Synthesis and Thermal Stability of New Ni-Based Bulk Glassy Alloy with Excellent Mechanical Properties

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The thermal stability, glass-forming ability (GFA) and mechanical properties of the Ni-Ta-Ti and Ni-Ta-Ti-Zr glassy alloys have been investigated. As the Ti content increases, the supercooled liquid region $\Delta T_x (= T_x - T_g)$ and reduced glass transition temperature (T_g/T_l) of $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ glassy alloys increase, showing maximum values of 63 K at 20%Ti and 0.59 at 25%Ti, respectively, and then gradually decrease. The addition of Zr to Ni-Ta-Ti alloys is effective for the increase in ΔT_x and T_g/T_l . The maximum ΔT_x and T_g/T_l values of 73 K and 0.60, respectively, are obtained for $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ alloy. The Ni-Ta-Ti-Zr glassy alloys were formed in the rod form with diameters of over 1.0 mm by copper mold casting. The Ni-Ta-Ti-Zr bulk glassy alloys exhibit excellent mechanical properties, *i.e.*, the compressive fracture strength ($\sigma_{c,f}$) of 3180–3220 MPa and the compressive plastic elongation ($\varepsilon_{c,p}$) of 0.2–0.4%. [doi:10.2320/matertrans.47.2358]

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1. Introduction

It is known that amorphous alloys have characteristic physical and chemical properties such as high strength, high corrosion resistance and good soft magnetic properties, which are significantly different from the corresponding crystalline alloys.¹⁾ However, the requirement of rapid solidification has led to strict limitation of their material shape to ribbons, wires and powders and its limitation has restricted further extension of their application fields. Since the findings of the stabilization of supercooled liquid in multi-component alloys consisting only of metallic elements in 1988, followed by the syntheses of bulk glassy alloys by use of the stabilization of supercooled liquid, much effort has been devoted to develop a new bulk glassy alloy exhibiting high glass-forming ability (GFA) and useful engineering properties. The development of bulk glassy alloys was focused on Mg-,²⁾ lanthanide-³⁾ and early transition metal (ETM)-based alloy systems^{4,5)} in the early stage period between 1988 and 1993, and then much attention has been paid to the late transition metal (LTM)-based bulk glassy alloys such as Fe-,^{6–9)} Co-,^{10,11)} Cu-^{12–18)} and Ni-^{19–24)} based alloys because of their more importance in engineering aspects. The advantage points for the LTM bulk glassy alloys include higher strength,^{7,11–24)} and good soft magnetic properties,^{8–11)} excellent corrosion resistance,²³⁾ and lower materials cost.^{6–9,12,14)} It is noticed that high fracture strength with good toughness can be obtained for the LTM-based bulk glassy alloys consisting only of metallic elements, such as Cu-^{12–18)} and Ni-^{20,21,23–25)} based systems, and the Ni-Nb-based bulk glassy alloy has the highest fracture strength.

The synthesis of Ni-Nb-based bulk glassy alloys has been reported in 2002.²⁰⁾ The Ni-based bulk glassy alloy rods with diameters of 1.5–3 mm were fabricated in the Ni-Nb-Ti ternary and Ni-Nb-Ti-based multi-component alloys, and exhibited high strength of ~ 3080 MPa,^{20,21,24,25)} distinct

plastic strains, high thermal stability, and excellent corrosion resistance in aggressive acids.²⁶⁾ In addition, their alloys are expected to replace the conventional graphite bipolar plates in fuel cells. Recently, we have investigated the effect of different elements on the corrosion resistance of the Ni-Nb-based glassy alloys, and found that substitution of Ta for Nb in the Ni-Nb-based glassy alloys was very effective for increasing the corrosion resistance in fluoride containing acid solution at a high temperature.²⁷⁾ However, little is known about the effect of substitution of Ta for Nb on the thermal stability of the supercooled liquid, glass-forming ability and mechanical properties of the Ni-Ta-based glassy alloys. The heats of mixing in the Ni-Nb and Ni-Ta pairs as well as the atomic sizes of Ta and Nb are similar with each other.^{28,29)} In addition, Ta metal has a much higher melting temperature than Nb. Therefore, a new type of Ni-Ta-based bulk glassy alloy is expected to exhibit higher mechanical strength and thermal stability than those of Ni-Nb-based bulk glassy alloys. This paper presents the thermal stability, glass-forming ability (GFA) and mechanical properties of the $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ ($x = 0$ to 40) and $\text{Ni}_{60}\text{Ta}_{40-x-y}\text{Ti}_x\text{Zr}_y$ ($y = 0$ to 30) glassy alloys. The reasons for the high thermal stability and mechanical properties for the Ni-Ta-based bulk glassy alloys are also discussed.

