Ce-Rich Misch Metal-Based Bulk Metallic Glasses with High Glass-Forming Ability

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Ce-rich misch metal (Mm)-based bulk metallic glasses (Mm consists of Ce, La, Pr and Nd) with high glass-forming ability are developed in Mm–Co–Al alloy system. The critical diameter for glass-formation is 10, 5 and 3 mm, and the supercooled liquid region \( \Delta T_g = T_c - T_g \) (where \( T_c \) is crystallization temperature and \( T_g \) is glass transition temperature) is 27, 90 and 79 K for Mm65Co25Al20 (Mm65), Mm60Co20Al20 (Mm60) and Mm55Co35Al20 (Mm55) alloys, respectively. The employment of the misch metal, which comprises multi-rare earth elements, instead of pure Ce in the Ce–Al–Co system can improve the glass-forming ability in spite of the tiny atomic size difference of the rare earth metals. The present alloy system is an exception to the criteria of mixing used for evaluating the relative GFA.

1. Introduction

Since La-based bulk metallic glass (BMG) was fabricated by copper mold casting, a number of bulk glass-forming alloy systems, e.g. Zr-, Mg-, Pd-, Fe-, Cu-, Ti-, Ni- and Co-based alloys, have been developed. When attention is paid to rare earth metal-based metallic glasses with high glass-forming ability (GFA), one can list La-, Nd-, Pr-, Y- and Ce-based alloys. Moreover, addition of rare earth metals can significantly improve glass-forming ability of some bulk glassy alloys, e.g. Fe- and Cu-based alloys. The effect of complete replacement of La by the misch metal in La–Al–Ni and La–Al–Ni–(Cu,Co) alloys on GFA has also been investigated and BMG matrix composites was fabricated. Ce-rich misch metal as the raw material of refined pure rare earth metals has an obvious advantage in price comparing with pure Ce. If Ce-rich misch metal alloys inheriting the relative low melting temperature of Ce with a high glass-forming ability (GFA) are developed, it would be energy efficient in industrial production since a simple heating and forming process would be feasible. Therefore the search for misch metal-based BMGs with high GFA is of significance not only for basic science but also for practical applications. In this paper, we report a new bulk metallic glass system Mm–Co–Al with high GFA, where Mm denotes a Ce-rich misch metal nominally consisting of La, Ce, Pr and Nd. Bulk glasses Mm65Co25Al20 (Mm65), Mm60Co20Al20 (Mm60) and Mm55Co35Al20 (Mm55) alloys can be produced with diameters up to 10, 5 and 3 mm, respectively, by copper mold casting. Studies on the thermal properties and GFA revealed that the present alloy system is an exception to the criteria extensively used for evaluating the relative GFA in a given alloy system, such as supercooled liquid region \( \Delta T_g \) (\( T_c - T_g \), \( T_g \) is crystallization temperature and \( T_g \) is glass transition temperature) reduced glass transition temperature \( T_g (T_g = T_g/T_m) \), \( T_m \) is melting temperature) and different atomic size distribution, as well as negative heat of mixing used for evaluating the relative GFA.

2. Experimental Procedure

Master alloys with nominal compositions of Mm65Co25Al20 (Mm65), Mm60Co20Al20 (Mm60) and Mm55Co35Al20 (Mm55) were prepared by arc-melting the mixture of a Ce-rich misch metal (Mm), Co and Al with a purity of \( >99 \) mass\%, 99.9 mass\%, 99.99 mass\% under an argon atmosphere. The Ce-rich misch metal nominally consists of 45.1 at\% Ce, 33.6 at\% La, 5.4 at\% Pr and 15.9 at\% Nd by neglecting impurities. From the master alloys, cylindrical rod samples were prepared by copper mold casting and ribbons were prepared by single-roller melt-spinning under an argon atmosphere. The structure of the samples was examined by X-ray diffraction (XRD) using a Siemens D500 X-ray diffractometry with Cu-K\( \alpha \) radiation. Thermal stability associated with glass transition, supercooled liquid region and crystallization was investigated by a Perkin-Elmer DSC-6 differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s. The melting behaviors of the alloys were measured using a Setaram Setsys 16/18 DSC at a heating rate of 0.17 K/s. High-resolution transmission electron microscopic (HRTEM) observation was carried out using a JEM-2010 TEM operated at 200 kV.

