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Heavy rare earth based bulk metallic glasses with high thermal stability

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Abstract

We report a family of ternary Gd–Al–Co alloys based on the heavy gadolinium rare earth element can be readily cast into fully glassy rod by a conventional casting method. It is found that the bulk metallic glasses (BMGs) have much high thermal stability (i.e. high glass transition temperature and crystallization temperature) and high moduli compared with those of other known rare-earth based BMGs. It is confirmed that, in addition to the strong chemical interaction among the components, the high bulk modulus of the base component in the BMGs is dominantly responsible for the high thermal stability. The thermal stability is correlated with the bulk modulus of the base element in the rare earth based BMGs.

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Keywords: A. Glasses, metallic; B. Thermal stability; Elastic properties

Recently, intensive efforts have been carried out for developing BMGs in various alloy systems [1–3]. Compared with transition metal (e.g. Zr, Fe, and Cu) based BMGs [1–6], which are admirable for a broad application as engineering materials due to their excellent mechanical properties and low cost, only few BMGs based on light rare earth element (RE), such as Pr-, Ce-, and Nd-based BMGs have been developed [7–10]. No heavy RE-based BMGs (atomic number larger than that of promethium) have been reported so far. On the other hand, the known RE-based BMGs have relatively low glass transition temperature T_g and crystallization temperature T_x which could limit some practical applications. Previous theoretical studies predicted that the thermal stability of metallic glasses would be enhanced with the higher bulk modulus of the base component [11]. As a heavy RE, Gd has a relatively high bulk modulus and melting point, and low chemical activity in lanthanide family. It is ferromagnetic with the Curie temperature round room temperature. Therefore, Gd-based BMGs could have high thermal stability and unique properties (e.g. magnetic and magneto-optical properties), which are attractive for application as functional materials. For example, Gd–TM (TM = Fe, Co, Ni) glassy films are of excellent magnetic cooling effect [12–15].

To confirm the theoretical prediction and exploring new RE-based BMGs with enhanced thermal stability, in the work, the heavy gadolinium element is selected as a base component. Guo et al. have reported that Y-based alloys have good glass forming ability (GFA) [16], and Y additions have been found to be very effective for improving the GFA and manufacturability of Zr-, and Fe-based glass-forming alloys [17]. Based on these considerations, Y and Al have been selected to add into the Gd–Co system to further enhance its GFA. We found that the heavy RE based Gd–(Y, Nd)–Al–Co alloy system can be readily cast into bulk glass. This BMG exhibits the highest T_g and T_x in all known RE-based BMGs. A correlation between thermal stability and elastic modulus is found. The result is of great importance for designing new glass-forming alloys with high thermal stability and for understanding the universal features of structural and physical properties of metallic glassy alloys.

The Gd–(Y, Nd)–Al–Co alloys with the nominal compositions listed in Table 1 were prepared by arc melting high-purity Gd, Y, Nd, Al, and Co metals in Ti-gettered argon atmosphere. The ingots were remelted several times to ensure the homogeneity of the samples, and then were suck-cast into a copper mold to obtain cylindrical rods. The structure of the as-cast alloys was identified by X-ray diffraction (XRD) using a MAC M03 diffractometer with Cu Kα radiation. Thermal properties were investigated in a Perkin–Elmer Differential

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Table 1
Thermodynamic parameters of the Gd-based BMGs

BMG	T_g (K)	T_x (K)	T_m (K)	T_l (K)	T_{rg} (K)	γ
$Gd_{56}Al_{24}Co_{20}$	576	630	954	978	0.60	0.405
$Gd_{36}Y_{20}Al_{24}Co_{20}$	603	658	1010	1048	0.60	0.398
$Gd_{40}Y_{16}Al_{24}Co_{20}$	598	653	972	995	0.62	0.410
$Gd_{50}Y_6Al_{24}Co_{20}$	587	645	957	979	0.61	0.412
$Gd_{36}Nd_{20}Al_{24}Co_{20}$	557	623	889	917	0.63	0.423
$La_{60}Cu_{20}Ni_{10}Al_{10}$	387	447	694	–	0.56	–
$Ce_{60}Cu_{20}Ni_{10}Al_{10}$	374	441	645	672	0.58	0.422
$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	417	469	708	810	0.59	0.382
$Nd_{60}Cu_{20}Ni_{10}Al_{10}$	438	478	728	755	0.60	0.401
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	623	672	932	996	0.67	0.415
$Fe_{61}Y_2Zr_8Co_6Al_1Mo_7B_{15}$	890	956	1444	1496	0.60	0.400
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	754	797	1133	–	0.63	–

The data of other RE-based BMGs and some typical BMGs are from Refs. [2,3,7,9,10,24].

