Thermal and mechanical properties of the Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8} based bulk metallic glass microalloyed with silicon

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Abstract

The amorphous alloy rods of (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} (x = 0.25, 0.5, 0.75, 1) with a diameter of 2−6 mm were prepared by drop casting method in an Ar atmosphere. The thermal properties, including glass forming ability (GFA) and thermal stability during isothermal annealing of these amorphous alloys, and the mechanical properties have been systematically investigated by the combination of DSC, XRD, SEM, TEM, and compression test. The result of X-ray diffraction reveals that these entire (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} alloy rods exhibit a typical amorphous diffraction pattern with only a broad maximum around 2θ around 40 degree. Both T\textsubscript{g} (glass transition temperature) and T\textsubscript{x} (crystallization temperature) of these (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} alloys increase with the silicon addition. In addition, both the activation energy of crystallization and the incubation time of isothermal annealing these (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} amorphous alloys indicate that the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{99.25}Si\textsubscript{0.75} alloy possesses the best thermal stability in the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} alloy system. In parallel, the result of compression test shows that the yield strength increases with the addition of Si content and reaches to a maximum value about 1750 MPa with 3% plastic strain for the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{99.25}Si\textsubscript{0.75} amorphous alloy.

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1. Introduction

Numbers of BMGs (bulk metallic glasses) reveal many attracting interests for scientific research and engineering application because of their exceptional properties, such as a high strength up to 5 GPa [1], high hardeness, high elastic strain up to 2%, good wear resistances, and near perfect as-cast surfaces [2–5]. Several intermetallic bulk glassy materials by consolidation of the base composition (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{99.25}Si\textsubscript{0.75} alloy system. In parallel, Jang et al. have reported that adding silicon into the Zr-base amorphous alloy can significant increase their thermal stability [10,11]. Therefore, the high GFA Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8} amorphous alloy which compositionally designed by thermodynamics and deep eutectic methodology [12] is selected as the base alloy for studying the effect of microalloying with silicon (an element can cause negative heat of mixing with the base composition) on its crystallization behavior and thermal stability.

2. Experimental procedure

The alloy ingots based on the compositions of (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} (x = 0.25, 0.5, 0.75, 1) by atomic percentage were firstly prepared by arc melting of the appropriate mixture of pure elements, including Zr (99.8 wt% purity), Ni (99.9 wt% purity), Cu (99.99 wt% purity), Al (99.99 wt% purity), and Si (99.99% purity), under a Ti-gettered argon atmosphere. Then the alloy ingots were remelted in an arc furnace under a purified argon atmosphere. After complete melting, the liquid alloy was drop cast into the water-cooled Cu mold to form alloy rods with diameter around 40 degree. Both T\textsubscript{g} (glass transition temperature) and T\textsubscript{x} (crystallization temperature) of these (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} alloys increase with the silicon addition. In addition, both the activation energy of crystallization and the incubation time of isothermal annealing these (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} amorphous alloys indicate that the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{99.25}Si\textsubscript{0.75} alloy possesses the best thermal stability in the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{100−x}Si\textsubscript{x} alloy system. In parallel, the result of compression test shows that the yield strength increases with the addition of Si content and reaches to a maximum value about 1750 MPa with 3% plastic strain for the (Zr\textsubscript{53}Cu\textsubscript{30}Ni\textsubscript{9}Al\textsubscript{8})\textsubscript{99.25}Si\textsubscript{0.75} amorphous alloy.

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an aspect ratio of 2:1 (height/diameter) are tested in compression under an initial strain rate of $2 \times 10^{-4} \text{s}^{-1}$ at room temperature by using a MTS 810 universal testing machine. Both ends of the specimens are polished to make them parallel to each other prior to the compression test. The fracture surfaces of the deformed specimens are examined by scanning electron microscopy (SEM, Hitachi S4700 FESEM) with EDS.

3. Results and discussions

Fig. 2(a) shows the X-ray diffraction patterns obtained from the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}$ ($x = 0.25, 0.5, 0.75, 1$) amorphous alloy rods with 4 mm in diameter. There is no resolvable crystalline peak in the $2\theta$ range of 20–80°, but only a broad maximum is observed in the range of 30–50° for all of the alloys in this study. In addition, the TEM observation also revealed that a uniform amorphous morphology in the as-quenched rod with diameter of 4 mm for the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{99.75}Si_{0.25}$ amorphous alloy, as shown in Fig. 2(b). This indicates that amorphous state of these alloys had been achieved by Cu-mold drop casting method. In addition, the typical outlook of the amorphous rods from 2 to 6 mm for the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}$ ($x = 0.25, 0.5, 0.75, 1$) alloy (as shown in Fig. 1(b) and (c)) shows the characteristic shining surface.

