"Soft" bulk metallic glasses based on cerium

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CeAlNiCu alloys can be readily cast into glassy rods with up to 5 mm in diameter. The Ce-based bulk metallic glasses (BMGs) exhibit a wide supercooled region up to 78 K, very low glass transition temperature (T_g=359 K), melting temperature (T_m=637 K), and Debye temperature (θ_D=144 K). Ultrasonic measurements demonstrate that these Ce-based BMGs are very soft, having the lowest elastic moduli in known BMGs. These features suggest that the "soft" BMGs are an ideal model system for investigating physical problems in glass transition, supercooled liquid and melt states, and have potential applications as a functional material as well. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1768308]

Recently, metallic glasses have regained considerable interest due to the fact that new metallic glass-forming families with a critical cooling rate of less than 100 K/s can be made glassy with dimensions of 1 mm or more.[1,2] Compared with conventional transition metal (e.g., Zr, Pd, Fe, Ni, Co, Ti, and Cu based bulk metallic glasses (BMGs), only few rare earth (RE) based BMGs, which could have promise for application as functional materials, have been developed and investigated.[2–5] Cerium is the most abundant RE metal on earth.[6] It is also one of the most reactive RE metal and oxidizes very readily even at room temperature.[6] Because Ce absorbs more oxygen then Zr does during the preparation process, to take using Ce as the based component instead of Zr to form BMGs would be of significance to extend the current understanding of the effects of oxygen on glass forming ability (GFA) of BMG-forming alloys. The oxygen content normally significantly deteriorates the GFA of an alloy.[1,2] Another intrinsic feature of cerium is its variable electronic structure and dual valency states, because of which only a small amount of energy is required to change the relative occupancy of the electronic levels. For example, when Ce is subjected to high pressure or low temperature a volume change of approximately 10% results.[6] Therefore the structural and physical properties of Ce-based BMGs should have intrinsic characteristics, which should be different from those of other known BMGs.

In this work, a family of Ce-based BMGs with excellent GFA is developed. These BMGs show the lowest glass transition temperature, T_g, melting point T_m, and elastic modulus of all the BMGs. Their elastic constants are comparable with those of polymers and other nonmetallic glasses. The "soft" BMGs offer conveniences for investigation of the nature of the glass transition, supercooled liquid and especially the metallic glass-forming melts, which has been less studied due to the experimental difficulties at higher temperatures. The formation of Ce-based BMGs is also of significance for understanding the universal features of structure and property of metallic glasses. The BMG itself has some promise for future applications such as phase change erasable optical storage.[7]

The Ce–Ni–Al–Cu alloys with nominal compositions listed in Table I were prepared by arc melting pure Cu, Ni, Al, Nb with industrial pure Ce in a Ti-gettered argon atmosphere. The purity of Ce is only about 99.5 wt%, which is much lower than that of other base elements of BMGs. The alloy ingots were remelted and suck cast into a Cu mold to get cylindrical rods in different diameters. The structure of the as-cast alloys was ascertained by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu $K\alpha$ radiation. Thermal analysis was carried out in a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) at a heating rate of 10 K/min. The acoustic velocities were measured using a pulse echo overlap method by a MATEC 6600 model ultrasonic system with a measuring sensitivity of 0.5 ns.[8] The density was determined by the Archimedean technique and the accuracy lies with 0.1%. Elastic constants (e.g., the Young's modulus E, the shear modulus G, the bulk modulus K, and the Poisson's ratio σ) and the Debye temperature θ_D were derived from the acoustic velocities and the density.[8]

Figure 1 shows the XRD patterns of the as-cast $Ce_{60}Al_{10}Ni_{10}Cu_{20}$ alloy. The XRD curve shows the broad diffraction maxima characteristic of an amorphous structure without appreciable diffraction peaks that may correspond to crystalline phases. The result indicates that the $Ce_{60}Al_{10}Ni_{10}Cu_{20}$ cylinder-shaped rod with diameter of 1 mm is amorphous. With the composition modification, the $Ce_{70}Al_{10}Ni_{10}Cu_{10}$, $Ce_{65}Al_{12.5}Ni_{12.5}Cu_{10}$, and $Ce_{60}Al_{15}Ni_{15}$

TABLE I. Values of the T_g, T_x, T_m, T_l, y, T_{rg}, and the critical diameters of fully amorphous rods of the Ce-based BMGs. The data for other BMGs adopted from Refs. 11, 13, and 17 are also listed.