Scanning Calorimeter (DSC) DSC-7 and Differential Thermal Analyzer (DTA) DTA-7 under a continuous argon flow. The values of T_g, T_x, the liquidus temperature, T_l, were determined from the thermal analysis traces with the accuracy of ± 1 K. The acoustic velocities at ambient temperature measured by using a pulse echo overlap method and the travel time of ultrasonic waves propagating through the sample with a 10 MHz frequency were obtained using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns [18]. The elastic constants (e.g. bulk modulus B, Young's modulus E, shear modulus G, and Poisson's ratio σ) were derived from the ultrasonic velocities and density [19].

Fig. 1 shows the XRD patterns of the typical as-cast $Gd_{56}Al_{24}Co_{20}$ and $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMGs with diameter of 2–3 mm. The broad diffraction peaks in the pattern indicate that the as-cast rod consists of a full amorphous phase. The inset a shows the DSC curve of the $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMG, which exhibits an obvious endothermic characteristic of the glass transition followed by three sharp crystallization peaks. The inset b is the DTA trace shows the melting process of this alloy. The single endothermal signal of the melting indicates that the multi-component alloy is in eutectic composition point. The T_g, T_x, melting temperature T_m, and T_l, are determined to be 603, 658, 1010 and 1048 K, respectively. The supercooled liquid region $\Delta T = T_x - T_g$, is 55 K. The reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_m$) [20], and the γ value ($\gamma = T_x/(T_g + T_l)$) [21], which are important parameters in evaluating the GFA of an alloy, are 0.60 and 0.398, respectively. The distinctive glass transition and sharp crystallization events as well as large values of ΔT, T_{rg} and γ further confirm the excellent GFA of the alloy. The adequate atomic radius difference between Gd (0.180 nm), and Al (0.143 nm), and Co (0.125 nm) [22], the large negative heat of mixing between Gd and Co (−32 KJ/mol) [23], and eutectic composition induce the good GFA of the alloys.

For comparison, thermal parameters of the Gd based and other RE based BMGs [7–10], as well as some typical BMGs [3,9,24], are listed in Table 1. It is seen that, T_g, T_x, and T_m of Gd based BMGs are relatively lower than those of Zr-, Fe-, and Cu-based BMGs, but are the highest among those of the all

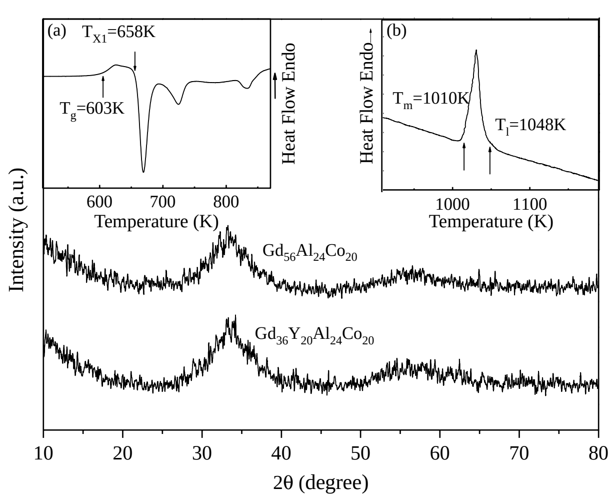

Fig. 1. XRD patterns of the as-cast $Gd_{56}Al_{24}Co_{20}$ alloy and $Gd_{36}Y_{20}Al_{24}Co_{20}$ alloy. DSC (inset a) and DTA (inset b) curves of the as-cast $Gd_{36}Y_{20}Al_{24}Co_{20}$ alloy show the distinct glass transition, crystallization and melting events. The scanning rate is 10 K/min.

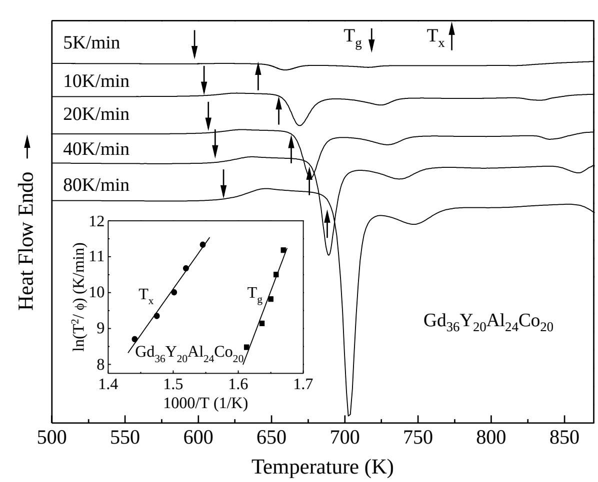

Fig. 2. DSC traces of the as-cast $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMG at different heating rates, of 5, 10, 20, 40, and 80 K/min. The inset is the Kissinger plot of the T_g and T_x of the BMG.

