Crystallization and fracture behavior of the Zr_{65-x}Al_{7.5}Cu_{17.5}Ni_{10}Si_x bulk amorphous alloys

J.S.C. Jang a,∗, Y.W. Chen a, L.J. Chang a, H.Z. Cheng a, C.C. Huang b, C.Y. Tsau c

a Department of Materials Science and Engineering, I-Shou University, Section 1, Shiucheng Road, Dashu Shiang, Kaohsiung County 84008, Taiwan, ROC
b Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC
c Department of Materials Science and Engineering, National Chen-Kung University, Tainan, Taiwan, ROC

Received 17 May 2004; received in revised form 10 August 2004; accepted 25 August 2004

Abstract

The crystallization behavior of amorphous Zr_{65-x}Al_{7.5}Cu_{17.5}Ni_{10}Si_x alloys, x = 0–10, was studied by means of differential scanning calorimetry, X-ray diffractometry, and TEM. The calculated T_g (T_l) for these amorphous alloys increases with increasing silicon content from 0.55 to 0.60, which indicates that the silicon addition could improve the GFA for the Zr_{65-x}Al_{7.5}Cu_{17.5}Ni_{10}Si_x alloys. The activation energy of crystallization of the alloy 4Si was about 365 ± 5 kJ mol⁻¹, both determined by the Kissinger and Avrami plot. This value is about 20% higher than the base alloy (314 kJ mol⁻¹), which implies that the silicon addition can increase the thermal stability for the Zr-based alloy. The average value of the Avrami exponent n were calculated to be 1.7–2.5 for the alloys in this study. In addition, the cube of crystal size as a function of isothermal annealing time presents a linear relationship for the Zr_{61}Al_{7.5}Cu_{17.5}Ni_{10}Si_4 alloy. During isothermal annealing the Zr_{61}Al_{7.5}Cu_{17.5}Ni_{10}Si_4 alloy at 698 K, the Zr_2Cu crystal with average size of 105 nm was first observed at the early stage (30% crystallization ratio) of crystallization. In addition, both nano-crystals of the ZrCu (∼100 nm) and the Zr_3Al (∼30 nm) were also observed to precipitate from the amorphous matrix upon the middle stage (50% crystallization ratio) of crystallization. The fracture surface presents typical ductile vein pattern for 4Si amorphous alloy ribbon after bented to 180°. However, a ductile–brittle transition phenomenon occurs at the amorphous ribbon after 50% crystallization ratio of isothermal annealing at the temperature between T_g and T_x.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Bulk amorphous; Zirconium-based alloy; Glass transition temperature; Crystallization kinetics; Fracture behavior

1. Introduction

A number of new bulk metallic glasses (BMGs) with a wide supercooled liquid region (defined as the difference between the glass transition temperature T_g and the onset crystallization temperature T_x, ΔT_x = T_x − T_g) before crystallization have been developed recently in La-based [1], Mg-based [2,3], Ti-based [4], and Zr-based [5–8] systems. Great attention has been devoted to the mechanism for the high stability of supercooled liquid in their special alloy systems. Among these metallic glasses, the Zr-based amorphous alloys are particularly interesting because they have high glass-forming ability with critical cooling rates as low as 1 K s⁻¹ [9] and have an extremely wide supercooled liquid region about 100 K [6]. This let these BMGs can be forged precisely in the supercooled liquid region into different shapes and still remain amorphous state. Another attractive characteristic of the BMG is its unique properties, such as high corrosion resistance, excellent elastic and mechanical properties [10,11] for Zr-based amorphous alloys and good soft magnetic properties for Fe-based [12] and Co-based [13,14] amorphous alloys. In addition, the tensile fracture strength of the Zr-based amorphous alloys reach 1600–1800 MPa at room temperature and their densities are around 5.9–6.7 Mg m⁻³ [15]. Therefore, a high specific strength of the BMG is expected to extend the application fields for bulk amorphous alloys.

0254-0584/$ – see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.matchemphys.2004.08.014
Based on the properties that the series of new amorphous alloys possesses a wide supercooled liquid region, Inoue [16] has proposed that the glass forming ability (GFA) of an alloy defined by the critical cooling rate $R_c$, which is the minimum cooling rate to obtain a BMG, can be evaluated by both values of $T_{rg}$ and $\Delta T_m$, where $T_{rg}$ is defined as $T_{lg}/2$ and $T_m$ is the onset melting temperature. Lu and Li [17] also showed recently that the best BMG forming alloys are at or near eutectic compositions, and the reduced glass transition temperature, $T_{rg}$, given by $T_{lg}/T_m$, reaches the highest value at the eutectic compositions, where $T_{lg}$ is the offset melting temperature. Since $T_{lg}$ plays the most influential role in glass formation, that one must look for regions of exceptionally low-lying $T_{lg}$ in the alloy phase diagram, such as the eutectic region.