3. Results and Discussion

The amorphous structure of the melt-spun Mm65, Mm60 and Mm55 ribbons was confirmed by XRD. DSC curves of the melt-spun ribbons exhibit distinct glass transition followed by supercooled liquid region prior to crystallization, as shown in Fig. 1. With the decrease in Mm content, \( T_g \) and \( T_c \) increase remarkably for the three alloys. The temperature intervals of the supercooled liquid region \( \Delta T_g \) of the glassy Mm65, Mm60 and Mm55 alloys are measured to be 27, 90 and 79 K, respectively. The heat release of the main

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crystallization peaks ($\Delta H_\text{c}$) for the Mm65 ribbon is evaluated to be $\sim 2.0 \text{kJ/mol}$, and the values are $\sim 4.6 \text{kJ/mol}$ for the Mm60 and $\sim 5.7 \text{kJ/mol}$ for Mm55, respectively. This indicates relatively small enthalpy difference between the glass and the crystal close to $T_g$ for the Mm65 alloy. For further confirmation of the glassy structure of the rapidly solidified Mm65 alloy, HRTEM observation was carried out. The HRTEM image and the corresponding selected area electron diffraction (SAED) pattern are shown in Fig. 2, revealing a single glassy phase without evidence for crystallization.

Figure 3 shows the melting behaviors of the alloys studied in this work. It is seen that the melting temperature $T_m$ changes indistinctively with the alloy composition variation. Accordingly, the reduced glass transition temperature ($T_g/\Delta H_e$) defined as $T_g/T_m$ increases with the decrease in Mm content with a value of 0.62, 0.65 and 0.69 for Mm65, Mm60 and Mm55, respectively. The distinct $T_g$ and high $T_g/T_m$ allow us to expect the present alloys to form bulk metallic glasses.

As an example, Fig. 4 shows the outer shape and surface appearance of Mm65 cast rods of 6, 8 and 10 mm in diameter. The rod surfaces are smooth and exhibit good mirror-like luster typical of metallic glasses. XRD patterns of the Mm-Co-Al BMGs with their respective critical diameters for glass-formation ($d_c$) are characteristic of a glassy phase, as shown in Fig. 5. The $d_c$ is 10 mm, 5 mm and 3 mm for Mm65, Mm60 and Mm55, respectively, in spite of $T_g/T_m$ increases with decreasing Mm content in the three alloys. Figure 6 shows the DSC curves of Mm65 as-cast rods with diameters of 6, 8 and 10 mm. For comparison, the DSC curve of the melt-spun ribbon is also included. There is no apparent difference in $T_g$, $T_x$ and $\Delta H_e$ among the ribbon and rod samples, conforming the fully glassy structure of the as-cast Mm65 rods with a diameter up to 10 mm. Such comparison of DSC curves for the Mm60 and Mm55 samples was also carried out and completely amorphous structure of the 5 mm diameter Mm60 rod and 3 mm diameter Mm55 rod was also confirmed. In addition to the reverse change trend of $d_c$ and $T_g$ with the alloy composition variation, the Mm65 alloy with a relatively small supercooled liquid region of 27 K
enhance the formation of glasses.4,5,19–22) F. Guo and S. J. elements with differing atomic radii and strong interactions exhibits rather higher glass-forming ability evidenced by the
Fig. 6 DSC curves of Mm65Co25Al20 rods with their critical diameters of 10, 5 and 3 mm, respectively.

The experimental results indicate that the GFA of the present Mm–Co–Al alloy system does not correlate with $T_G/T_m$ and $\Delta T_x$, although the parameters are useful indicators of relative GFA for many glass-forming alloy systems.4,5,16–18) Moreover, the Mm65Co25Al10 alloy developed in this work exhibits relatively high GFA in the rare earth metal-based BMGs, as seen in Table 1, which lists the thermal parameters and critical diameters of the present Mm–Co–Al glassy alloys and other typical rare earth metal-based BMGs.1,9,10,24,25) It is also notable that the addition of the misch metal for replacing Ce in the Ce–Co–Al alloy can improve the GFA, which is evidenced by an increase in the critical diameter from 2 mm of Ce60Co25Al10 to 10 mm of Mm65Co25Al10.24) It has been suggested that alloying elements with differing atomic radii and strong interactions enhance the formation of glasses.4,5,19–22) F. Guo and S. J. Poon reported that the addition of Sc to the Y–Co–Al alloy can enhance the GFA because of the good distribution of atomic size in multi-component system improving atomic packing efficiency.9) However, for the present Mm–Co–Al alloy system, there is only a slight difference in the atomic size of La, Ce, Pr and Nd (183, 181.8, 182.4 and 181.4 pm, respectively).26) The heat of mixing ($\Delta H_{mix}$) between the rare earth metals is zero, and there is no considerable difference in $\Delta H_{mix}$ among the atomic pairs of Ln–Co as well as among those of Ln–Al (Ln = Ce, La, Pr, Nd).27) Therefore it does not seem that the higher GFA of the Mm–Co–Al alloys could be explained well with respect to the atomic size and chemical bonding. Theoretically, electronic effect also governs the formation and stability of metallic glasses.6,28–30) Considering the electron configurations of La, Ce, Pr and Nd are [Xe]5d$^1$6s$^2$, [Xe]4f$^4$5d$^1$6s$^2$, [Xe]4f$^4$6s$^2$ and [Xe]4f$^5$6s$^2$, respectively and the number of valence electrons increases in sequence, we suggest that the diversity in electron configuration of the rare earth metals may be related to the higher GFA of the Mm65Co25Al10 alloy in comparison with the Ce60Co25Al10 alloy. The cooperation of the valence electrons of La, Ce, Pr and Nd included in the misch metal of an appropriate content in the resultant multi-component alloy system could play a role in stabilizing the glassy phase during the solidification from liquid to solid state under a certain condition and therefore be favorable for achieving high GFA. Dong et al. have proposed an empirical $e/a$ parameter ($e/a$ is the effective conduction electron concentration) to predict the BMG forming composition in a given alloy system,6,30) which could be correlated to the GFA in the present system and facilitate our further investigation.