Alloy system	Critical diameter (mm)	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT (K)	T_{rg}	y
$Ce_{60}Al_{10}Ni_{10}Cu_{20}$	1	374	441	645	672	67	0.58	0.422
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	3	359	377	639	714	18	0.56	0.351
$Ce_{65}Al_{12.5}Ni_{12.5}Cu_{10}$	3	371	402	644	709	31	0.58	0.372
$Ce_{60}Al_{15}Ni_{15}Cu_{10}$	3	390	468	644	685	78	0.61	0.435
$Ce_{65}Al_{10}Ni_{10}Cu_{10}Nb_5$	5	359	384	637	702	25	0.56	0.362
$Ce_{57}Al_{10}Ni_{12.5}Cu_{15.5}Nb_5$	2	369	415	638	677	46	0.58	0.397
$Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$	–	656	735	1108	1168	79	0.59	0.403
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{12.5}$	–	623	672	932	996	49	0.67	0.415
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	–	575	670	804	840	95	0.72	0.473

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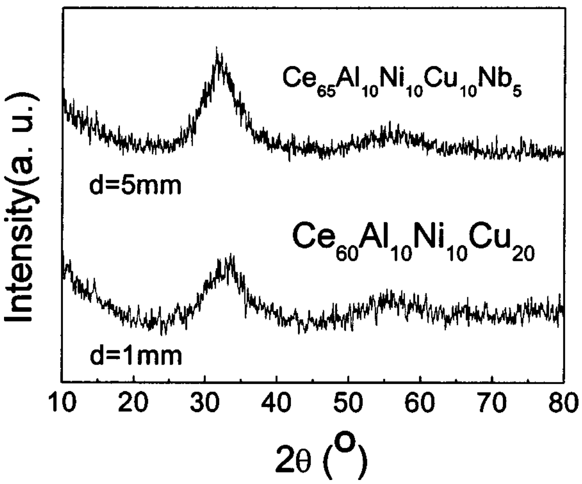

FIG. 1. XRD patterns of the as-cast 5 mm diameter rod of $Ce_{65}Al_{10}Ni_{10}Cu_{10}Nb_5$ and 1 mm diameter rod of $Ce_{60}Al_{10}Ni_{10}Cu_{20}$ alloys.

Cu_{10} BMG rod size extends to 3 mm in diameter. If more components such as Nb are introduced, the BMG rod size can be further extended to 5 mm as shown in Fig. 1. The transimission electron microscope (TEM) confirms the glassy structure (not shown here), high resolution TEM image shows that a small amount of nanocrystallites less than 5 nm in the amorphous matrix which cannot be detected by XRD. In particular, the Ce-based BMGs, unlike other BMGs such as Zr-based BMGs,[1,2] can be easily obtained with low-purity base component because their GFA is not so sensitive to oxygen and other impurities. In fact, RE addition is found to be very effective to enhance the oxygen resistance during the glass formation of the Zr-, Fe-, and Mg-based BMG forming alloys, and Mg-based BMG with RE addition even can be cast in air condition.[9] The beneficial effects have not been well understood yet. Cerium has been widely used as a good scavenging flux in the steel cast process, because the reaction between Ce and O is thermodynamically favored compared to that between O and Fe. A small part of Ce in the alloys should have the role of scavenging and deoxidization in the melting and cast processes. The Ce-based ingots actually have obvious impurities on the surface (not be cast)