2. Experimental Procedure

Multi-component Ni-based alloy ingots with nominal composition of $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ ($x = 0$ to 40) and $\text{Ni}_{60}\text{Ta}_{40-x-y}\text{Ti}_x\text{Zr}_y$ ($y = 0$ to 30) were prepared by arc melting the mixtures of pure Ni, Ta, Zr and Ti metals in an argon atmosphere. The purity of metals was over 99.5 mass%. Alloy ingots were re-melted five times to ensure chemical homogeneity. The mass losses were measured for each ingot after melting and were less than 0.1 mass%. The glassy alloy was produced by copper mold casting for bulk cylindrical rods with diameters up to 1.5 mm and by melt spinning for ribbons with a cross section of 0.02×1.2 mm². The glassy phase was identified by X-ray diffractometer using Cr-K α

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Fig. 1 DSC curves of melt-spun $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ ($x = 0$ to 40 at%) glassy alloys.

radiation and thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The melting and liquidus temperatures were measured with a differential thermal analyzer (DTA) at a heating rate of 0.33 K/s. Mechanical properties were measured with an Instron testing machine. The gauge dimension of specimens was 1 mm in diameter and 2 mm in height for compressive test and the strain rate was $5 \times 10^{-4} \text{ s}^{-1}$. The fracture surface was examined by scanning electron microscopy (SEM).

3. Results

The X-ray diffraction patterns and DSC curves showed that the melt-spun $\text{Ni}_{100-x}\text{Ta}_x$ ($x = 35$ to 45) ribbons were composed of a glassy single phase. However, the supercooled liquid region (ΔT_x) and the reduced glass transition temperature (T_g/T_l) are below 40 K and 0.58, respectively, indicating that the Ni-Ta binary glassy alloys do not have high thermal stability of supercooled liquid and high GFA.^{30,31)}

We examined the effect of Ti addition on the thermal stability of supercooled liquid in the glassy alloy series of $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$. Figure 1 shows DSC curves of the melt-spun $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ ($x = 0$ to 40) glassy alloys. The glass transition temperature (T_g) and crystallization temperature (T_x) decrease from 1005 to 861 K and 1042 to 903 K, respectively, with increasing Ti content from 0 to 30 at%, while the ΔT_x increases from 38 to 63 K with increasing Ti content from 0 to 20 at% and then decreases to 42 K with a further increase in Ti content to 30 at%. No glass transition is observed for $\text{Ni}_{60}\text{Ti}_{40}$. We further measured the liquidus temperature (T_l) by DTA. The T_l and T_g/T_l were plotted as a function of Ti content for the $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ glassy alloys in Fig. 2. It can be seen that the T_l values of the ternary alloys

Fig. 2 Liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) as a function of Ti content for the $\text{Ni}_{60}\text{Ta}_{40-x}\text{Ti}_x$ ($x = 10$ to 40 at%) glassy alloys.

significantly decrease with increasing Ti content. However, the T_g/T_l increases from 0.57 to 0.59 with increase of Ti content from 10 to 25 at%, and then decreases with a further increasing Ti content. The large ΔT_x values exceeding 60 K and high T_g/T_l above 0.58 are simultaneously obtained in the Ti concentration range of 20–25 at%. It is therefore concluded that the addition of Ti to Ni-Ta binary glassy alloys is effective in increasing the stability of supercooled liquid and GFA. We examined the GFA of Ni-Ta-Ti ternary alloys by copper mold casting, but the critical rod diameter for formation of the glassy phase was below 1.0 mm.

