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Erbium- and cerium-based bulk metallic glasses

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Abstract

We report that the elastic constants of available bulk metallic glasses (BMGs) show a correlation with a weighted average of the elastic constants for the constituent elements. Based on the correlation, we report the formation of two families of erbium- and cerium-based BMGs with controllable elastic properties.

Keywords: Metallic glasses; Elastic properties

1. Introduction

The mechanism of glass formation is one of the central issues in condensed matter physics and materials science. Substantial progress has been made in understanding these issues over the past decades, yet many key questions remain [1–5]. One of the general guiding principles for designing alloys to form bulk metallic glasses (BMGs) is to pick multiple elements (more than three different elements) with dramatic differences in size, which leads to increased complexity and size of the crystal unit cell and reduces the energetic advantage of forming crystalline phases [1,3]. A complicated structure with an atomic configuration corresponding to a higher degree of dense randomly packed structure leads to high viscosity and slow crystallization of supercooled liquid. Although some empirical rules, based on thermodynamics and kinetics, give useful directions in general [1,3–5], the development of new BMGs is still a very time-consuming process of selection and screening of different combinations of elements. The development of BMGs has always been "hit or miss" as to whether the resulting glass has excellent glass-forming ability (GFA) or turns out to have excellent mechanical properties. Therefore, finding a more specific criterion for BMG formation is very important and would lead to smart searches for new BMGs with desirable properties rather than the trial-and-error method.

In this work, we tried to collect all available relevant data on bulk metallic glasses to show that there are correlations between the elastic constants of BMGs and a weighted average of the elastic constants for the constituent elements. We have attempted to develop two new families of Er-based and Ce-based BMGs with desirable properties based on the correlations.

2. Experimental

BMGs exhibit isotropic elastic constants that can be determined from the longitudinal and transverse sound velocities (using a pulse echo overlap method with a 10 MHz at a MATEC 6600 ultrasonic system) [5]. The bulk modulus B, Young's modulus E, the shear modulus G and Poisson's ratio v are derived from the acoustic velocities with an accuracy better than 5% [5]. Table 1 includes all available relevant data on typical BMGs based on different elements with representative compositions.

3. Results and discussion

Our previous studies show that the elastic constants (M) of some BMGs can be calculated in the form [6,7]:

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Table 1
Calculated and experimental elastic constants for various BMGs, all the elastic constants from Refs. [5,7,18]

BMGs	B (GPa)		G (GPa)		E (GPa)		B/G	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	114.75	114.99	37.44	47.10	101.30	105.47	3.06	2.44
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	113.38	113.69	35.20	47.61	95.71	103.94	3.22	2.39
$Zr_{53}Ti_5Cu_{20}Ni_{12}Al_{10}$	106.78	106.93	32.12	37.33	87.58	84.80	3.32	2.86
$Zr_{48}Nb_8Cu_{12}Be_{24}Fe_8$	113.38	116.10	35.20	45.57	95.71	100.41	3.22	2.55
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	107.67	107.41	31.98	36.63	87.30	82.63	3.37	2.93
$Zr_{65}Al_{10}Ni_{10}Cu_{15}$	106.65	103.40	30.27	35.73	82.96	79.11	3.52	2.89
$Nd_{60}Al_{10}Fe_{20}Co_{10}$	46.54	45.88	19.44	22.16	51.20	57.18	2.39	2.07
$Pd_{77.5}Cu_6Si_{16.5}$	174.65	156.64	32.91	35.00	92.91	96.37	5.31	4.48
$La_{55}Al_{25}Cu_{10}Ni_5Co_5$	44.13	41.32	15.60	19.12	41.86	50.77	2.83	2.16
$La_{66}Al_{14}Cu_{10}Ni_{10}$	34.91	37.48	13.44	17.88	35.72	47.38	2.60	2.10
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	128.23	122.33	36.93	41.38	101.10	103.09	3.47	2.96
$Pr_{55}Al_{12}Fe_{30}Cu_3$	41.38	44.40	18.20	21.95	47.61	54.85	2.27	2.02
$Mg_{65}Cu_{25}Tb_{10}$	44.71	53.15	19.61	20.84	51.32	55.09	2.28	2.55
$Cu_{50}Zr_{50}$	101.2	114.32	32	39.11	87	89.29	3.16	2.92
$(Cu_{50}Zr_{50})_{96}Al_4$	113.7	112.1	32.39	38.34	88.73	88.32	3.51	2.92
$(Cu_{50}Zr_{50})_{90}Al_7Gd_3$	117.1	104.35	32.4	36.94	89.0	86.02	3.61	2.82
$Gd_{40}Y_{16}Al_{24}Co_{20}$	58.0	53.48	23.5	27.60	62.2	70.63	2.47	1.94
$Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$	58.5	55.76	24.4	29.31	64.2	74.14	2.40	1.90
$Ni_{50}Nb_{50}$	168.3	174.9	48.2	50.7	132	137.7	3.49	3.45
$Ce_{68}Al_{10}Cu_{20}Fe_2$	31.0	30.0	11.8	17.0	30.8	42.0	2.60	1.76
$Er_{50}Y_6Al_{24}Co_{20}$	65.07	58.49	26.98	31.19	71.10	80.22	2.41	1.88

