Thermal stability and corrosion behavior of Cu–Zr–Al–Y bulk metallic glass

S.F. Chen, S.L. Lin*, J.K. Chen, Y.L. Lin

Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei 106, Taiwan, ROC

ARTICLE INFO

Article history:
Received 17 November 2009
Received in revised form 28 January 2010
Accepted 27 February 2010
Available online 30 March 2010

Keywords:
B. Glasses, metallic
B. Glass-forming ability
B. Corrosion

A B S T R A C T

In this study, (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-x}Y_x (0 \leq x \leq 8, in at.%) alloy ribbons and rods are prepared by single roller melt-spinning method and suction casting method. X-ray spectra show that the obtained alloy ribbons with X = 0, 2, 4, 8 and alloy rods with X = 0 and 4 at.% Y are fully amorphous. Amorphous rod of 4 at.% Y containing alloy up to 6 mm diameter can be achieved and has a large supercooled region (∆T_f) up to 75 K. In contrast, alloy rods with either X = 2 or 8 at.% Y contain small amount of crystallites. In H_2SO_4 solution, the Cu–Zr–Al–Y metallic glass rods form uniform oxide films on surface and have corrosion rate of 0.051–0.073 mm/yr. Pitting occurs when the glass rods are immersed in 3% NaCl solution and sea water and the corrosion rate ranges from 0.194 to 0.286 mm/yr. In all solutions, the corrosion resistance of Cu–Zr–Al–Y bulk metallic glass outperforms 304 L stainless steel.

1. Introduction

Recently bulk metallic glasses (BMGs) have attracted considerable interest due to their unique physical, mechanical and chemical properties [1–4]. Among various bulk metallic glasses, Cu-based alloys exhibit a large supercooled liquid region, ∆T_f = (∆T_m − T_g), characterizing their excellent glass-forming ability. Multi-component Cu-based alloy with composition of Cu_{42}Zr_{42}Al_{16} showing large supercooled liquid region has been obtained by several groups of scientists [5–7]. It is reported that the glass-forming ability of some bulk metallic alloy can be further improved by additions of large atoms, such as Ag, Au, Pd, Be, Nb, Gd, and Y [8–15]. Yttrium has been widely used in some bulk metallic alloy as a minor addition element. Lu et al. [14,15] reported that the GFA of Fe-based alloy could be improved by the addition of 2 at.% yttrium. The beneficial effects of Y on GFA are twofold: (i) Y adjusts the compositions closer to the eutectic point and lowers liquid temperature, and (2) Y improves the manufacturability of these alloys by scavenging the oxygen impurity via the formation of innocuous yttrium oxides. In current study, Yttrium (Y) is added to Cu_{42}Zr_{42}Al_{16} alloy system. Xu et al. [6] also reported that the Yttrium can scavenge oxygen from the Cu–Zr–Al alloys via innocuous Y oxide formation (∆G_{Cu_2O_288K} = −1904 kJ/mol, ∆G_{CuO_298K} = −155 kJ/mol, ∆G_{ZrO_298K} = −944 kJ/mol, and ∆G_{Al_2O_3_298K} = −1675.7 kJ/mol). The reduction of free oxygen increases the liquid phase stability and suppresses crystalline phase formation in supercooled liquids. Meanwhile, the atomic radius of Y is larger than the other major elements (Cu: 0.128 nm, Zr: 0.160 nm, Al: 0.143 nm, Y: 0.182 nm) and Y has negative heats of mixing with Cu and Al (−22 kJ/mol for Y–Cu and −31 kJ/mol for Y–Al). These are in consistent with the three empirical rules of BMG formation proposed by Inoue [16]: (i) multi-component systems consist of more than three elements; (ii) three main constituent elements have over 12% of difference in atomic size; and (iii) negative heats of mixing exist among the three main constituent elements. Therefore, Y is beneficial in increasing the density of random packed structure and solid/liquid interfacial energy, leading to the improved glass-forming ability (GFA).

In order to consider the Cu-based BMGs as industrial materials, the resistance to environment attacks should also be studied. The corrosion of metallic alloys is significantly influenced by the microstructure. In general, the amorphous structure is known to improve the corrosion resistance due to fewer defects and optimized chemical homogeneity. In this paper, effects of rare-earth element Y addition on both the GFA and corrosion properties of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-x}Y_x (X = 0, 2, 4 and 8) alloys are investigated.