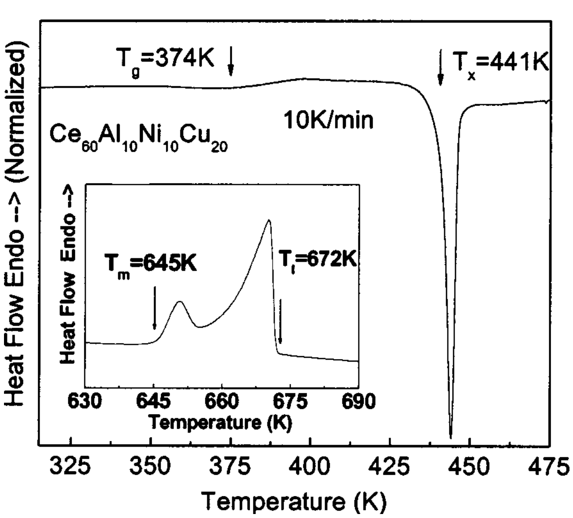

FIG. 2. DSC trace of the $Ce_{60}Al_{10}Ni_{10}Cu_{20}$ BMG showing the glass transition and crystallization as well as the melting.

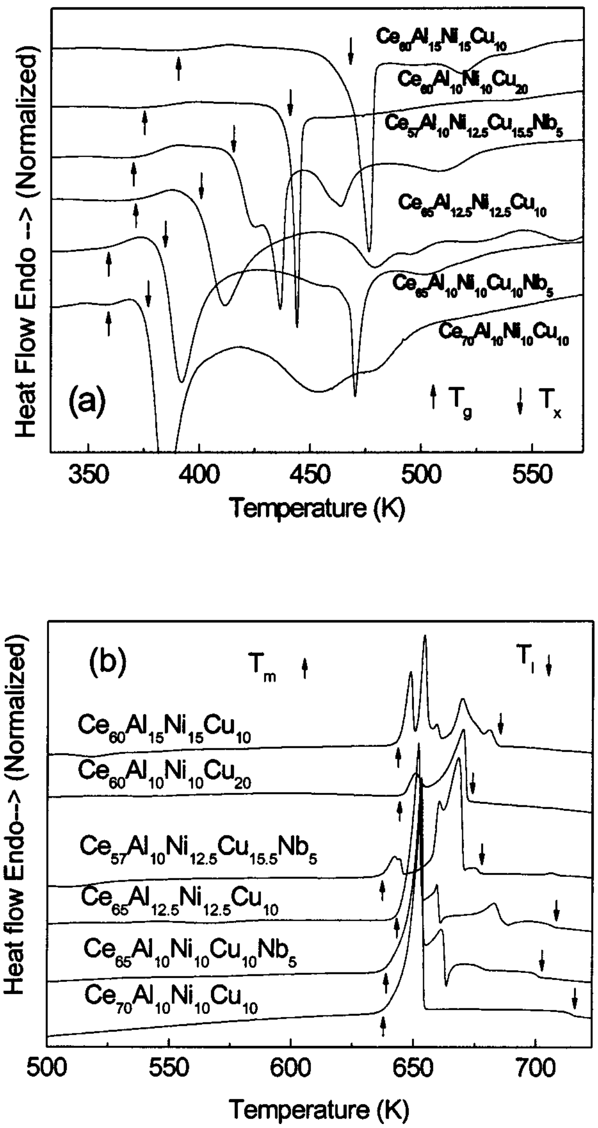

FIG. 3. (a) DSC traces of the Ce-based BMGs with different compositions; (b) DSC traces of the Ce-based BMGs showing the melting processes upon different compositions.

which demonstrates the scavenging role of Ce.

Figure 2 is the DSC trace of the $Ce_{60}Al_{10}Ni_{10}Cu_{20}$ BMG. The crystallization process is a single exothermic reaction indicating a one-step transformation from the glass into the crystalline state. The remarkable features of the trace is an obvious endothermic feature before crystallization indicating a glass transition with onset at 374 K and a large supercooled liquid region of 67 K($\Delta T = T_x - T_g$). With composition modification the T_g of the $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMG reaches 359 K, which is the lowest value for the known BMGs to date. From the endothermal signal of melting, we can deduce that the alloy is not close to eutectic point. The T_x, T_m, and liquidus temperature, T_l are determined to be 441, 645, and 672 K, respectively. The reduced glass transition temperature $T_{rg}(T_{rg} = T_g/T_m)$,[10] and the γ value $[\gamma = T_x/(T_g + T_l)$[11]] which are critical parameters in determining the GFA of an alloy, are 0.58 and 0.422, respectively. The distinct glass transition and the sharp crystallization as well as large values of T_{rg} and γ further confirm the glassy structure and the high GFA of the alloy. For comparison, thermal parameters of the

TABLE II. Acoustic data and elastic constants and θ_D for the Ce-based BMGs, amorphous carbon, nonmetallic glasses, and $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG. The data for other glass are adopted from Refs. 6, 16, and 17.