$$M^{-1} = \sum f_i \cdot M_i^{-1}, \tag{1}$$

where M_i and f_i denote any elastic constant and the atomic percentage of the constituent element, respectively. We tried to apply Eq. (1) to a variety of available BMGs and the calculated elastic constants are listed in Table 1. For the elastic constants of the constituent elements, we used the data of Ref. [8]. Fig. 1 shows the ratio between the experimental and calculated E, G, B and B/G (or alternatively v) for a variety of BMGs. The elastic constants ratios range from 0.70 to 1.4 (for E and K the ratio is closer to 1.0, the ratios for G have relatively larger deviations) indicating that the elastic constants of the BMGs calculated using Eq. (1) are roughly in agreement with those obtained by the ultrasonic method. The elastic constants of the BMGs show a correlation with a weighted average of the elastic constants for the constituent elements. The results imply that the elastic moduli of the BMGs depend on their metallic components, and the base element makes the predominant contribution to the elastic moduli. Thus we can approximately adopt the calculated results even if the experimental data of a BMG are not known.

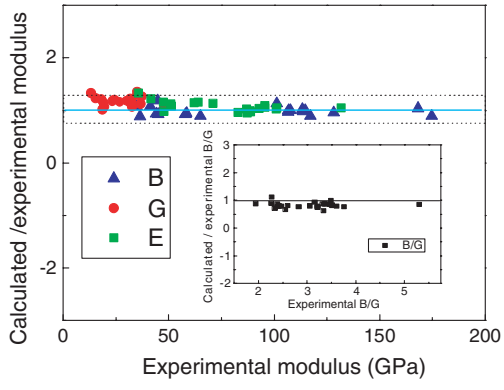

Fig. 1. The ratio of calculated elastic constants to experimental results for various BMGs. The inset is the ratio of calculated B/G to experimental B/G.

Sufficient data on elastic moduli, mechanical properties and glass transition of various BMGs show that there are clear correlations between fracture strength σ and E ($E/\sigma \approx 50$), and Vicker's hardness Hv and E ($E/Hv \approx 25$) [4,5]. On the other hand, the elastic constants and T_g of BMGs show correlations: the correlation between B and T_g can be expressed as [9] $T_g = 6.14 \times 10^{-3}\langle\Omega\rangle\langle B\rangle/k_B$, where $\langle\Omega\rangle$ is the average local volume, k_B is the Boltzmann constant. The E and T_g have an empirical correlation of $T_g \propto 2.5E$ (Refs. [4,5]). Correlations between shear modulus G and T_g for various BMGs have also been reported [10]. Moreover the relationship between elastic constants and melting temperature, T_l can be described as [11] $E = 97.9 \times q(RT_l/V_m)$, where q is the number of atoms in the chemical formula, V_m is the molar volume and R is the gas constant. More intriguingly, the relative strength of bulk and shear moduli B/G, can be a measure of fragility, m, of a glass-forming liquid [12].

A good rule of thumb, associated with the ratio of T_g and T_l, has for many years been proposed for evolution of GFA [13]: that is, good metallic glass formers require T_g/T_l to be higher than 0.67. It is a successful empirical rule for finding a new metallic glass system [1–5]. The T_g and T_l themselves are correlated with elastic constants. That indicates that the GFA is connected with the elastic properties, and the GFA, which is often characterized by the thermo-

dynamic and kinetic criteria, can be evaluated from the point of view of elastic moduli and avoids the need to measure the thermodynamic parameters.

Thus the above result implies that the elastic constant in metallic glasses appears to be a parameter that monitors or controls the GFA and properties, even fragility of the glass-forming alloys. We established correlations, associated with elastic moduli, and since the moduli of glasses scale with those of their elemental components, they may provide useful guidelines for the development of new BMGs with desirable properties by the selection of elements with suitable elastic moduli as constituents.

As a case study we designed new rare earth-based BMGs on the basis of the above results. To develop a rare earth-based BMG with higher thermal stability and moduli, we tried to produce BMGs based on erbium. In the rare earth family, Er has the highest elastic moduli ($E = 70$ GPa, $B = 44$ GPa, and $G = 28$ GPa) [8]. We have developed the Er-based BMG with superior GFA by means of the elastic moduli criterion combining the addition method. We first prepare an Er–Co alloy because of the large negative enthalpy of formation between them (~−40 kJ/mole) [14]. With the addition of Al and Y (some rare earth and transition metals have been found to be very effective for improving the GFA of the BMG-forming alloys [15]), we find that the GFA of the Er–Co alloy can be greatly improved and a new family of Er-based BMGs has been developed. The right inset of Fig. 2 presents the X-ray diffraction (XRD) patterns (using a MAC M03 diffractometer with Cu-Kα radiation) of typical as-cast ErAlCoY BMGs prepared by a conventional casting method with diameter of 5–8 mm (for the details of preparation see Refs. [1–5]). The broad diffraction peaks in the pattern indicate that the as-cast rod consists of fully amorphous phase within the sensitivity limits of XRD. Fig. 2 shows the differential scanning calorimeter (DSC) curves (Perkin–Elmer DSC-7) of the BMGs, exhibiting an obvious glass transition followed by two sharp crystallization peaks. The left inset is the differential thermal analyzer (DTA) traces (Perkin–Elmer DTA-7), showing the melting process of these alloys. The single endothermal signal of the melting indicates that the multi-component alloy is near the eutectic composition point. The T_g, T_x, T_l, T_{rg} T_g/T_l, $\Delta T = T_x - T_g$ and $\gamma = T_x/(T_g + T_l)$ [16] are listed in Table 2. The distinctive glass transition and sharp crystallization events, as well as the large values of ΔT, T_{rg} and γ, further confirm the excellent GFA of the alloys [1–5,16]. The elastic constants of the new Er-based BMGs (included in Table 1) fit the correlation well as shown in Fig. 1.