2. Experimental procedure

Alloy ingots of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-x}Y_x (X = 0, 2, 4 and 8, in at.%) were prepared by arc melting pure Cu (99.8 wt.% purity), Zr (99.9 wt.% purity), Al (99.8 wt.% purity), and Y (99.9 wt.% purity) under argon atmosphere. The alloys were then molten using a vacuum induction melting furnace at 1 × 10^−4 torr before injecting onto a 200 mm diameter copper wheel rotating at 4000 rpm to form rapidly solidified ribbon specimens of 3 mm width and about
30 μm thickness. The rod specimens were prepared by suction casting method into 4 and 6 mm diameter × 70 mm length in size. The microstructures of (Cu0.46Zr0.46Al0.08)100−xYX alloy ribbons and rods were analyzed by XRD (Rigaku DMAX2200VK/PC) and SEM (Hitachi-S4700). The glass transition temperature (Tg) and onset crystallization temperature (Tc) of alloy ribbons and rods were measured with DSC (TA Instruments SDT2960 Simultaneous DSC-TGA). Corrosion tests were performed on alloy rods of (Cu0.46Zr0.46Al0.08)100−xYX by immersing in 1 M H2SO4, 3.5 wt.% NaCl solution, and real sea water for fourteen days. The weight loss was measured to calculate the average corrosion rate [17]. The corroded surfaces were also observed using SEM.

3. Results and discussion

XRD and SEM microstructures of (Cu0.46Zr0.46Al0.08)100−xYX (X = 0, 2, 4, and 8) alloy ribbons are shown in Figs. 1 and 2. The XRD spectra demonstrate a broad diffraction peak without any detectable Bragg peaks. The SEM micrographs (Fig. 2) show no clear contrast, either. These indicate that the alloy ribbons prepared by rapid solidification are amorphous. Fig. 3 shows the XRD spectra of (Cu0.46Zr0.46Al0.08)100−xYX (X = 0, 2, 4, and 8) alloy rods. For 4 mm alloy rod of X = 0 and 6 mm alloy rod of X = 4, broad diffraction peaks indicate they are both fully metallic glassy. The larger rod size of 6 mm also implies that alloy of X = 4 has better glass-forming
ability than that without Y addition. For alloy rods with $X = 2$ and 8, sharp Bragg peaks are observed in their XRD spectra which correspond to the metastable AlCu$_2$Zr and CuZr phases (Fig. 3), indicating small crystalline phase forms in the amorphous matrix. Based on the simple relationship between the maximum thickness of glassy alloy and critical cooling rate ($R_c$) suggested by Lin and Johnson [18], the critical cooling rate ($R_c$) for glassy phase formation is estimated to be less than 111 K/s with 4 at.% Y addition in current alloy system.

Fig. 4 shows the DSC curves of (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{100-x}$Y$_x$ (X = 0, 2, 4, and 8) alloy ribbons. Their glass transition temperatures ($T_g$), onset crystallization temperatures ($T_X$), and the supercooled liquid region ($\Delta T_X = T_X - T_g$) are summarized in Table 1. For all four alloy ribbons, obvious endothermic peaks of the glass transition temperature range from 617 K to 680 K. Exothermic peaks are shown in the same curves indicating that $T_g$ and $\Delta T_X$ change from 747 K and 67 K to 773 K and 101 K, respectively. Among all alloy ribbons, the (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{96}$Y$_4$ alloy bears the largest supercooled liquid region (Table 1) and has the optimum glass-forming ability.

Table 1

<table>
<thead>
<tr>
<th>X in (Cu$<em>{0.46}$Zr$</em>{0.46}$Al$<em>{0.08}$)$</em>{100-x}$Y$_x$</th>
<th>Ribbons/rods</th>
<th>$T_g$ (K)</th>
<th>$T_X$ (K)</th>
<th>$\Delta T_X$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>671/718</td>
<td>770/778</td>
<td>99/60</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>664/733</td>
<td>753/777</td>
<td>89/45</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>672/702</td>
<td>773/777</td>
<td>101/75</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>680/704</td>
<td>747/762</td>
<td>67/58</td>
<td></td>
</tr>
</tbody>
</table>

4 at.% optimum atomic packing configuration may be achieved, therefore (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{96}$Y$_4$ alloy rods remain high glass-forming ability. Apparently, 8 at.% of Y addition overdoses and again increases free volume, so the supercooled liquid region decreases.

Fig. 5 shows the DSC curves of (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{100-x}$Y$_x$ (X = 0, 2, 4, and 8) alloy rods. Their $T_g$, $T_X$, and $\Delta T_X$ are summarized in Table 1. $\Delta T_X$ ranges from 45 K to 75 K, similar in trend to (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{100-x}$Y$_x$ alloy ribbons. According to the study by Lu [14] and Xu et al. [6], with 2 at.% of Y addition, the atomic structure may be expanded to make the atomic structure less closely packed. The crystal structures of the alloy rods contain many free volumes with less dense atomic configuration, therefore atoms diffuse more easily and the supercooled liquid region decreases. When X further increases to 4 at.% optimum atomic packing configuration may be achieved, therefore (Cu$_{0.46}$Zr$_{0.46}$Al$_{0.08}$)$_{96}$Y$_4$ alloy rods remain high glass-forming ability. Apparently, 8 at.% of Y addition overdoses and again increases free volume, so the supercooled liquid region decreases. |
In summary, the 4 at.% Y addition to the Cu_{46}Zr_{46}Al_{8} alloy system increases the ΔT_{X} by 2 K and 15 K for alloy ribbon and rod, respectively. Y addition dramatically enhances the thermal stability of glass-forming liquid, and consequently, the glass-forming ability of Cu_{46}Zr_{46}Al_{8} alloy.