Table 2
The elastic constants, thermodynamics parameters, and the activation energy for the $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMG and other RE-based BMGs, and some typical BMGs (Refs. [3,9,10,26])

Glass	T_g (K)	E_g (eV)	T_x (K)	E_x (eV)	E (GPa)	G (GPa)	K (GPa)
$Gd_{36}Y_{20}Al_{24}Co_{20}$	603	4.13	658	2.21	62.2	23.6	57.4
$Gd_{40}Y_{16}Al_{24}Co_{20}$	598		653		62.2	23.5	58.0
$Pr_{60}Al_{10}Ni_{10}Cu_{20}$	417	2.61	469	1.35	37.17	13.64	45.16
$La_{66}Al_{14}Cu_{10}Ni_{10}$	405	–	431	–	35.72	13.44	34.91
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	359	–	377	1.33	30.3	11.5	27.0
$Nd_{60}Al_{10}Fe_{20}Co_{10}$	485	2.2	610	1.4	54.1	20.7	46.5
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	623	5.8	672	2.0	101.2	37.4	114.1
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	754	–	797	5.77	101.1	36.9	128.2

known RE based BMGs. The increase in T_g, T_x, and T_m with the substitution of Gd by Y from 6 to 20 at%. The thermal ability is distinctly improved by the addition of Y. The increase in T_x and T_g means high thermal stability and large application temperature range of the BMGs. Kinetic analysis of crystallization and glass transition of the Gd-based BMGs were performed using Kissinger's method [25]. Fig. 2 shows the DSC curves obtained from the $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMG at different heating rates. The Kissinger's plots of T_g and T_x are shown in the inset. The values of the effective activation energy for glass transition, E_g and crystallization E_x are then determined to be 4.13 and 2.21 eV, respectively. Compared with other RE based BMGs listed in Table 2 [10,11], Gd-based BMGs have much larger values of E_g and E_x. This means that the atoms of Gd-based BMGs need larger additional energy for the transition from glassy state to crystallization state.

The elastic constants of the typical Gd-based and other RE-based BMGs available, as well as some typical BMGs [3,9,10, 26] are listed in Table 2. The E, G, and B of the as-cast $Gd_{36}Y_{20}Al_{24}Co_{20}$ BMG is 62.2, 23.6, and 57.4 GPa, respectively, which are distinctively larger than those of other RE-based BMGs, while lower than those of Zr- and Cu-based BMGs. The elastic constants of an alloy can be correlated with the individual elastic constants of its components as [26]: $M^{-1} = \sum f_i M_i^{-1}$, where M is elastic constants and f_i the atomic percentage of component. From the correlation, one can see that the base element has predominant contribution to M of an alloy. Egami [11] suggested that the bulk modulus attributed dominantly to base element of a metallic glass has a correlation with its thermal parameters. The relation between the T_g and B of glasses was described in terms of the atomic level stresses. This concept originates from the realization that in glasses most of the interatomic distance are non-ideal, being either stretched or compressed, resulting in the pressure between the atoms. As the local atomic pressure has closely correlated with the local bulk modulus depending on the interatomic potential, it is deduced that the T_g was positively related to B of metallic glasses, which applies well for a large number of conventional metallic glasses [27]. The rule is also fit for various RE-based BMGs. As shown in Fig. 3, T_g of the BMGs (with similar atomic percentage) is intimately linked to B of the RE base metals. It is found that not only T_g but also T_x of the BMGs increase with B of the RE base. Gd with a relatively high bulk modulus (38 GPa) has high T_g, T_x and large activation energies for the glass transition and crystallization resulting from the chemical interaction among the components. The addition of Y further increases T_g and T_x of Gd-based BMG [shown in the inset of Fig. 3] since Y has a high bulk modulus (41 GPa). While the addition of Nd with low bulk modulus (32 GPa) decreases the T_g and T_x of the BMG (see Table 1). Thus, the results confirm that the thermal stability is correlated with the bulk modulus at least in rare earth based BMGs. The high bulk modulus of the base component can lead to high thermal stability for the BMGs. It is note that other BMG systems such as Zr-, Fe- and Cu-based BMGs also satisfy the correlation.