Inoue and Masumoto [16,18,19] also revealed the relationship between the thermal stability of amorphous phase and their topological short-range ordering. It is generally thought that the increase in packing density causes an increase in the thermal stability and mechanical strength of an amorphous phase. Therefore, the low values of $T_{lg}$ and $\Delta T_m$ for the binary amorphous alloys are presumably because their amorphous structure has a looser atomic packing density than the corresponding crystalline phases. Inoue and Turnbull [20] also showed that one must look for regions of exceptionally low-lying $T_{lg}$ in the alloy phase diagram, such as the eutectic region.

In order to control the thermal stability and mechanical strength of an amorphous phase, the packing density of the series of new amorphous alloys is varied from 0 to 10 at.% silicon content. Fig. 1 shows the reduced glass transition temperature $T_{rg}$ of the Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$Si$_x$ alloys as a function of silicon content.

### 3. Results and discussion

#### 3.1. Calorimetry analysis

Fig. 1 shows the liquidus temperature, $T_{li}$, for the pre-alloyed Zr$_{65-x}$Al$_x$Cu$_{17.5}$Ni$_{10}$Si$_{10}$ alloys that measured by DTA. The liquidus temperatures for the alloys with 2–8 at.% silicon content are shown to be lower than others. However, the liquidus temperature increases slightly when the silicon content increases to 10 at.%.

According to the analyses of Turnbull [20], the best composition for metallic glass forming alloys, which with the highest reduced glass transition

### Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Annealing time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_0$</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$</td>
<td>550 ± 20</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$Si$_2$</td>
<td>700 ± 20</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$Si$_4$</td>
<td>715 ± 20</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$Si$_6$</td>
<td>700 ± 20</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$Si$_8$</td>
<td>695 ± 20</td>
</tr>
<tr>
<td>Zr$<em>{65}$Cu$</em>{17.5}$Al$<em>{17.5}$Ni$</em>{10}$Si$_{10}$</td>
<td>720 ± 20</td>
</tr>
</tbody>
</table>

Unit: Hv. The $t_0$, $t_1$, and $t_2$ are defined as the annealing time required for obtaining the 30, 50, and 80 vol.% of crystallization for each alloy, respectively.
temperature, \( T_g \), are at or near the deep eutectic point. This implies that the Zr-based alloys with silicon content 2–10 at.\% are analogous to the Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\) base alloy with high glass forming ability.

The \( T_g \), \( T_x \), and \( \Delta T_x \) (temperature interval between \( T_g \) and \( T_x \)) measured by DSC analyses as a function of silicon content was shown as Fig. 2. The crystallization temperature, \( T_x \), exhibits an increasing trend as the silicon content increases up to 10 at.\%. In addition, the value of calculated \( T_{50} \) for base alloy was 0.57; the 2Si and the 4Si alloys present the same value of about 0.57. However, the 6Si, the 8Si and the 10Si alloys present higher value of \( T_{50} \) about 0.60. This indicates the additions of silicon in the Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\) base alloy would retain a high glass forming ability.

The activation energy for crystallization of the Zr\(_{65}\)−\(x\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)Si\(_{x}\) alloys were determined by means of the Kissinger plot [21],

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

where \( b \) is the heating rate, \( T \) the specific temperature, \( R \) the gas constant, and \( E_a \) the activation energy. By using the value of \( T_p \) (peak temperature of crystallization), the plot of the ln \((b/T^2)\) versus 1/\(T_p\) yielded a straight line, as shown in Fig. 3, and the activation energy of crystallization can be calculated. Fig. 4 show the activation energy of crystallization calculated by Kissinger plot as a function of silicon content for Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)Si\(_{x}\) alloys. The activation energy reaches the maximum for the 4Si alloy. This indicates that the silicon may improve the thermal stability for the Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\) based alloy.