Glasses	ρ (g/cm^3)	V_l (km/s)	V_s (km/s)	E (GPa)	G (GPa)	K (GPa)	σ	θ_D (K)
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	6.670	2.521	1.315	30.3	11.5	27.0	0.313	144
Amorphous carbon	1.56	3.88	2.407	21.4	9.01	11.4	0.187	338
Nylon	-	-	-	4.0	1.43	6.54	0.40	-
Polypropylene	-	-	-	4.13	1.54	4.37	0.34	-
Polyethylene	-	-	-	2.55	0.91	4.54	0.41	-
Fused quartz	2.201	5.96	3.75	72.7	31.0	36.9	0.17	496
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	6.125	5.174	2.472	101.2	37.4	114.1	0.352	327

Ce-based BMG and other typical BMGs[4,12–14] are listed in Table I. Compared with the other typical BMGs with high GFA, the Ce-based BMGs do indeed have excellent GFA and much lower T_g and T_m. According to the BMG formation criterions,[1,2] the sufficient atomic radius differences between Ce (atomic radius 2.70 Å) and Al, Ni, and Cu, the larger negative heat of mixing between Ce and Ni (−43 kJ/mol[15]) and multicomponents result in the excellent GFA of the Ce-based alloys.

Figure 3 shows the DSC results of the BMGs with different compositions. Their values of T_g, T_x, T_m, T_l, ΔT, T_{rg}, and γ are listed in Table I. The crystallization and melting proceses of these BMGs are sensitive to the composition as shown in Fig. 3. The $Ce_{60}Al_{15}Ni_{15}Cu_{10}$ alloy has the highest T_g(390 K), the largest ΔT_x(78 K), the largest T_{rg}, (0.61) and y(0.435) among Ce-based BMGs. However, the melting trace in Fig. 3(b) shows that the $Ce_{60}Al_{15}Ni_{15}Cu_{10}$ alloy is far from the eutectic point. There is a large melting interval (41 K) between T_m and T_l comprising more than three melting steps. The addition of Nb can enhance the GFA, further decrease T_g and increase ΔT of the Ce-based alloys. From Table I, the values of T_{rg}, y and the GFA (represented by critical diameter) do not show a consistent trend as other BMGs do.[11,12]

The elastic constants and θ_D of the typical BMGs calculated from the acoustic data and other BMGs,[16,17] amorphous carbon,[16] fused quartz,[16] and polymers[18] and listed in Table II. The E, G, K, and θ_D of the representative $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMG are 30.3 GPa, 11.5 and 27.0 GPa and 144 K, respectively. To our knowledge, these are the lowest elastic constants values among metallic glasses known so far, and they are comparable to those of amorphous carbon and oxides fused quartz, and close to those of polymers list in Table II, indicating that the BMGs exhibit elastic properties similar to those of nonmetallic glasses, and have much "softer" elastic constants than other BMGs.[16,17] The extremely small value of θ_D also reveals that the BMG is much less rigid than other BMGs. However, the value of σ of the Ce-based BMG is much larger than that of nonmetallic glasses and similar to that of other BMGs. The σ value directly reflects the bonding forces of a material. The result reveals that the BMGs short-rant structure is still based on metallic bonds like for other BMGs.[8] The Ce-based BMG with the structural characteristics of metallic glass exhibits elastic properties similar to those of nonmetallic glasses. Ce has a special variable electronic structure and dual valency states, so the structural and physical properties of Ce-based BMGs should be intrinsically different from other BMGs Related properties studies are still in progress. We believe that the new and soft Ce-based BMGs, which have high GFA, a large supercooled liquid region, and the lowest values of T_g, T_m, θ_D, and elastic constants, offer an ideal material to study the nature of the glass transition and metallic melt with a large accessible time and temperature windows in very low temperature region. The BMGs with unique features also have potential applications as functional materials such as information storage materials and biomaterials.

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