Bulk metallic glasses based on binary cerium and lanthanum elements

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The authors reported the formation and dynamic and thermodynamic properties of bulk metallic glasses (BMGs) based on binary Ce and La elements, in which the compositions of Ce and La can be gradually changed in the range from 0 to 100 at. % without deteriorating the glass-forming ability. The properties of the binary base glasses can be tuned by modification of the Ce and La compositions. The BMGs with unique features and tunable properties might provide a model system to investigate some long-standing issues in BMG-forming alloys. The approach has implication for designing BMGs with tunable properties. © *2007 American Institute of Physics*.
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The bulk metallic glasses (BMGs) have attracted a lot of interest because of their extraordinary properties that have both engineering and functional application potentials.[1,2] Finding BMGs with the desired properties is a long-standing but important issue for both scientists and engineers. The general strategy for developing BMG alloys is to select one element as a base. So, up to now, most multicomponent BMGs have been developed based on one element such as Zr, Cu, and Ce.[2] We then come up with an idea that if a BMG bases on two or more elements with different properties, and the composition of the base elements can be gradually changed in a large composition range without deteriorating the glass-forming ability, we can probably tune its properties by arbitrarily adjusting the proportion of the two base elements. The BMGs with unique features and tunable properties might provide a model system to investigate some long-standing issues in metallic glasses. The approach may also have implication for searching BMGs.[3]

The cerium and lanthanum have similar atomic radii and different properties because of their different electronic structures. For example, they have markedly different magnetic properties (Ce has $4f$ electrons). The La- and Ce-based BMGs are of different liquid fragility (the La-based BMGs are more fragile than Ce-based BMGs), while both the Ce and La elements are the good BMG-forming bases.[4] It is found that the cheap misch (including La and Ce and other rare earth elements) based BMGs can be formed.[5–7] So, as an example, the Ce and La were used as the binary bases with gradually changed Ce and La compositions to identify the idea.

In this letter, a series of $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ BMGs based on the Ce–La has been obtained through gradually changed Ce and La compositions. The properties and fragility of the series BMGs have been investigated. The results are used to validate the correlation between Poisson's ratio and fragility.[8,9]

The $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ alloys ($x=0-100$ at. %, increasing step of 10%) were prepared by arc-melting pure Ce, La, Cu, Al, and Co in a Ti-gettered argon atmosphere. The alloy ingots were melted and suck cast into a Cu mold to get cylindrical rods in 3 mm diameters. The glassy 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 different heating rates, ranging from 5 to 100 K/min. The acoustic velocities were measured using a pulse echo overlap method by a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns.[10] The density ρ was determined by the Archimedean technique and the accuracy lies within 0.1%. Elastic constants (e.g., Young's modulus E, shear modulus G, bulk modulus K, and Poisson's ratio σ) were derived from the acoustic velocities and the density.[10] The values of fragility (m) were determined according to the method in Ref. 11. The crystallization activation energy (E_x) of the BMGs was evaluated using Kissinger's method.[12]

Figure 1 shows the XRD patterns of the as-cast cylinder-shaped rod $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ alloys with diameter of 3 mm. The broad diffraction maxima in the XRD curves show characteristic of an amorphous structure. Unlike

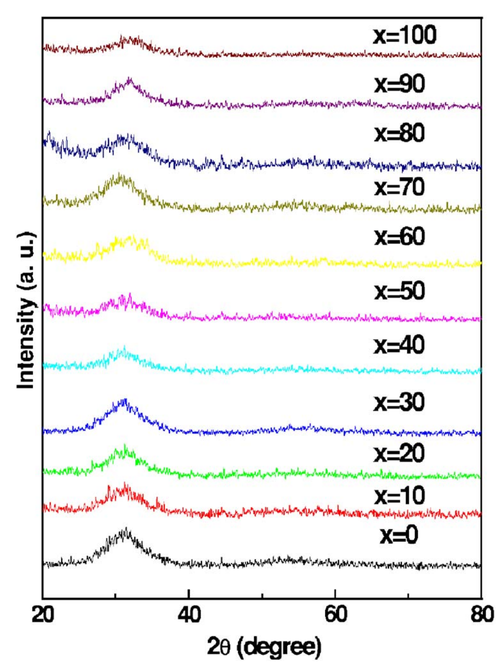

FIG. 1. (Color online) XRD patterns of the $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ BMGs (x ranges from 0 to 100 with a step of 10%).

