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Gd–Ni–Al bulk glasses with great glass-forming ability and better mechanical properties

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Abstract A series of Gd–Ni–Al ternary glassy alloys with the maximum diameter of 4 mm were obtained by common copper mold casting. The maximum values of the reduce glass transformation temperature (T_g/T_m) and the distance of supercooling region ΔT_x of these alloys in this study were 0.648 and 50 K, respectively. The compressive fracture strength (σ_f) and Young's modulus (E) of Gd–Ni–Al glassy alloys were 1,240–1,330 MPa and 63–67 GPa, respectively. The magnetic properties of these BMGs were investigated. The Gd–Ni–Al bulk glassy alloys with great glass forming ability and good mechanical properties are promising for the future development as a new type of function materials.

Introduction

As a new class of materials, bulk metallic glasses (BMGs) have been widely investigated and various alloy systems have been developed in the past several decades. These new alloys exhibit attractive properties as potential structural and functional materials, such as high yield strength, high corrosion-resistant, exceptionally large elastic strain limit and excellent soft-magnetic properties [1–3].

Among the available BMGs systems, rare earth (RE)-based bulk metallic glass system is one of the most important and valuable alloy systems. Since the first Ln–TM–Al (Ln = lanthanide metals, TM = VI ~ VIII group transition metal) alloy system was produced by Inoue's group in 1989 [4, 5], a number of RE-based bulk amorphous alloys/bulk metallic glasses (BMG) were obtained in the Nd-, Pr-, Sm-,Y-, Ce- and heavy RE-based alloy systems [6–12]. For instance, Nd/Pr-based bulk amorphous alloys with hard magnetic properties at room temperature were obtained by Inoue's group in 1995 [6–8], Sm- and Y-based bulk metallic glasses were developed by Gou et al. [9, 10]. Zhang and Wang et al. prepared the Ce-based bulk metallic glasses with polymerlike thermoplastic behavior caused by their extraditionally low glass transition temperature T_g, which is similar to or lower than that of many polymers [11]. Furthermore, the heavy RE-based alloy systems were mainly obtained by Wang and his coworkers in the recent years [12]. Among these new RE-based BMGs, the Gd-based BMG is worthy to note for its high thermal stability and unique properties (e.g., magnetic and magneto-optical properties), which are attractive for application as functional materials. Some Gd-based BMGs were obtained by Li and Wang et al. in the last year [13, 14]. Almost at the same time, we have successfully developed a series of Gd–TM–Al (TM = Fe, Co and Ni) ternary bulk amorphous and bulk metallic glasses [15–17]. In this study, some Gd–Ni–Al bulk metallic glasses with great glass forming ability were obtained by copper mold casting and their mechanical properties were investigated.

Experimental

The master alloys of Gd–Ni–Al alloy systems with composition range of 50–70 Gd and 10–40 Al were prepared by induction-melting a mixture of pure Gd, Co and Al metals in an argon atmosphere. The amorphous ribbons with a thickness of about 20–30 μm and a width of 1 mm were

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produced by single-roller melt spinning method in argon atmosphere. Based on fundamental data of the Gd–Co–Al amorphous alloy ribbons, the bulk metallic glasses of $Gd_{50-65}Ni_{10-30}Al_{15-30}$ (at.%) were prepared as cylindrical samples with a length of about 50 mm and diameters ranging from 1 to 5 mm by injection casting of the molten alloy into copper molds with cylindrical cavities.

The structure of the as-cast cylindrical samples was examined by X-ray diffractometry. The thermal stability associated with crystallization and melting was measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Magnetic properties were measured by a vibrating sample magnetometer (VSM) under an applied field of 1,432 kA/m at room temperature. Compressive testing was performed with an Instron testing machine at a strain rate of 5×10^{-4} s^{-1}. The gauge dimension of the specimen was 2 mm in diameter and 4 mm in height.

Results and discussion

Figure 1 presents the XRD patterns of the as-cast $Gd_{60}Ni_{15}Al_{25}$ cylinders up to 5 mm in diameter which shows the highest glass-forming ability of Gd–Ni–Al system in the present study. As shown in Fig. 1, the broad diffraction peaks confirm for $Gd_{60}Ni_{15}Al_{25}$ glassy alloys with the diameters from 1 to 5 mm. These broad diffraction peaks indicate the formation of an amorphous phase in the as-cast rods. Therefore, the maximum diameter of the BMG is up to 4 mm for $Gd_{60}Ni_{15}Al_{25}$ glassy alloy.

