Ce–Cu–Fe–Al–Si Bulk Metallic Glass Alloys With High Glass Forming Ability

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New Ce–Cu–Fe–Al–Si bulk metallic glasses (BMGs) with high glass formation ability (GFA) and large supercooled liquid regions (ΔT_g, ΔT_x = T_x – T_g) were developed. Investigation shows that the addition of Fe and Si elements is very effective to improve the glass formation ability of Ce-based BMGs. For an optimizing composition, the ΔT_g value is 95 K and the alloy can be prepared into bulk metallic glass rods with the diameters of at least 10 mm. In the Ce–Cu–Al–Fe alloys, the glass transition temperature (T_g), crystallization temperature (T_x) and ΔT_x increase with increasing Fe content. The reduced glass transition temperature (T_r = T_g/T_x) of the present BMG system is about 0.5–0.6 and is much lower than that of other metal base BMG systems with high GFA. Compressive fracture strength (σ) and Young’s modulus (E) of the Ce–Cu–Al–Fe BMGs are ~930 MPa and ~45 GPa, respectively, and increase with increasing Fe content.

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1. Introduction

In 1988, multicomponent Ln-based(1) and Mg-based(2,3) metallic glass alloys with large supercooled regions and high glass formation ability (GFA) were found and bulk metallic glasses (BMGs) were prepared firstly. These findings show that the alloys with large supercooled liquid regions (ΔT_g, ΔT_x = T_x – T_g) defined by the difference between the glass transition temperature (T_g) and crystallization temperature (T_x) have very high GFA and can be prepared into bulk metallic glass samples with larger sizes. On the other hand, from the viewpoint of the application, it is also very important to search for metallic glass alloys with larger ΔT_g and much more stable supercooled liquid for precision forming process of BMGs by use of viscous flow deformation behavior in the supercooled liquid regions. It is well-known that metallic glasses display softening phenomenon and superplasticity on their ΔT_g temperature ranges. This is highly useful for realizing high-performance micro-structures and micromachines to fabricate various microdevices as well as nanodevices as functional or structural parts. In recent years, many kinds of BMG systems have also been developed, for example, Zr-,(4) Cu-,(5) Fe-,(6) Co-,7) Ni-,(8,9) Ti-,(10) Pd-,(11) Nd-,12) Pr-,13) Pr-,14) and so like. For Zr-, Cu-, Ni-, and Ti-based BMGs,4,5,8-10) they exhibit good mechanical properties, like high fracture strength and high yield strength, and are ideal candidates for structural materials. Moreover, Fe-based BMGs have excellent soft magnetic properties6) and Nd-based12) (or Pr-based13) BMGs exhibit some hard magnetic properties. However, these metallic glasses have very high glass transition temperatures and increase significantly the technical complexity of micro-machines, and limit their fabrication and application as micro- or nanodevices. Among these alloys, La-1) and Pd-based BMGs are proper candidates for micromachines as its low T_g (less than 600 K) and large ΔT_x.15,16) More recently, Ce-based BMGs with lower T_g, larger and much more stable supercooled regions to realize the aim. In this paper, we further developed new Ce-based metallic glasses on the basis of Ce72Cu28 binary eutectic alloy. We found that the addition of Fe and Si elements is very effective to improve the glass formation ability and enlarge the supercooled liquid regions of Ce-based alloys. In an optimized composition, the supercooled liquid region is above 90 K and bulky metallic glass samples with the diameters of at least 10 mm can be prepared easily by copper mold casting. Moreover, mechanical properties of Ce-based BMGs were also investigated in detail, including fracture strength and elastic modulus, and so like.

2. Experimental Procedure

Ingots with nominal composition of (Ce_{0.72}Cu_{0.28}Al_{0.01}Fe_{x}Si_{y}) were prepared by arc melting mixtures of high purity Ce (99.99%), Cu (99.9%), Al (99.9%), Fe (99.9%) and Si (99.9%) under a Ti-gettered purified Ar atmosphere. Ce-based BMGs in a cylindrical rod form with the diameters of ~10 mm were produced by the copper mold casting method. The glassy phase was examined by X-ray diffraction (XRD) with Cu Kα radiation. 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 point and liquidus temperature of Ce-based alloys were measured by differential thermal analysis (DTA). To measure mechanical properties of the BMGs, the BMG rods with a diameter of 2 mm were cut to specimens of 4 mm length, and were polished carefully. The strain gauge was glued strongly on the surface of the specimens by using the special strain gauge cement. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height. Compressive testing was performed with an Instron testing machine and the strain rate was 5 × 10^{-4} s^{-1}.