The kinetic study of crystallization was performed by using the Johnson–Mehl–Avrami (JMA) [22] isothermal analysis for volume fraction \( x \) transformed as a function of time based on the following Eq. (2):

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

The samples were annealed isothermally at several temperatures between \( T_g \) and \( T_x \). For each annealing temperature \( T_a \), three values of time to reach 30, 50, and 80% crystallization were selected to plot curves of ln \((t)\) versus 1/\(T_a\), as shown in Fig. 5, then the activation energies were determined by the slope. The highest activation energy about 371 kJ mol\(^{-1}\) obtained from the slope of these curves occurs at the 4Si alloy, which is similar to the result calculated from Kissinger plot. In parallel, the incubation time as a function of isothermal temperature, as shown in Fig. 6, exhibits an increasing trend with silicon addition except the 6Si alloy. This implies that the addition of silicon presents a positive effect on improving the thermal stability of the Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\) based alloy.
In addition, Eq. (2) can be written as:

\[
\ln \left( \frac{\ln(1 - x)}{1 - x} \right) = n \ln(k) + n \ln(t) \tag{3}
\]

where \( k \) is the effective rate constant and \( n \) is the Avrami exponent. The Avrami plots of \( \ln(1 - x) \) versus \( \ln(t) \), constructed for \( 0.1 \leq x \leq 0.9 \) at several different temperatures are shown in Fig. 7. The average value of the Avrami exponent \( n \) is around 1.7–2.5. This implies that these alloys present similar crystallization process, with a decreasing nucleation rate [23].

4. Microstructure analysis

Fig. 8 shows X-ray diffraction patterns of the Zr\(_{65-x}\)Al\(_{3}\)Cu\(_{17.5}\)Ni\(_{10}\)Si\(_{x}\) alloys. A broad maximum around low angle area was observed for almost all of the alloys in this study. However, a few small peaks were observed in the alloys with 2–10 at.% silicon content. These sharp peaks were identified to be the Zr\(_2\)Cu-type and the Zr\(_2\)Ni-type crystalline phases. The former phase is the tetragonal structure with lattice constant of \( a = 0.4536 \) nm and \( c = 0.3716 \) nm, whereas the latter phase is the tetragonal structure with lattice constant of \( a = 6.499 \) nm and \( c = 5.270 \) nm. This is also confirmed by TEM observation as shown in Fig. 9(a–c). Some ultra fine crystalline particles with random orientation, of size about 10–20 nm, were embedded in the amorphous matrix. In addition, some larger crystalline particles with size of 20–50 nm were observed in some area of the as-quenched alloy, as shown in Fig. 9(a–c).
shown in Fig. 9(d and e). By the selected area diffraction (SAD) analysis of nano electron beam, the crystalline particle was identified to be the tetragonal-structured Zr₂Cu-type crystalline phase.

Since the Zr₆₁Al₇.₅Cu₁₇.₅Ni₁₀Si₄ alloy presents the highest activation of crystallization, this alloy was selected as the base alloy for the kinetics study of isothermal annealing. The X-ray diffraction patterns of the Zr₆₁Al₇.₅Cu₁₇.₅Ni₁₀Si₄ alloy, isothermally annealed at 678 K at different time are shown as Fig. 10. The diffraction peaks are identified to be the Zr₂Cu-type and the Zr₂Ni-type crystalline phases. The particle size calculated by Scherrer’s formula exhibits a good linear relationship between the annealing times tₐ and the cube of particle size of both the Zr₂Cu-type and the Zr₂Ni-type crystalline phases, as shown in Fig. 11. This can be described by the following Eq. (4):

\[ D₃₃ - D₀₃ = k tₐ \]

where, \( D₀₃ \) is the particle size in diameter at \( tₐ = 0 \), \( D₃₃ \) is the particle size at \( tₐ \), and the rate constant \( k \) depends on temperature in the Arrhenius relation. This result is analogous
Fig. 10. X-ray diffraction patterns of the Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_{4}$ alloy isothermal annealed at 678 K for different time.

Fig. 11. Cube crystal size as a function of annealing time for the Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_{4}$ alloy.

Fig. 12. TEM images of Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_{4}$ alloy annealed at 678 K for 1180 s (about 30 vol.% of crystallization): (a) bright field image, (b) nano-beam SAD of Br [012] of Zr$_{2}$Cu nanoparticle.

Fig. 13. TEM images of Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_{4}$ alloy annealed at 678 K for 1270 s (about 50 vol.% of crystallization): (a) bright field image, (b) nano-beam SAD of Br [112] of Zr$_{2}$Al nanoparticle, and (c) nano-beam SAD of Br [011] of ZrCu particle.
128


Fig. 14. Fracture surface of bending the Zr61Al7.5Cu17.5Ni10Si4 amorphous ribbon 180° after different crystallization ratio; (a) 0%, (b) 30%, (c) 50%, and (d) 80%.

to the growth behavior with thermal activation process of Arrhenius type by Saida [24].

