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_x , $\Delta T_x = T_x - T_g$) 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_x 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 ($T_{rg} = T_g/T_i$) 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_f) 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-based¹⁾ 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_x , $\Delta T_x = T_x - T_g$) 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_x 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_x 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⁾ Pt-,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-based)¹³⁾ BMGs exhibit some hard magnetic properties. However, as 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 glass transition temperatures have been formed.^{17,18)} So low T_g means that Ce-based bulk metallic glasses soften even if these samples are put into boiling water. It suggests that Ce-based BMGs are appropriate materials of micromachines for fabricating various nanodevices. At present, it is important to find new 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})_{100-x-y}Al₁₀Fe_xSi_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 K α 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}-

Fig. 1 DSC curves of $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ glassy alloys.

Fig. 2 Dependence of T_g , T_x , ΔT_x , and T_l on Fe content in $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x}\text{Al}_{10}\text{Fe}_x$ glassy alloys.

Table 1 T_g , T_x , ΔT_x , T_p , D , T_m , T_l and T_{rg} of $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ glassy alloys.

Alloy	T_g (K)	T_x (K)	ΔT_x (K)	T_p (K)	D (mm)	T_m (K)	T_l (K)	T_g/T_m	T_g/T_l
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{95}\text{Al}_5$	330	373	43	379	2.0	630	660	0.524	0.500
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90}\text{Al}_{10}$	348	411	63	420	5.0	625	663	0.557	0.525
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{87.5}\text{Al}_{10}\text{Si}_{2.5}$	370	448	78	450	8.0	627	658	0.590	0.562
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Fe}_5$	361	437	76	441	6.0	622	652	0.580	0.554
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Fe}_{7.5}$	369	452	83	456	8.0	620	650	0.595	0.568
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{80}\text{Al}_{10}\text{Fe}_{10}$	377	465	88	469	10.0	615	649	0.613	0.581
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{75}\text{Al}_{10}\text{Fe}_{15}$	386	455	69	458	5.0	614	646	0.629	0.598
$(\text{Ce}_{0.72}\text{Cu}_{0.28})_{78.5}\text{Al}_{10}\text{Fe}_{10}\text{Si}_{1.5}$	382	477	95	480	>10.0	609	645	0.627	0.592

$\text{Al}_{10}\text{Fe}_x\text{Si}_y$ glassy alloys at a heating rate of 0.083 K s^{-1} . It is obvious that the addition of Fe and Si elements causes the significant increase in the supercooled liquid region (ΔT_x) of the alloys. The results of the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ glassy alloys, including glass transition temperature (T_g), crystallization temperature (T_x), ΔT_x , 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 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90}\text{Al}_{10}$ glassy alloy [Fig. 1(a)], the T_g , T_x and ΔT_x are 348, 411 and 63 K, respectively. The addition of small amount of Si element increases ΔT_x greatly. For the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{87.5}\text{Al}_{10}\text{Si}_{2.5}$ glassy alloy, the T_g , T_x and ΔT_x 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 ΔT_x (shown in Table 1). For the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Fe}_5$ glassy alloy, the T_g , T_x and ΔT_x 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 ΔT_x are, respectively, 369, 452 and 83 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Fe}_{7.5}$ glassy alloy, 377, 465 and 88 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{80}\text{Al}_{10}\text{Fe}_{10}$ glassy alloy, and 386, 455 and 69 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{75}\text{Al}_{10}\text{Fe}_{15}$ 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 ΔT_x on Fe content in the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x}\text{Al}_{10}\text{Fe}_x$ 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.¹⁸⁾ 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 ΔT_x also increase with increasing Fe content, but when the Fe content is above 10 at%, the T_x and ΔT_x start to decrease [Figs. 2(b)(c)]. From Fig. 1 and Table 1, one can also notice that the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{78.5}\text{Al}_{10}\text{Fe}_{10}\text{Si}_{1.5}$ glassy alloy displays much larger ΔT_x , namely, the T_g , T_x and ΔT_x are 382, 477 and 95 K, respectively. Large ΔT_x of 95 K suggests that the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{78.5}\text{Al}_{10}\text{Fe}_{10}\text{Si}_{1.5}$ 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 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ 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 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ alloys at a heating rate of 0.083 K s^{-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

Fig. 3 XRD patterns of Ce-based bulk metallic glasses with different diameters.