3. Results and Discussion

Figure 1 shows DSC curves of the (Ce_{0.72}Cu_{0.28})_{90-x-y}}-


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AlFeFe$_2$Si$_y$ glassy alloys at a heating rate of 0.083 Ks$^{-1}$. It is obvious that the addition of Fe and Si elements causes the significant increase in the supercooled liquid region ($\Delta T_s$) of the alloys. The results of the (Ce$_{0.72}$Cu$_{0.28}$)$_{90-x}$Fe$_x$Al$_{10}$Fe$_3$Si$_y$ glassy alloys, including glass transition temperature ($T_g$), crystallization temperature ($T_x$), $\Delta T_s$, peak temperature ($T_p$), critical diameter of samples ($D$), melting point ($T_m$), and liquidus temperature ($T_l$), are listed in Table 1. For the (Ce$_{0.72}$Cu$_{0.28}$)$_{90-x}$Al$_{10}$ glassy alloy [Fig. 1(a)], the $T_g$, $T_x$, and $\Delta T_s$ are 330, 373, and 43 K, respectively. The addition of small amount of Si element increases $\Delta T_s$ greatly. For the (Ce$_{0.72}$Cu$_{0.28}$)$_{90}$Al$_{10}$Si$_{25}$ glassy alloy, the $T_g$, $T_x$, and $\Delta T_s$ are 370, 448, and 78 K, respectively. The addition of Fe element into Ce–Cu–Al alloy system also causes the significant increase in $T_g$, $T_x$, and $\Delta T_s$ (shown in Table 1). For the (Ce$_{0.72}$Cu$_{0.28}$)$_{85}$Al$_{10}$Fe$_5$ glassy alloy, the $T_g$, $T_x$, and $\Delta T_s$ are 361, 437, and 76 K, respectively. With increasing Fe content, the $T_g$ increases and the exothermic peaks shift to a higher temperature side. The $T_g$, $T_x$, and $\Delta T_s$ are, respectively, 369, 452, and 83 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{80}$Al$_{10}$Fe$_{10}$ glassy alloy, 377, 465, and 88 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{75}$Al$_{10}$Fe$_{15}$ glassy alloy, and 386, 455, and 89 K for the (Ce$_{0.72}$Cu$_{0.28}$)$_{70}$Al$_{10}$Fe$_{20}$ glassy alloy. One can notice that $T_g$ is also very low for Ce–Cu–Al–Fe glassy alloys. Figure 2 shows the dependence of $T_g$, $T_x$, and $\Delta T_s$ on Fe content in the (Ce$_{0.72}$Cu$_{0.28}$)$_{90-x}$Al$_{10}$Fe$_y$ glassy alloys. The $T_g$ increases with increasing Fe content [Fig. 2(a)]. We have discussed some factors of affecting $T_g$ in Ce–Cu–Al glassy alloys. The $T_g$ of Ce-based glassy alloys changes with the variation of Ce content and increases with the reduction of Ce content. In the present Ce–Cu–Al–Fe alloy system, the Fe addition causes the decrease in Ce content and leads to the increase in $T_g$. Both $T_x$ and $\Delta T_s$ also increase with increasing Fe content, but when the Fe content is above 10 at%, the $T_x$ and $\Delta T_s$ start to decrease [Figs. 2(b)(c)]. From Fig. 1 and Table 1, one can also notice that the (Ce$_{0.72}$Cu$_{0.28}$)$_{75}$Al$_{10}$Fe$_{10}$Si$_{15}$ glassy alloy displays much larger $\Delta T_s$ than that of the Ce-based alloys. The $T_g$, $T_x$, and $\Delta T_s$ are 382, 477, and 95 K, respectively. Large $\Delta T_s$ of 95 K suggests that the (Ce$_{0.72}$Cu$_{0.28}$)$_{25}$Al$_{10}$Fe$_{10}$Si$_{15}$ glassy alloy has very stable supercooled liquid and very high glass formation ability. Figure 3 shows XRD patterns of the Ce–Cu–Al–(Fe,Si) BMG rods with different diameters. Bulky metallic glass samples of Ce-based alloys with the diameter of 10 mm were prepared by copper mold casting. Only main broad peaks are seen in the diffraction patterns, indicating that these samples consist of a glassy phase basically. Figure 4 shows the external appearance of the cylindrical (Ce$_{0.72}$Cu$_{0.28}$)$_{90-x}$Al$_{10}$Fe$_x$Si$_y$ alloy samples with diameters of 6 and 10 mm. These bulk alloys have a good luster typical for metallic glass alloys, indicating the formation of bulk metallic glass structure even for the cylindrical sample with the large diameter of 10 mm.