### 4. Conclusions

Bulk metallic glasses based on a Ce-rich misch metal (Mm) consisting of Ce, La, Pr and Nd with a high glass-forming ability are developed in Mm–Co–Al alloy system. Mm65Co25Al10 alloy can be produced in a bulk glassy form with a diameter reaching 10 mm, for which $\Delta T_x$ ($= T_x-T_g$) is 27 K and $T_g$ ($= T_g/T_m$) is 0.62. Critical diameter for glass formation is 5 and 3 mm, respectively, for Mm65Co25Al20 and Mm65Co25Al30 alloys with $\Delta T_x$ of 90 K and 79 K and $T_g$ of 0.65 and 0.69, respectively. The employment of misch metal comprising Ce, La, Pr and Nd for replacing pure Ce in the Ce–Al–Co system significantly improves the glass-forming ability. The criteria, $\Delta T_x$, $T_g/T_m$ and atomic size

<table>
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<tr>
<th>Alloy (at%)</th>
<th>$d_c$/mm</th>
<th>$T_g$/K</th>
<th>$T_x$/K</th>
<th>$T_m$/K</th>
<th>$\Delta T_x$/K</th>
<th>$T_g/T_m$</th>
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<tr>
<td>Mm65Co25Al20</td>
<td>3</td>
<td>488</td>
<td>567</td>
<td>706</td>
<td>79</td>
<td>0.69</td>
</tr>
<tr>
<td>Mm65Co25Al20</td>
<td>5</td>
<td>458</td>
<td>548</td>
<td>707</td>
<td>90</td>
<td>0.65</td>
</tr>
<tr>
<td>Mm65Co25Al10</td>
<td>10</td>
<td>430</td>
<td>457</td>
<td>698</td>
<td>27</td>
<td>0.62</td>
</tr>
<tr>
<td>Ce60Co25Al10</td>
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<td>—</td>
<td>411</td>
<td>680</td>
<td>—</td>
<td>0.57</td>
</tr>
<tr>
<td>La55Ni5Co15Al10</td>
<td>2.5</td>
<td>465</td>
<td>545</td>
<td>—</td>
<td>70</td>
<td>0.68</td>
</tr>
<tr>
<td>Ce60Ni15Cu15Al10</td>
<td>3</td>
<td>390</td>
<td>468</td>
<td>644</td>
<td>78</td>
<td>0.61</td>
</tr>
<tr>
<td>Ce60Ni10Cu10Nb10Al10</td>
<td>5</td>
<td>359</td>
<td>384</td>
<td>637</td>
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</tr>
<tr>
<td>Y25Sc65Co20Al14</td>
<td>25</td>
<td>645</td>
<td>760</td>
<td>976</td>
<td>115</td>
<td>0.69</td>
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Fig. 5 X-ray diffraction patterns of glassy Mm65Co25Al20, Mm65Co25Al20 and Mm65Co25Al10 rods with critical diameters of 10, 5 and 3 mm, respectively.

Fig. 6 DSC curves of Mm65Co25Al10 melt-spun ribbon and cast rods with diameters of 6, 8 and 10 mm.
distribution etc., used for evaluating the relative GFA are not applicable to the GFA of the present Mn–Co–Al alloy system.

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