New Ce-Cu-Al-Zn Bulk Metallic Glasses with High Oxidation Resistance

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We reported the effect of Zn addition on the glass formation ability (GFA), thermal stability, melting behavior and oxidation behavior of Ce-based bulk metallic glasses (BMGs). The Ce-Cu-Al alloys with Zn addition also have high glass formation ability (GFA) and large supercooled liquid regions ($\Delta T_x$, $\Delta T_y$, $T_x$, $T_y$ are the onset crystallization temperature and $T_y$ is the glass transition temperature). The $T_x$, $T_y$ and $\Delta T_y$ are, respectively, 368, 437 and 69 K for the Ce$_{72}$Cu$_{28}$Al$_{10}$Zn$_{5}$ alloy, and 394, 467 and 73 K for the Ce$_{72}$Cu$_{28}$Al$_{10}$Zn$_{5}$-Al$_{12}$Zn$_{5}$ alloy. The $\Delta T_y$ of the Ce$_{72}$Cu$_{28}$Al$_{10}$Zn$_{5}$ alloys was above 70 K and the BMGs with diameters up to ~6 mm could be produced successfully. The critical diameters and $\Delta T_y$ of the alloys increase with increasing Zn content, and have maximum values of 6 mm and 73 K, respectively, at 7.5 at% Zn, and then decreases in the higher Zn content range. The melting behavior shows that the addition of Zn element causes the significant increase of both $T_x$ and $T_y$. The investigation of oxidation behavior shows that the addition of Zn element is effective for the enhancement of the oxidation resistance.

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Keywords: cerium base bulk metallic glass, zinc addition, glass formation ability, oxidation behavior

1. Introduction

In the past 18 years, many kinds of bulk metallic glass (BMG) alloys have been developed, for example, La-1, Mg-2,3) Zr-4) Cu-5) Fe-6) Co-7) Ni-8,9) Ti-10) Pd-11) Nd-12) Pr-13) Pt-14) and so like. Among these BMGs, different base systems have also been developed, such as La-, Pr-, Dy-, and Nd-based BMGs.1,12,13,15) Recently, Ce-based BMGs with high glass formation ability, thermal stability, melting behavior and oxidation behavior of Ce-Cu-Al-Zn alloys. Thermal stability associated with glass transition, supercooled liquid region and crystallization temperature was examined by differential scanning calorimetry (DSC) in a Seiko DSC 6200 (Exstar 6000, Seiko Instruments Inc.). The melting and liquid temperatures were measured by differential thermal analysis (DTA, TM 9000) with high vacuum system at a heating rate of 0.083 K s$^{-1}$. The BMG samples with a diameter of 2 mm were cut to the length of 3.0–3.2 mm and used for the measurement of oxidation behavior. In a purified Ar atmosphere, the BMG samples were heated in a furnace at a heating rate (0.083 K s$^{-1}$) so as to cause the oxidation behavior on the surface. The weight variation of BMG samples was recorded in real time by a computer and used to evaluate the oxidation resistance.

2. Experimental Procedure

An Ingot with nominal composition of Ce$_{72}$Cu$_{28}$ was prepared by arc melting mixtures of high purity Ce (99.99%) and Cu (99.9%) under a Ti-gettered purified Ar atmosphere. Multi-component (Ce$_{72}$Cu$_{28}$)$_{100-x}$Al$_{10}$Zn$_x$ were prepared by high frequency induction melting a mixture of (Ce$_{72}$Cu$_{28}$) eutectic alloy, Al metal (99.9%) and Zn metal (99.9%) in a purified Ar atmosphere. Ce-based BMGs in a cylindrical rod form with diameters up to 6 mm were produced by copper mold casting. Ce-based glassy alloy ribbons were prepared by the melt-spinning technique. The glassy phase was examined by X-ray diffraction (XRD) with Cu $K_{\alpha}$ radiation.

3. Results and Discussion

Figure 1 shows DSC curves of the Ce$_{72}$Cu$_{28}$Al$_{10}$Zn$_x$ glassy alloys at a heating rate of 0.083 K s$^{-1}$. The glass transition temperature ($T_g$), crystallization temperature ($T_c$) and supercooled liquid region ($\Delta T_x$, $\Delta T_y = T_x - T_y$) of the alloys were shown in Table 1. The $T_c$, $T_x$ and $\Delta T_x$ of the

![Fig. 1 DSC curves of (Ce$_{72}$Cu$_{28}$Al$_{10}$Zn$_x$)](image-url)
Table 1 Parameters of (Ce$_{0.72}$Cu$_{0.28}$)$_{10-x}$Al$_{10}$Zn$_x$ glassy alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_g$</th>
<th>$T_x$</th>
<th>$\Delta T$</th>
<th>$D$</th>
<th>$T_{g}/T_{x}$</th>
<th>$T_{g}/T_{x}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$</td>
<td>348</td>
<td>411</td>
<td>63</td>
<td>5</td>
<td>625</td>
<td>663</td>
<td>0.557</td>
</tr>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$Zn$_{2.5}$</td>
<td>368</td>
<td>437</td>
<td>69</td>
<td>5</td>
<td>625</td>
<td>680</td>
<td>0.589</td>
</tr>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$Zn$_{5}$</td>
<td>383</td>
<td>454</td>
<td>71</td>
<td>6</td>
<td>668</td>
<td>685</td>
<td>0.599</td>
</tr>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$Zn$_{7.5}$</td>
<td>394</td>
<td>467</td>
<td>73</td>
<td>6</td>
<td>676</td>
<td>697</td>
<td>0.605</td>
</tr>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$Zn$_{10}$</td>
<td>402</td>
<td>463</td>
<td>61</td>
<td>4</td>
<td>689</td>
<td>721</td>
<td>0.603</td>
</tr>
<tr>
<td>(Ce$<em>{0.72}$Cu$</em>{0.28}$)$<em>{10}$Al$</em>{10}$Zn$_{15}$</td>
<td>414</td>
<td>458</td>
<td>44</td>
<td>3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