Figure 5 shows DTA curves of the (Ce$_{0.72}$Cu$_{0.28}$)$_{90-x}$Al$_{10}$Fe$_y$Si$_y$ alloys at a heating rate of 0.083 Ks$^{-1}$. The melting behavior of the Ce-based alloys is rather complex and at least have two stages. We define the melting point of the first stage as the melting point of these alloys, as
shown in Fig. 5(f). The definition of liquidus temperature is also shown in Fig. 5(f). The results of the DTA measurement are also shown in Table 1. The addition of Fe as well as Si elements causes the variation of both melting point (Tm) and liquid temperature (Tl). For the (Ce0.72Cu0.28)90Al10 alloy [Fig. 5(a)], the Tm and Tl are 625 and 663 K, respectively. A small amount of addition of Fe element reduces Tm and Tl [shown in Fig. 2(d)]. The Tm and Tl, respectively, are 622 and 652 K for the (Ce0.72Cu0.28)85Al10Fe5 alloy, 615 and 649 K for the (Ce0.72Cu0.28)80Al10Fe10 alloy, 614 and 646 K for the (Ce0.72Cu0.28)75Al10Fe15 alloy. A small amount of addition of Si element also reduces Tl of the alloys. The Tl of the (Ce0.72Cu0.28)87.5Al10Si2.5 alloy is 658 K. For the (Ce0.72Cu0.28)78.5Al10Fe10Si1.5 alloy, the Tl is much lower and is 645 K. The reduced glass transition temperature Tg, which is defined from the ratio of Tg/Tl, is an important parameter that estimates the glass formation ability of the alloys. In some BMG alloy systems, for example Cu-based BMGs (Tg = 0.62),19 Pt-based BMGs (Tg = 0.64),20 and Pd-based BMG systems (Tg = 0.672),21 a larger Tg value suggests that the alloy has a higher GFA and can be prepared into metallic glass samples with larger sizes. From Table 1, it is obvious that the Tg values of the present Ce-based alloys increase with increasing Fe content and the ΔTg values also increase greatly. This is consistent with the above description. However, one can also notice that the Tg values are rather low and are less than 0.6 in the present alloys. The results suggest that Ce-based alloys with lower Tg values also have very high glass formation ability. This is different with other metal base BMGs with high GFA and high Tg. The reason that high glass-forming Ce-based alloys have lower Tg is not clear. It is possible to speculate22,23 that cerium metal has an excellent ability to purify the melt and further to improve the GFA of the present alloys. Further research work, including the mechanism of low Tg, oxygen content of Ce-based BMGs, microstructure of Ce-based BMGs, and so like, will be investigated in detail.

Figure 6 shows compressive stress-strain curves of the (Ce0.72Cu0.28)90−x−yAl10Fe10−x−y bulk metallic glasses with the diameter of 2 mm. From the curves, it is noticed that compressive fracture strength of the Ce-based BMGs is not high, but their elastic modulus is very low. For the (Ce0.72Cu0.28)85Al10Fe2.5 BMG, the compressive fracture strength (σf) and Young’s modulus (E) are 760 MPa and 35 GPa, respectively. But, with increasing Fe content, the σf and E are, respectively, 815 MPa and 39 GPa for the (Ce0.72Cu0.28)82.5Al10Fe7.5 BMG, 880 and 41 MPa for the (Ce0.72Cu0.28)80Al10Fe10 BMG. Figure 7 shows the dependence of compressive fracture strength (σf) and Young’s modulus (E) of the (Ce0.72Cu0.28)90−x−yAl10Fe10 BMGs on Fe...
content. The $\sigma_f$ and $E$ of the Ce-based BMGs increase with increasing Fe content. The increase in the fracture strength is due to the decrease in the Ce content. We also observe SEM fracture morphology of the Ce–Cu–Al–Fe BMGs. The Ce-based BMGs also display typical fracture morphology of bulk metallic glass alloys, like 45° degree angle fracture surface, vein-like patterns, and so like. This is consistent with compressive fracture morphology of other high strength BMGs, like Zr- and Cu-based BMGs, although the strength of Ce-based BMGs is much lower.

4. Conclusions

Ce–Cu–Fe–Al–Si bulk metallic glasses with high glass forming ability and large supercooled liquid region of 95 K were developed. The addition of Fe and Si elements is very effective to improve the $\Delta T_s$ and GFA of the Ce-based glassy alloys. Investigation shows that the Ce-based BMGs have very low $T_g$, $T_m$, and $T_f$. The reduced glass transition temperature, $T_{g\text{-}f}$, is less than 0.6. It means that the alloy system with low $T_{g\text{-}f}$ also has high glass-forming ability and can be prepared into bulk glass samples. This gives us a new design concept to develop new bulk metallic glass alloys, especially RE-based bulk metallic glasses (RE = Rare Earth). Compressive fracture strength ($\sigma_f$) and Young’s modulus ($E$) of the Ce–Cu–Al–Fe BMGs are ~930 MPa and ~45 GPa, respectively, and increases with increasing Fe content.

REFERENCES