We further examined the effect of Zr addition on the thermal stability of supercooled liquid and GFA of the Ni-Ta-Ti ternary glassy alloys. Figure 3 shows DSC curves of the melt-spun $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{25-x}\text{Zr}_x$ ($x = 0$ to 25) glassy alloys. It can be seen that the ΔT_x increases with increasing Zr content from 0 to 5 at%, and then decreases with a further increase in Zr content to 25 at%. The 5 at% Zr alloy shows a maximum ΔT_x of 73 K. Figure 4 shows the changes in the T_l and T_g/T_l with Zr content for the $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{25-x}\text{Zr}_x$ ($x = 0$ to 25) and $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{20-x}\text{Zr}_x$ ($x = 0$ to 20) glassy alloys. The lowest T_l at 5 at% Zr causes the highest T_g/T_l of 0.60 for both the alloy series, and the further increase in Zr content results in a decrease in T_g/T_l . The large ΔT_x of over 60 K as well as the high T_g/T_l of 0.60 for the $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ alloys indicates that the choice of their alloy compositions may lead to the formation of bulk glassy alloys by copper mold casting.

The cast $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ rods with a diameter of 1.0 mm were produced. The XRD patterns of the alloy rods were shown in Fig. 5. The XRD patterns of the rods consist only of a broad peak, and no diffraction peak

Fig. 3 DSC curves of melt-spun $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{25-x}\text{Zr}_x$ ($x = 0$ to 25 at%) glassy alloys.

Fig. 4 Liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) as a function of Ti content for the $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{25-x}\text{Zr}_x$ ($x = 0$ to 25) and $\text{Ni}_{60}\text{Ta}_{20-x}\text{Ti}_{20-x}\text{Zr}_x$ ($x = 0$ to 20) glassy alloys.

corresponding to a crystalline phase is seen, indicating that a glassy phase is formed. The further increase in the rod diameter to 1.5 mm resulted in the precipitation of crystalline phases. It is therefore concluded that the critical rod diameter for formation of the glassy phase lies between 1.0 and

Fig. 5 X-ray diffraction patterns of $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ alloy rods with a diameter of 1.0 mm.

Fig. 6 Compressive stress-elongation curves of cast $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ glassy rods with diameters of 1.0 mm.

1.5 mm. We also measured the T_g , T_x and heat of crystallization ΔH_c of these cast alloy rods on the basis of DSC curves. It was confirmed that the T_g , T_x and (ΔH_c) are nearly the same between the bulk and ribbon samples, being consistent with the result obtained by XRD.

Figure 6 shows the stress-elongation curves under a compressive applied load for the bulk glassy $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ alloy rods of 1.0 mm in diameter. The alloys exhibit excellent mechanical properties. That is, the compressive fracture strength ($\sigma_{c,f}$) and compressive plastic elongation ($\varepsilon_{c,p}$) are 3180 MPa and 0.4%, respectively, for the former alloy, and 3220 MPa and 0.2%, respectively, for the latter alloy. The fracture behavior and fracture surface appearance are exemplified for the $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ glassy alloy rod in Fig. 7. The fracture occurs along the maximum shear plane, which is declined by about 40 degrees to the direction of applied load (Fig. 7(a)), and the fracture surface consists mainly of a well-developed vein pattern (Fig. 7(b)) typical to other bulk glassy alloys with good ductility.^{20,30} Many shear bands which are marked with arrows are also observed on the rod surface (Fig. 7(c)). The appearance of the plastic strain can thus be attributed to the generation of the shear bands.

Fig. 7 Fracture surface appearance of the cast glassy $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ alloy rod.