When the Zr61Al7.5Cu17.5Ni10Si4 alloy annealed at 698 K for 1180 s (about 30 vol.% of crystallization) a crystalline phase with average particle size about 105 nm nucleated from the amorphous matrix was observed by TEM, as shown in Fig. 12. The crystalline particles were identified to be the tetragonal Zr2Cu-type phases with lattice constant of \( a = 0.321 \) nm and \( c = 1.135 \) nm, which is in good agreement with the data of JCPDS file No. 18-0466 and the result of the XRD measurement. However, two other nano-crystalline phases were observed to embed in some area of the amorphous matrix for the alloy annealed at 698 K for 1270 s (about 50 vol.% of crystallization), as shown in Fig. 13. They were identified to be the ordered fcc Zr3Al with lattice constant of 0.429 nm and the ordered fcc ZrCu phase with lattice constant of 0.628 nm. Since the atomic radius of Al is larger than Cu (0.143 nm for Al and 0.128 nm for Cu), that the diffusivity in Zr matrix of Al would be smaller than that of Cu. Therefore the crystal size of Zr3Al particles (with average crystal size of 30 nm) comes out much smaller than the ZrCu particles (with average crystal size of 100 nm).

5. Hardness test and fracture surface observation

Table 1 shows the results of microhardness for the Zr61−xAl7.5Cu17.5Ni10Si4 alloys for different annealing time at the temperature of 15 K above \( T_g \) for each alloy. The \( t_1 \), \( t_2 \), and \( t_3 \) are defined, as the annealing time required obtaining the 30, 50, and 80 vol.% of crystallization for each alloy, respectively. The hardness of amorphous Zr61−xAl7.5Cu17.5Ni10Si4 alloys exhibits an increasing trend as the silicon content increases. The average hardness of silicon-added alloys is about 30% higher than the base alloy. This fact may contribute to the effect of large negative heat of mixing between atom pairs of Si–Zr, Si–Ni, and Si–Cu on the bonding strength. In addition, the hardness of each alloy decreases as the volume fraction of crystallization increases. The change in hardness may vary with different crystalline phases, such as Zr2Cu, Zr2Si, etc.

The fracture surface of bending the as-quenched Zr61Al7.5Cu17.5Ni10Si4 amorphous ribbon 180° presents the typical ductile vein pattern, as shown in Fig. 14. The larger diameter of the veins also implies an increase in the thickness of the shear deformation region, which induces an increase in energy required for plastic deformation and final fracture [25]. However, a ductile–brittle transition phenomenon occurs at the amorphous ribbon after 50% crystallization ratio of the isothermal annealing at the temperature between \( T_g \) and \( T_x \).

6. Conclusion

According to the results of DTA, DSC, X-ray diffraction, and TEM observation for the zirconium-based alloy with different silicon content, the effect of silicon on the glass forming ability and thermal stability can be summarized as:

(1) The lower liquidus temperatures occur around the alloys with 2–8 at.% silicon content. In addition, the value of calculated \( T_L \) for base alloy was 0.57; the 2Si and the
4Si alloys present the same value of about 0.57, the 8Si and the 10Si alloys present higher value of $T_{rg}$ about 0.60. This indicates the addition of silicon in the Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ base alloy can retain a high glass forming ability.

(2) The activation energy of crystallization for the alloy 4Si was about 365 ± 5kJmol$^{-1}$ determined both by the Kissinger and the Arrhenius plot. These values are 20% higher than the activation energy of crystallization for the based alloy. In addition, the incubation time as a function of isothermal temperature exhibits an increasing trend with silicon addition except the 6Si alloy. These two facts imply that the addition of silicon presents a positive effect on improving the thermal stability of the Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si base alloy.

(3) The average value of the Avrami exponent $n$ is around 1.7–2.5 for both these alloys in this study. This indicates these alloys present similar nucleation mechanism of crystallization.

(4) The change in particle size with increasing annealing time shows a good linear relationship between annealing time and the cube of particle size of the Zr$_2$Cu-type and the Zr$_2$Ni-type crystalline phases. This indicates that the crystal growth of the Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_4$ alloy belongs to thermal activation process of Arrhenius type.

(5) During isothermal annealing the Zr$_{61}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$Si$_4$ alloy at 698 K, the Zr$_2$Cu crystal with average size of 105 nm was first observed at the early stage (30% crystallization ratio) of crystallization by TEM. In addition, both nano-crystals of the ZrCu ($\sim 100$ nm) and the Zr$_3$Al ($\sim 30$ nm) were also observed to precipitate from the amorphous matrix upon the middle stage (50% crystallization ratio) of crystallization.

(6) A ductile–brittle transition phenomenon occurs when the amorphous ribbon reaches 50% crystallization ratio of the isothermal annealing at the temperature between $T_g$ and $T_x$.

Acknowledgements

The authors would like to gratefully acknowledge the sponsorship from the National Science Council of ROC under the project NSC91-2216-E-214-015. The authors are also very grateful for the assistance of TEM studies by Ms. Liang-Chu Wang.

References