In conclusion, the first heavy RE-based Gd–(Y, Nd)–Al–Co BMGs family with good GFA and high stability are obtained by a conventional casting method. The correlation between thermal stability and bulk modulus of BMGs is found at least in rare earth based BMGs system. The link established can assist in understanding the formation mechanism and the universal features of structural and physical properties in metallic glasses, and in guiding BMG-forming alloy design to enhance thermal stability.

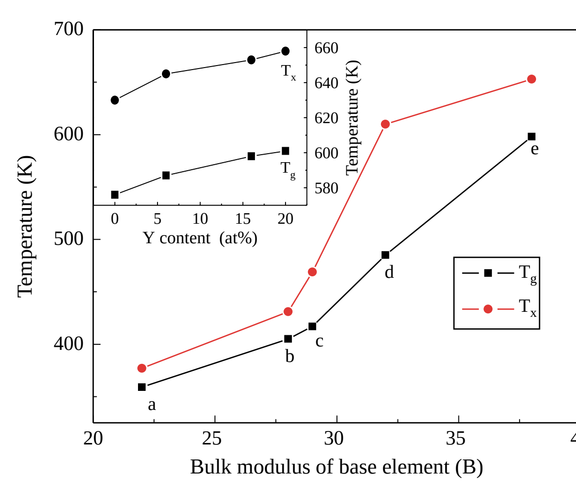

Fig. 3. The relationship between T_g, T_x, and the bulk modulus of the base elements of the RE-based BMGs. The (*a–e*) refers to $Ce_{70}Cu_{10}Ni_{10}Al_{10}$, $La_{66}Cu_{10}Ni_{10}Al_{14}$, $Pr_{60}Cu_{20}Ni_{10}Al_{10}$, $Nd_{60}Fe_{20}Co_{10}Al_{10}$, and $Gd_{40}Y_{16}Al_{24}Co_{20}$, respectively. The inset is the dependence of the T_g and T_x on the content of Y ranging from 0 to 20%.

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References

[1] Johnson WL. JOM 2002;54:40.
[2] Inoue A. Acta Mater 2000;48:279.
[3] Wang WH, Dong C, Shek CH. Mater Sci Eng R 2004;44:45.
[4] Ponnambalam V, Poon SJ. Appl Phys Lett 2003;83:1131.
[5] Eckert J, Mattern N, Seidel M. Mater Trans JIM 1998;39:623.
[6] Greer AL. Science 1995;267:1947.
[7] Wei BC, Wang WH, Pan MX. Phys Rev B 2001;64:012406.
[8] Schneider S, Bracchi A, Samwer K. Appl Phys Lett 2002;80:174.
[9] Zhao ZF, Zhao DQ, Wang WH. Appl Phys Lett 2003;82:4699.
[10] Zhang B, Pan MX, Wang WH. Appl Phys Lett 2004;85:61.
[11] Egami T. Mater Sci Eng A 1997;226:261.
[12] Mohammed KA, Lanchester PC. J Magn Magn Mater 1986;60:275.
[13] Liu P, Yang QQ, Yang YS. Electrochim Acta 2000;45:2147.
[14] Liu XY, Barclay JA, Bose TK, Combe J. J Appl Phys 1996;79:1630.
[15] Chevalier B, Bobet JL. Appl Phys A 2003;10:1007.
[16] Guo FQ, Poon SJ, Shiflet. Appl Phys Lett 2003;83:2575.
[17] Lu ZP, Liu CT, Thompson JR, Porter WD. Phys Rev Lett 2004;92:245503. Zhang Y, Zhao DQ, Wang RJ, Wang WH. Mater Trans JIM 2000;41:1423.
[18] Wang WH, Wang RJ, Pan MX. Appl Phys Lett 1999;74:1803.
[19] Schreiber D. In: Elastic constants & their measurement. New York: McGraw-Hill; 1973.
[20] Turnbull D. Contemp Phys 1969;10:473.
[21] Lu ZP, Liu CT. Phys Rev Lett 2003;91:115505.
[22] Senkov ON, Miracle DB. MRS Bull 2001;36:2183.
[23] De Boer FR, Miedema AR, Niessen AK. In: Cohesion in metals. Amsterdam: North-Holland; 1988.
[24] Lu ZP, Liu CT, Porter WD. Appl Phys Lett 2003;83:2581.
[25] Kissinger HE. J Res Natl Bur Stand 1956;57:217.
[26] Zhang Z, Wang RJ, Wang WH. J Phys Condens Matter 2003;15:4503.
[27] Egami T. Rep Prog Phys 1984;47:1601.