(Ce$_{0.72}$Cu$_{0.28}$)$_{10-x}$Al$_{10}$ glass alloy are 348, 411 and 63 K, respectively. The addition of Zn element increases the $T_g$, $T_x$ and $\Delta T_x$. The $T_g$, $T_x$ and $\Delta T_x$ are, respectively, 368, 437 and 69 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{87.5}$Al$_{10}$Zn$_{2.5}$ alloy, 383, 454 and 71 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{85}$Al$_{10}$Zn$_{5}$ alloy, and 394, 467 and 73 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{82.5}$Al$_{10}$Zn$_{7.5}$ alloy. With further increasing Zn content, the $T_g$ still increase, while the $T_x$ and $\Delta T_x$ begin to reduce. The $T_g$, $T_x$ and $\Delta T_x$ are, respectively, 402, 463 and 61 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{80}$Al$_{10}$Zn$_{10}$ glassy alloy, and 414, 458 and 44 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{75}$Al$_{10}$Zn$_{15}$ glassy alloy. The critical diameters ($D$) of Ce-based BMGs with different Zn content for (Ce$_{0.72}$Cu$_{0.28}$)$_{10-x}$Al$_{10}$Zn$_x$ BMGs. For comparison, the result of (Ce$_{0.72}$Cu$_{0.28}$)$_{80}$Al$_{10}$Fe$_{2.5}$ BMG was also shown in (b).
BMGs prepared by copper mold casting are also summarized in Table 1. The $D$ is 5 mm for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{87.5}\text{Al}_{10}\text{Zn}_{2.5}$ alloy. With increasing Zn content, the $D$ also increases. The $D$ is 6 mm for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Zn}_{5}$ and $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Zn}_{7.5}$ alloys. In the higher Zn content range, the $D$ begins to decrease. Figure 2 shows XRD patterns of the Ce-Cu-Al-Zn BMG rods with different diameters up to 6 mm. Only main broad peaks are observed in the diffraction patterns, indicating that these samples consist of a glassy phase basically. The $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Zn}_{7.5}$ BMG with a diameter of $\sim$6 mm also displays a smooth outer surface with bright metallic luster, which is typical for bulk metallic glass alloys.

DTA curves of the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{100-x}\text{Al}_{10}\text{Zn}_x$ alloys were also measured at a heating rate of 0.083 K s$^{-1}$. The melting point ($T_m$) and liquid temperature ($T_l$) of the alloys are also summarized in Table 1. The $T_m$ and $T_l$ are 625 and 680 K, respectively, for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{87.5}\text{Al}_{10}\text{Zn}_{2.5}$ alloy, 668 and 685 K, respectively, for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Zn}_{5}$ alloy, and 676 and 697 K, respectively, for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Zn}_{7.5}$ alloy. It is clear that both $T_m$ and $T_l$ increase significantly with increasing Zn content. Based on the results of both $\Delta T_s$ and GFA, it is worthwhile to notice that the $\Delta T_s$ and GFA increase with increasing $T_l$. This is different from other Ce-based BMGs. For Ce-Cu-Al BMGs and Ce-Cu-Al-Fe BMGs, with increasing Al and Fe contents, the $\Delta T_s$ and GFA increase greatly, while the $T_l$ decreases.\textsuperscript{16,17} The reduced glass transition temperature $T_{rg}$, which is defined from the ratio of $T_g/T_l$, is an important parameter to estimate the glass formation ability.\textsuperscript{18} The $T_{rg}$ values of the

![Fig. 6 SEM images of oxidized surfaces of (a) and (b) $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90}\text{Al}_{10}$ glassy alloy ribbon and (c) $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Zn}_{7.5}$ glassy alloy ribbon exposed in air for 20 months.](image)
Ce-Cu-Al-Zn BMGs with high glass formation ability (GFA), a large supercooled liquid region (ΔTc) and high oxidation resistance were developed. The Zn addition to Ce-Cu-Al alloys improves GFA, enlarges ΔTc, and also increases both Tg and Tt. The maximum ΔTc and critical diameters of the alloys are 73 K and 6 mm, respectively. The reduced glass transition temperature (Tg) and the γ parameter also increase with increasing Zn content when Zn content is less than 7.5 at%, but these parameters begin to reduce in the higher Zn content range. The Zn addition was also beneficial to enhance the oxidation resistance of Ce-based BMGs. This is expected to provide a new chance for applications of the Ce-based BMGs in the future.

REFERENCES