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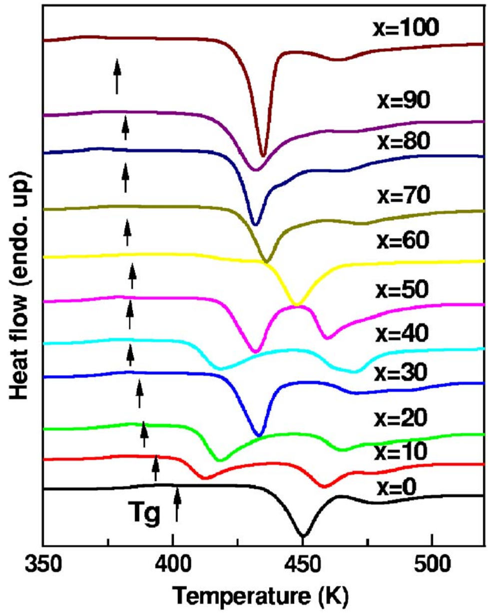

FIG. 2. (Color online) DSC traces focusing on the glass transition and crystallization of the $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ BMGs (the heating rate is 20 K/min).

Ti-based BMGs that exhibit phase separation,[13] no evidence of phase separation in these as-cast glasses is found. Figure 2 shows the DSC scans of the glass alloys using a heating rate of 20 K/min. These as-cast samples have distinct glass transition and sharp crystallization peaks in their DSC traces, confirming the glassy structure. The single glass transition process in each curve confirms that no phase separation happens. These BMGs show distinct different crystallization processes. The XRD and DSC results indicate that the Ce–La based BMGs are prepared. A summary of the thermal properties of the (CeLa) based glassy alloys is listed in Table I. The variations of the supercooled liquid region ΔT ($\Delta T = T_x - T_g$, in which T_x is the onset temperature of the first crystallization event and T_g is the glass transition temperature) and the crystallization activation energy (E_x) with the changing composition of Ce or La are determined. These BMGs show good thermal stability characterized by large supercooled liquid regions of over 50 K. The values of E_x are relatively low compared with those of other BMGs.[14,15]

The elastic constants and fragility of the Ce–La based BMGs are obtained and also listed in Table I. The BMGs show three distinct features. The first is that both G and E do not significantly change and remain nearly constant at ~11 and ~31 GPa, respectively, with the Ce composition changing. According to the cooperative shear model theory,[16] for a fixed glass configuration the barrier height for shear flow is proportional to the isoconfigurational G. The similar shear modulus of the Ce–La based BMGs indicates that these alloys have similar configurational potential energy.[16] Secondly, ρ, K, T_g, and δ are very sensitive to changes in composition, as shown in Fig. 3 [to show the changing tendency, the data of each parameters are normalized to their corresponding values of $Ce_{68}Al_{10}Cu_{20}Co_2$ ($x=100$)]. With the increasing percentage of Ce, the K, T_g, and δ of the BMGs decrease nearly monotonously. For example, the K of the Ce–La based BMGs decreases by about 38% from 38 to 30 GPa. On the contrary, ρ monotonously increased with the increase of the content of Ce. Thirdly, these BMGs have markedly different values of m ranging from 50 to 30.

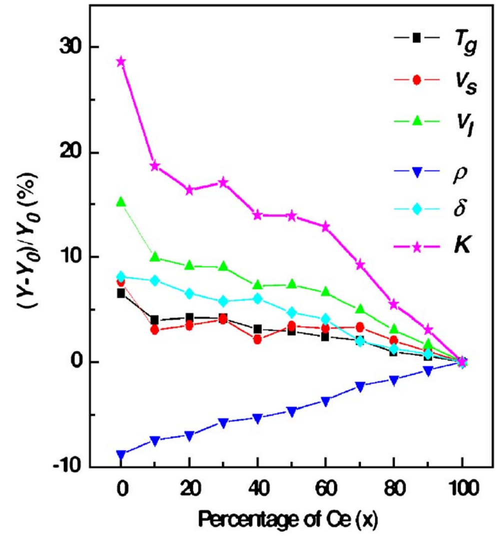

FIG. 3. (Color online) Relative changes $\Delta Y = (Y - Y_0)/Y_0$ ($Y = T_g$, V_s, V_l, ρ, δ, and K) vary with the raise of the percentage of Ce (x). Y_0 is the value of T_g, V_s, V_l, ρ, δ, and K of $Ce_{68}Al_{10}Cu_{20}Co_2$ ($x=100$).

These alloys exhibit glass transition temperature below 375 K and relatively wide supercooled liquid regions of 40–75 K. The low shear modulus also corresponding to the low T_g in these BMGs and the stable supercooled liquid state indicate the polymerlike thermoplastic behavior of the BMGs, which is desirable for both scientific significance and practical applications.[4,5] It is found that the BMGs with an

TABLE I. Thermodynamic parameters, elastic constants, and fragility for the Ce–La based BMGs.