The DSC scans of the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}$ amorphous alloys rods with diameter of 4 mm are shown in Fig. 3. All of the samples exhibit a clear glass transition followed by a supercooled liquid region and then exothermic reaction due to crystallization. In addition, the lowest liquidus temperature (about 1132 K) occurs at the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{99.75}Si_{0.25}$ alloy, as shown in Table 1. According to the analyses of Turnbull [13], the best metallic glass forming alloys are at or near deep eutectic composition and also result in obtaining highest reduced glass transition temperature $T_{rg} (T_{rg} = T_g / T_l)$. This implies that the alloy $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{99.5}Si_{0.5}$ would retain a high glass forming ability.

According to the result of DSC analysis in Table 1, the value of GFA index, $\gamma$ ($\gamma = T_x / T_g + T_l$) [14] and $\gamma_m$ ($\gamma_m = T_x / T_g + T_l$) [15] all exhibit an increasing trend with the silicon additions. As increases Si content to 0.5 at.% to 1.0 at.%, the $\gamma$ and $\gamma_m$ of the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}$ ($x = 0.5, 0.75, 1.0$) amorphous alloys reach to the highest value of 0.430 and 0.774, respectively. This suggests that the optimum GFA would occur at the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{99}Si_{1}$ amorphous alloy. In comparison the value of $\gamma$ and $\gamma_m$ with the base alloy, it is suggested that the Si element present a positive effect on increasing GFA in the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})$ alloy system.

| Thermal parameters of the $(Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}$ ($x = 0-1$) alloys. |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $T_x$ (K) | $T_g$ (K) | $T_l$ (K) | $\Delta T_x$ | $T_{rg}$ (K) | $\gamma$ | $\gamma_m$ |
| 0 at.% Si | 698 | 773 | 1135 | 75 | 0.614 | 0.421 | 0.747 |
| 0.25 at.% Si | 691 | 773 | 1136 | 82 | 0.608 | 0.423 | 0.752 |
| 0.5 at.% Si | 716 | 789 | 1132 | 73 | 0.632 | 0.426 | 0.761 |
| 0.75 at.% Si | 702 | 786 | 1137 | 84 | 0.617 | 0.427 | 0.765 |
| 1 at.% Si | 711 | 794 | 1132 | 83 | 0.628 | 0.430 | 0.774 |
The activation energy of crystallization for the \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_{x} \) alloys was determined by means of the Kissinger plot \([16]\),

\[
\ln \left( \frac{b}{T_p^2} \right) = -\frac{E_a}{RT} + \text{constant} \tag{1}
\]

where \( b \) is the heating rate, \( T \) is the specific temperature, \( R \) is the gas constant, and \( E_a \) is the activation energy. By substituting \( T \) with \( T_p \) (peak temperature of crystallization) in equation (1), the activation energy of crystallization can be determined from the slope of a plot of the \( \ln \left( \frac{b}{T_p^2} \right) \) as a function of \( 1/T_p \). The \( \ln \left( \frac{b}{T_p^2} \right) \) as a function of \( 1/T_p \) is plotted in Fig. 4(a). Fig. 4(b) shows the activation energy of crystallization calculated by Kissinger plot as a function of Si content for \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_{x} \) alloys. The activation energy of these \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_{x} \) alloys decreases with Si content at beginning and then reaches to the maximum (295 kJ/mol) at the \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75} \) amorphous alloy. This implies that the \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75} \) may have the best thermal stability for the \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_{x} \) alloy system.

By using the Johnson-Mehl-Avrami (JMA) isothermal analysis for volume fraction \( x \) transformed as a function of time \( t \) based on the following equation (2):

\[
x(t) = 1 - \exp\left[-(kt)^{n}\right] \tag{2}
\]

\( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_{x} \) amorphous alloys were annealed isothermally at several temperatures between \( T_g \) and \( T_x \). To construct the JMA plots, the volume fraction of crystallization at time \( t \) was assumed to be the same as that of heat released. Therefore, the volume fraction of crystallization \( x \) which obtained by measuring the partial area under peak up to time \( t \) versus as the annealing time is plotted as shown in Fig. 5. In parallel, the incubation time as a function of isothermal annealing temperature exhibits an increasing trend with Si addition as shown in Fig. 6. Base on the result of incubation time, the optimum thermal stability occurs at the \( (\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75} \) amorphous alloy. Since the covalent atomic radius of Si (0.132 nm) is just between the atomic group of \([\text{Zr} \ (0.160 \text{ nm}), \text{Al} \ (0.143 \text{ nm})]\) and \([\text{Cu} \ (0.128 \text{ nm}), \text{Ni} \ (0.125 \text{ nm})]\), that the addition of Si would increase the packing density of the base alloy. In addition, both the Zr–Si (−67 kJ/mol) and Ni–Si (−23 kJ/mol) binary system have a large negative heat of mixing \([17]\) which can form strong atomic bonding of Zr–Si and Ni–Si.
Fig. 7. Hardness as a function of Si addition for \((Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}\) \((x = 0 – 1)\) BMG rods with diameter of 4 mm.

Fig. 8. Compression stress–strain curves of the \((Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}\) BMG rods with diameter of 4 mm.

Fig. 9. SEM images of different type vein pattern at some area of the fracture surface for the \((Zr_{53}Cu_{30}Ni_{9}Al_{8})_{100-x}Si_{x}\) BMG rods with diameter of 4 mm after compression test.
atomic pairs. Therefore, the increase of thermal stability for the base alloy with Si addition is suggested contributing by the increase of their atomic packing density as well as their Zr–Si and Ni–Si strong atomic bonding. This evidence is in agreement with the previous report [10,18]. Si would present a positive effect on improving the thermal stability of some Zr-based BMGs.

The result of hardness test for these \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) amorphous alloys exhibits a clearly increasing trend with Si addition and reaches to the value about 580 in Hv for the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99}\text{Si}_1\) amorphous alloy as shown in Fig. 7. This is presumed to be caused from an increase in the packing density by adding the smaller Si atom in the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100}\text{Si}_1\) alloy system [19]. On the other hand, the result of compression test exhibits similar increasing trend with the Si content on the yield strength and the maximum yield strength about 1750 MPa with 3% plastic strain occurs at the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75}\) amorphous alloy (Fig. 8).

The entire fracture surface of these \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) BMG rods after compression test exhibits more or less area of typical vein pattern. However, the fracture surface of the BMG rods with different Si content presents quite different morphology of vein pattern, such as the area fraction of vein pattern and the width of vein size. SEM images of different type vein pattern at some area of the fracture surface for the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) BMG rods with diameter of 4 mm after compression test are shown in Fig. 9. The densest of vein pattern with average vein size around 30 μm was found from the fracture surface of the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100}\text{Si}_1\) base BMG rod, which performs the largest plastic strain. This is in agreement with the suggestion by Inoue [20]. The increase in the fraction of veins area on the fracture surface suggests the increase in the area of shear deformation region which results in increasing the energy required for plastic deformation and the final fracture.

4. Conclusion

Base on the results of thermal analyses, X-ray diffraction, and TEM observation for the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) (x = 0.25, 0.5, 0.75, 1) amorphous alloys, the effect of microalloying with Si on the glass forming ability and thermal properties can be summarized as follows:

(1) The value of GFA index, γ and γ_m all exhibit an increasing trend with the silicon additions. As the Si content increases to 0.5–1.0 at.% the γ and γ_m of the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) (x = 0.5, 0.75, 1.0) amorphous alloys reach to the value more than 0.426 and 0.761. This suggests that the Si element present a positive effect on increasing GFA in the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) alloy system.
(2) Both the activation energy of crystallization and the incubation time of isothermal annealing these \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) amorphous alloys indicate that the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75}\) alloy posses the best thermal stability in the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100-x}\text{Si}_x\) alloy system. The increase of thermal stability for the base alloy with Si addition is suggested contributing by the increase of their atomic packing density as well as their Zr–Si and Ni–Si strong atomic bonding.
(3) The result of compression test shows that the yield strength increases with the addition of Si content and reaches to a maximum value about 1750 MPa with 3% plastic strain for the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{99.25}\text{Si}_{0.75}\) amorphous alloy.
(4) The densest of vein pattern with average vein size around 30 μm was found from the fracture surface of the \((\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_{9}\text{Al}_{8})_{100}\text{Si}_1\) base BMG rod, which performs the largest plastic strain. The increase in the fraction of veins area on the fracture surface suggests the increase in the area of shear deformation region which results in increasing the energy required for plastic deformation and the final fracture.

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