Fig. 6(a) shows the SEM micrograph of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} (X = 0, 2, 4, and 8) alloy rods after immersion in 3.5 wt.% NaCl solution for 14 days. Apparently, no passive layer is observed on the surface. The alloys are susceptible to pitting corrosion by Cl^{-}.

Table 2 lists the effects of Y on corrosion rates of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} rods. The corrosion rates decrease with the increasing Y addition in 3.5 wt.% NaCl solution from 0.210 mm/yr to 0.194 mm/yr, and the corrosion resistance ability elevates by 7.6%. On the other hand, the 2 at.% Y addition increases the corrosion rates from 0.037 mm/yr to 0.051 mm/yr and from 0.207 mm/yr to 0.286 mm/yr in 1 M H_{2}SO_{4} and real sea water, respectively. The alloy rods of X = 4 then show lower corrosion rate than 2 at.% added alloy rods in all solutions tested.

By comparing the corrosion resistance of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} BMGs in three solutions, the chlorine ion containing solution corrodes the alloys about 4 times higher than that of 1 M H_{2}SO_{4}. In comparison with 304 L stainless steel, the (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} BMGs have much lower corrosion rate in all solutions. 304 L stainless steel exhibits about 1000 times higher corrosion rate than the (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} BMGs in 1 M H_{2}SO_{4} solution. 304 L stainless steel also shows about 4 times higher corrosion rate than the (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} BMGs in Cl^{-} containing solutions. It is clear that these Cu-based alloy rods demonstrate better corrosion resistance in comparison with the 304 L stainless steel. The results confirm the excellent corrosion resistance of bulk metallic glasses.

### Table 2

<table>
<thead>
<tr>
<th>Avg. corrosion rate (mm/yr)</th>
<th>1 M H_{2}SO_{4}</th>
<th>3.5 wt.% NaCl</th>
<th>Sea water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_{46}Zr_{46}Al_{8}</td>
<td>0.037</td>
<td>0.210</td>
<td>0.207</td>
</tr>
<tr>
<td>(Cu_{46}Zr_{46}Al_{8})<em>{100-2}Y</em>{2}</td>
<td>0.051</td>
<td>0.204</td>
<td>0.229</td>
</tr>
<tr>
<td>(Cu_{46}Zr_{46}Al_{8})<em>{100-4}Y</em>{4}</td>
<td>0.046</td>
<td>0.194</td>
<td>0.218</td>
</tr>
<tr>
<td>(Cu_{46}Zr_{46}Al_{8})<em>{100-8}Y</em>{8}</td>
<td>0.047</td>
<td>0.194</td>
<td>0.286</td>
</tr>
<tr>
<td>304 L SS</td>
<td>53.28</td>
<td>0.753</td>
<td>0.856</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In this study, (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} (X = 0, 2, 4, and 8) bulk metallic glasses are fabricated by single roller melt-spinning method and suction casting method to form alloy ribbons and rods, respectively. Effects of Yttrium (Y) addition on glass-forming ability and corrosion resistance of Cu-based alloys are discussed. The results obtained are summarized as follows:

1. Alloy ribbons with X = 0, 2, 4, and 8 and alloy rods with X = 0 and 4 show broad X-ray diffraction spectra without any detectable sharp Bragg peaks, indicating that they are amorphous. In alloy rods of X = 2 and 8, the peaks of AlCu_{2}Zr and CuZr crystalline phases are visible, indicating that these alloy rods consist of amorphous matrix and small crystalline phases.

2. Concerning the glass-forming ability, 4 at.% Y appears to be the optimum addition which elevates thermal stability of metallic glass by expanding supercooled liquid region. The (Cu_{0.46}Zr_{0.46}Al_{0.08})_{96}Y_{4} bulk metallic glass demonstrates larger supercooled liquid region (101 K for ribbons and 75 K for glassy alloy rods) in comparison with the non-Y added Cu_{46}Zr_{46}Al_{8} alloy (99 K for ribbons and 60 K for glassy alloy rods).

3. On the corrosion resistance ability, the (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} BMGs corrode easier in solution with chloride ion than in 1 M H_{2}SO_{4}. In all solutions, the corrosion resistance of (Cu_{0.46}Zr_{0.46}Al_{0.08})_{100-X}Y_{X} bulk metallic glass outperforms 304 L stainless steel.

### References