Alloy system	T_g (K)	T_x (K)	ΔT (K)	E_x (eV)	ρ (g/cm^3)	V_l (km/s)	V_s (km/s)	K (GPa)	G (GPa)	E (GPa)	σ	m
$La_{68}Al_{10}Cu_{20}Co_2$	374	439	65	1.31	6.210	2.971	1.391	38.77	12.02	32.68	0.360	48
$(Ce_{10}La_{90})_{68}Al_{10}Cu_{20}Co_2$	365	403	38	1.46	6.303	2.836	1.332	35.77	11.18	30.38	0.358	33
$(Ce_{20}La_{80})_{68}Al_{10}Cu_{20}Co_2$	366	409	43	1.47	6.334	2.815	1.337	35.07	11.33	30.69	0.354	36
$(Ce_{30}La_{70})_{68}Al_{10}Cu_{20}Co_2$	366	421	55	1.28	6.418	2.812	1.345	35.29	11.61	31.38	0.352	33
$(Ce_{40}La_{60})_{68}Al_{10}Cu_{20}Co_2$	362	408	45	1.44	6.447	2.766	1.320	34.35	11.24	30.39	0.353	33
$(Ce_{50}La_{50})_{68}Al_{10}Cu_{20}Co_2$	362	419	57	1.41	6.492	2.769	1.337	34.32	11.60	31.27	0.348	37
$(Ce_{60}La_{40})_{68}Al_{10}Cu_{20}Co_2$	360	411	51	1.38	6.558	2.749	1.334	31.41	11.67	32.93	0.346	35
$(Ce_{70}La_{30})_{68}Al_{10}Cu_{20}Co_2$	357	426	67	1.27	6.653	2.707	1.335	32.93	11.86	31.77	0.339	38
$(Ce_{80}La_{20})_{68}Al_{10}Cu_{20}Co_2$	355	424	69	1.56	6.694	2.659	1.319	31.79	11.64	31.13	0.337	41
$(Ce_{90}La_{10})_{68}Al_{10}Cu_{20}Co_2$	353	422	69	1.07	6.755	2.621	1.306	30.75	11.51	31.07	0.335	32
$Ce_{68}Al_{10}Cu_{20}Co_2$	351	427	76	1.63	6.806	2.579	1.292	30.13	11.36	30.28	0.333	29

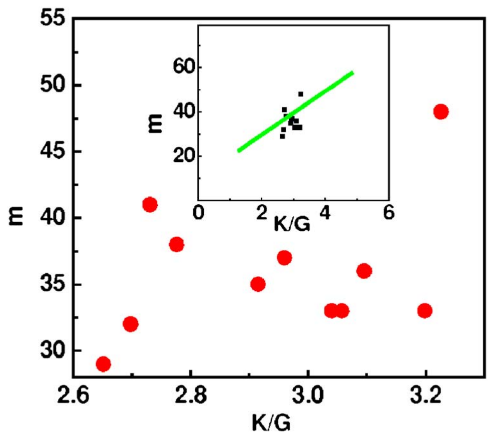

FIG. 4. (Color online) Correlation between fragility and the ratio of bulk to shear modulus of the $(Ce_xLa_{100-x})_{68}Al_{10}Cu_{20}Co_2$ BMGs. Inset: enlarged coordinates. The green line is the Sokolov-Novikov correlation.

inherent and strong structural disorder show the heavy fermion behavior, and their heavy fermion behavior can be tuned by the composition and structural relaxations.[17] The composition modification of Ce with 4f electrons and La without 4f electrons can induce the delocalization of the Ce 4f electrons in the BMGs and produce internal variation from the Kondo regime to the valence fluctuation regime, with the heavy fermion behavior at the crossover.[17] The glasses might provide a model system to investigate some long-standing issues with electron strong correlation in complex alloys.

Whether there exists a correlation between the liquid fragility and Poisson's ratio σ (or the ratios between the shear modulus and the bulk modulus, K/G) of glasses is still on debate.[8,9,18] The difference and similarity of the Ce–La based BMGs make them suitable for studying and identifying the relationships between the fragility and other physical properties such as the relations between the fragility and Poisson's ratio without taking the free electron's contribution into account,[9,19] because the free electron's contribution to the bulk modulus in the as-cast BMGs is almost the same. Figure 4 shows the relationship between the fragility and Poisson's ratio of these BMGs. As we can see, it appears that Poisson's ratio and the fragility of these BMGs did not show a similar changing tendency. In contrast to the expectation from the results reported by Novikov and Sokolov,[8,9] there is no obvious correlation between them. It is noted that the result does not mean the invalidity of the Sokolov-Novikov equation,[9] because the K/G ratios of BMGs are close to the ideal value of $8/3$,[20] and the fragility scan of the Ce–La based BMGs is not wide enough. Adding our data to the Sokolov-Novikov correlation figure with large fragility scale, we find that the data very approximately abide the trend in larger fragility scale[9] (see the inset figure).

In summary, we developed BMGs with their base containing binary Ce–La elements and the base composition tunable. By adjusting the percentage of the base elements of these glasses, BMGs with desired properties can be obtained. These BMGs, which might be desirable for both scientific significance and practical applications, are a model system to identify the correlations found in BMGs. The strategy is applicable to a wide variety of metallic alloys and may serve as a design consideration for the development of BMG materials with tunable properties.

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