Fig. 4 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ bulk metallic glasses with diameters of 6 and 10 mm.

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 (T_m) and liquid temperature (T_l). For the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90}\text{Al}_{10}$ alloy [Fig. 5(a)], the T_m and T_l are 625 and 663 K, respectively. A small amount of addition of Fe element reduces T_m and T_l [shown in Fig. 2(d)]. The T_m and T_l , respectively, are 622 and 652 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Fe}_5$ alloy, 615 and 649 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{80}\text{Al}_{10}\text{Fe}_{10}$ alloy, 614 and 646 K for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{75}\text{Al}_{10}\text{Fe}_{15}$ alloy. A small amount of addition of Si element also reduces T_l of the alloys. The T_l of the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{87.5}\text{Al}_{10}\text{Si}_{2.5}$ alloy is 658 K. For the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{78.5}\text{Al}_{10}\text{Fe}_{10}\text{Si}_{1.5}$ alloy, the T_l is much lower and is 645 K. The reduced glass transition temperature T_{rg} , which is defined from the ratio of T_g/T_l , is an important parameter that estimates the glass formation ability of the alloys. In some BMG alloy systems, for example Cu-based BMGs ($T_{rg} = 0.62$),¹⁹ Pt-based BMGs ($T_{rg} = 0.64$),²⁰ and Pd-based BMG systems ($T_{rg} = 0.672$),²¹ a larger T_{rg} 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 T_{rg} values of the present Ce-based alloys increase with increasing Fe content and the ΔT_x values also increase greatly. This is consistent with the above description.

Fig. 5 DTA curves of $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x-y}\text{Al}_{10}\text{Fe}_x\text{Si}_y$ alloys.

Fig. 6 Compressive stress-strain curves of $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x}\text{Al}_{10}\text{Fe}_x$ bulk metallic glasses.

However, one can also notice that the T_{rg} values are rather low and are less than 0.6 in the present alloys. The results suggest that Ce-based alloys with lower T_{rg} values also have very high glass formation ability. This is different with other metal base BMGs with high GFA and high T_{rg} . The reason that high glass-forming Ce-based alloys have lower T_{rg} is not clear. It is possible to speculate^{22,23} 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 T_{rg} , 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 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x}\text{Al}_{10}\text{Fe}_x$ bulk metallic glassy alloys 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 $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{85}\text{Al}_{10}\text{Fe}_{2.5}$ BMG, the compressive fracture strength (σ_f) and Young's modulus (E) are 760 MPa and 35 GPa, respectively. But, with increasing Fe content, the σ_f and E are, respectively, 815 MPa and 39 GPa for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{82.5}\text{Al}_{10}\text{Fe}_{7.5}$ BMG, 880 and 41 MPa for the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{80}\text{Al}_{10}\text{Fe}_{10}$ BMG. Figure 7 shows the dependence of compressive fracture strength (σ_f) and Young's modulus (E) of the $(\text{Ce}_{0.72}\text{Cu}_{0.28})_{90-x}\text{Al}_{10}\text{Fe}_x$ BMGs on Fe

Fig. 7 Dependence of fracture strength (a) and elastic modulus (b) of Ce–Cu–Al–Fe BMGs on Fe content.

content. The σ_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 ΔT_x and GFA of the Ce-based glassy alloys. Investigation shows that the Ce-based BMGs have very low T_g , T_m , and T_i . The reduced glass transition temperature, T_{rg} , is less than 0.6. It means that the alloy system with low T_{rg} 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 (σ_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.

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