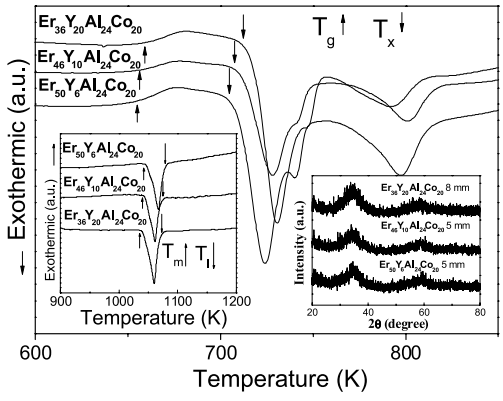

Fig. 2. DSC traces of the ErAlCoY alloys showing the sharp glass transition and crystallization events. The scanning rate is 10 K/min. The left inset shows DTA traces of the Er-based alloys showing the melting behavior. The scanning rate is 10 K/min. The right inset is the XRD patterns of the as-cast ErAlCoY alloys.

Table 2
Thermodynamic parameters of the Er- and Ce-based BMGs

BMGs	T_g (K)	T_x (K)	T_l (K)	ΔT (K)	T_{rg}	γ	Diameter (mm)
$Er_{36}Al_{24}Co_{20}Y_{20}$	661	719	1071	58	0.617	0.415	>8
$Er_{46}Al_{24}Co_{20}Y_{10}$	653	711	1073	58	0.609	0.412	5
$Er_{50}Al_{24}Co_{20}Y_6$	651	702	1079	51	0.603	0.406	5
$Ce_{68}Al_{10}Cu_{20}Fe_2$	352	423	708	71	0.497	0.399	5

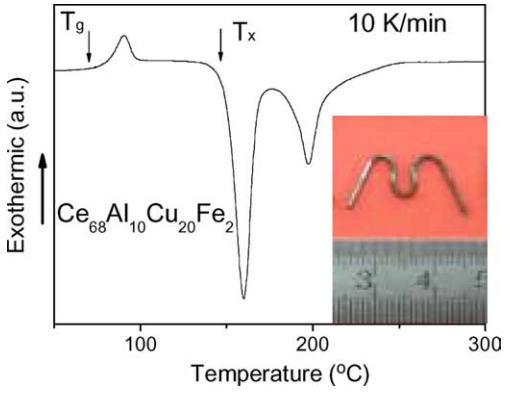

Fig. 3. DSC trace of the $Ce_{68}Al_{10}Cu_{20}Fe_2$ BMG with large supercooled liquid temperature region. Its T_g is lower than 100 °C. The inset shows the letter "M" of a Ce-based BMG formed by hand in near boiling water, indicating the deformability of the BMG.

Similarly, to produce BMG with low T_g and moduli, we develop BMGs based on cerium because Ce has lower moduli ($E = 34$ GPa, $B = 22$ GPa, and $G = 14$ GPa [8]). We obtained the Ce-based BMGs (see Fig. 3; the thermal parameters are listed in Table 2) with excellent GFA, exceptionally low T_g (below 100 °C), large ΔT (71 K) and low moduli, which are close to silicate glasses and polymers (listed in Table 1). The unique Ce-based BMG makes it possible to observe the intrinsic viscous behavior of the supercooled liquid near ambient temperature. For example, the Ce-based BMG bar can be hand-shaped, molded and imprinted in near-boiling water [17] (the inset of Fig. 3 is an example). Such superplasticity (similar to polymeric thermoplastic), which is not expected in crystalline alloys, indicates some potential applications.

4. Conclusions

We find that the elastic constants of available BMGs show a rough correlation with a weighted average of the elastic constants for the constituent elements. Based on the correlation, we show that the elastic moduli can assist in the selection of alloying components for controlling the elastic properties and glass-forming ability of the BMGs, and thus can guide BMG design. As a case study, we report the formation of two families of erbium- and cerium-based BMGs with controllable properties. Even through theoretical works are needed for understanding the physical origin for the correlations, we believe that the model could provide useful guidelines for the development of new BMGs, which is topic of current academic and application interest.

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