4. Discussion

We discuss the reason for the significant effect of Ti and Zr additions on the improvement of thermal stability and glass-forming ability of the Ni-Ta glassy alloys. It has been reported that the high thermal stability of supercooled liquid and high GFA leading to the formation of a bulk glassy alloy is obtained in the multi-component alloy systems satisfying the following three empirical component rules,^{30,31)} *i.e.*, (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12% among the main three elements, and (3) negative heats of mixing among the main elements. In the Ni-Ta-Ti-Zr system, their atomic sizes change in the order of Zr (0.162 nm) $\gg$ Ta (0.147 nm) $>$ Ti (0.143 nm) $\gg$ Ni (0.125 nm).²⁸⁾ Furthermore, the heats of mixing have been estimated to be -29 kJ/mol for Ni-Ta, -49 kJ/mol for Ni-Zr and -39 kJ/mol for Ni-Ti.²⁹⁾ The present combinations of atomic sizes can produce an efficiently dense random packing structure, which is often associated with low interfacial energy and high viscosity of liquids. In this glassy structure, the atomic diffusivity is also reduced, leading to the suppression of nucleation and growth reactions of a crystalline phase from liquid. In addition, the formation of the unique glassy structure is also attributed to the existence of the strongly attractive bonding Ni-Ta, Ni-Zr and Ni-Ti pairs, which can improve the local packing efficiency and restrain long range diffusion of atoms. Thus, these factors lead to the high thermal stability of the supercooled liquid against crystallization.³¹⁾

It is also noticed that the compressive fracture strength $\sigma_{c,f}$ is much higher than those for the other metal-metal type of bulk glassy alloys, *e.g.*, 600–900 MPa for Ln- and Mg- based bulk glassy alloys,^{32,33)} 1500–2500 MPa for Zr- and Cu-based bulk glassy alloys,^{12–14,16,31)} and 2700–3085 MPa for other Ni-based bulk glassy alloys.^{21,22,25)} With the aim of investigating the origin for the high $\sigma_{c,f}$ of the Ni-based bulk glassy alloys, the relation between $\sigma_{c,f}$ and T_g for typical bulk glassy alloys including the present Ni-Ta-Ti-Zr glassy alloys is shown in Fig. 8. One can see a clear tendency for $\sigma_{c,f}$ to increase with increasing T_g . Considering the previous concept that the T_g of the glassy alloys reflects the bonding force among the constituent elements,³⁴⁾ it is concluded that the high $\sigma_{c,f}$ value of the present Ni-based Ni-Ta-Ti-Zr bulk glassy alloy originates from the strong bonding nature among the constituent elements.

Fig. 8 Relation between compressive fracture strength ($\sigma_{c,f}$) and glass transition temperature (T_g) for the $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ glassy alloy rod. The data of other metal-metal type of bulk glassy alloys are also shown for comparison. (1) $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_5\text{Co}_5$; (2) $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$; (3) $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$; (4) $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$; (5) $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$; (6) $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$; (7) $\text{Ni}_{40}\text{Ti}_{20}\text{Zr}_{25}\text{Al}_{10}$; (8) $\text{Ni}_{60}\text{Nb}_{20}\text{Ti}_{15}\text{Zr}_5$; (9) $\text{Ni}_{60}\text{Nb}_{25}\text{Ti}_{15}$; (10) $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$.

5. Summary

The thermal stability and GFA of Ni-Ta-based glassy alloys increase by the addition of Ti and Zr. The large ΔT_x exceeding 60 K and high T_g/T_l of over 0.59 were obtained in a composition range of 15–25 at% Ta, 20–25 at% Ti, and 5–10 at% Zr. The new Ni-based bulk glassy alloys with a diameter of 1.0 mm were fabricated for the $\text{Ni}_{60}\text{Ta}_{20}\text{Ti}_{15}\text{Zr}_5$ and $\text{Ni}_{60}\text{Ta}_{15}\text{Ti}_{20}\text{Zr}_5$ alloys. The Ni-Ta-Ti-Zr bulk glassy alloys exhibit excellent mechanical properties, *i.e.*, compressive fracture strength of ~ 3180 – 3220 MPa, and plastic elongation of ~ 0.2 – 0.4% . The fracture strength reported in this paper may be the highest among the ductile bulk glassy alloys ever obtained.

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