy rods with diameters up to 2 mm. The bulk alloy exhibits high fracture strength of 2770 MPa in conjunction with E of 156 GPa and plastic elongation of 0.8%. The fracture mode in agreement with that for other bulk glassy alloys with good ductility. The fracture strength is much higher than those of the bulk glassy alloys in other alloy systems. The strength was found to have a proportional relation with E, T_g and T_l. The bonding force among the constituent elements is concluded to be a dominant factor for the high strength.

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