The DSC curves of some as-cast Gd–Ni–Al bulk amorphous alloy cylinders with a diameter of 1 mm are presented in Fig. 2. The content of Gd is fixed at 60 at.% (a), while the content of Al is fixed at 25 at.%.(b), respectively. The thermal stabilities of these Gd–Ni–Al bulk amorphous alloys bulk metallic glasses are summarized in Table 1. As shown in Fig. 2 and Table 1, the supercooled liquid region (ΔT_x) and the reduce glass transition temperature T_{rg},($=T_g/T_m$) (T_g and T_m are the glass transition temperature and melting temperature, respectively)of Gd–Ni–Al BMGs are 26–50 K and 0.628 to 0.648. And the glass transition temperature (T_g), crystallization temperature (T_x) and (T_m) for the $Gd_{60}Ni_{15}Al_{25}$ glassy alloy are 572, 617, and 928 K, respectively, so ΔT_x and T_{rg} are 45 K and 0.648. Obviously, comparing with the values of ΔT_x and T_{rg} of the typical BMG alloy systems which is normally more than 50 K [1–3], the Gd-based BMGs in the present study is smaller. The reason why the Gd-based alloys of high glass-forming ability show lower ΔT_x and T_{rg} is not clear yet. It is possible that the alloy composition is near the eutectic point and the Gd element has an excellent ability to purify the melt and further improve the glass-forming ability of the present alloys. Further research work about it will be carried out in detail. Furthermore, it was considered that the ΔT_x could serve more proper as a parameter of the thermal stability of the supercooled liquid than as a parameter of the glass forming ability of Gd–Ni–Al alloy system in present study. The reason is based on the experimental results that the bulk metallic glasses $Nd_{61}Al_{11}Ni_8Co_5Cu_{15}$ and $Mg_{65}Y_{10}Cu_{15}Ag_5Pb_5$ with small values of ΔT_x of 24 K and 32 K can be formed in cylinders with the diameters range from 6 to 12 mm [18–20]. Furthermore, the thermal stability is different from the GFA, the former indicates the resistance against the crystallization from the supercooled liquid when heating, while the GFA shows the suppression of the crystallization from the liquid in the cooling processes [21].

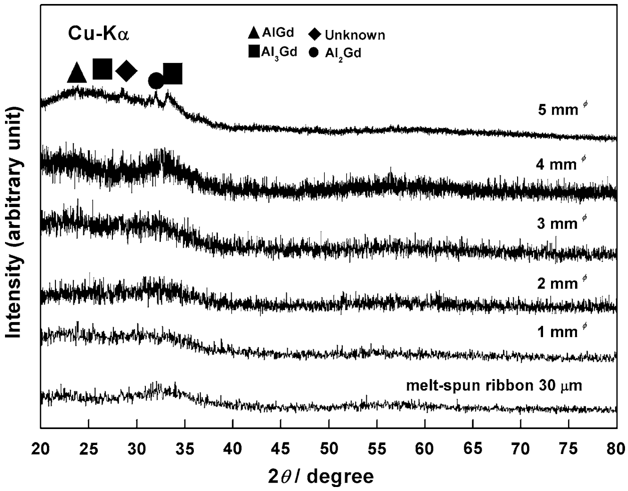

Fig. 1 XRD patterns of the as-cast $Gd_{60}Ni_{15}Al_{25}$ cylinders with different diameters together with the data of the amorphous ribbons shown for comparison

On the basis of the results of Ref. [17] and the present study, it can be found that the Gd–Ni–Al alloy systems exhibit better glass forming ability than Gd–Fe–Al alloy system. The maximum diameters of these two Gd-based alloy systems are 4 mm for the former and only 2 mm for the latter. The results can be explained on the basis of the three empirical rules for the achievement of high amorphous/glass forming ability suggested by professor Inoue [1], i.e. (1) the multi-component system consisting of more than three elements, (2) significantly different atomic size mismatch exceeding 12% among the main constituent elements, and (3) suitable negative heats of mixing among these elements.

Table 2 shows the data of mixing heat and the atomic radius of the elements of Gd–Fe–Al and Gd–Ni–Al alloy systems [21, 22]. As seen from the Table 2, the negative mixing heats of Gd–Fe and Fe–Al are smeller than that of the Gd–Ni and Ni–Al, respectively. Therefore, the negative mixing heat of Gd–Fe–Al alloy systems is smeller than

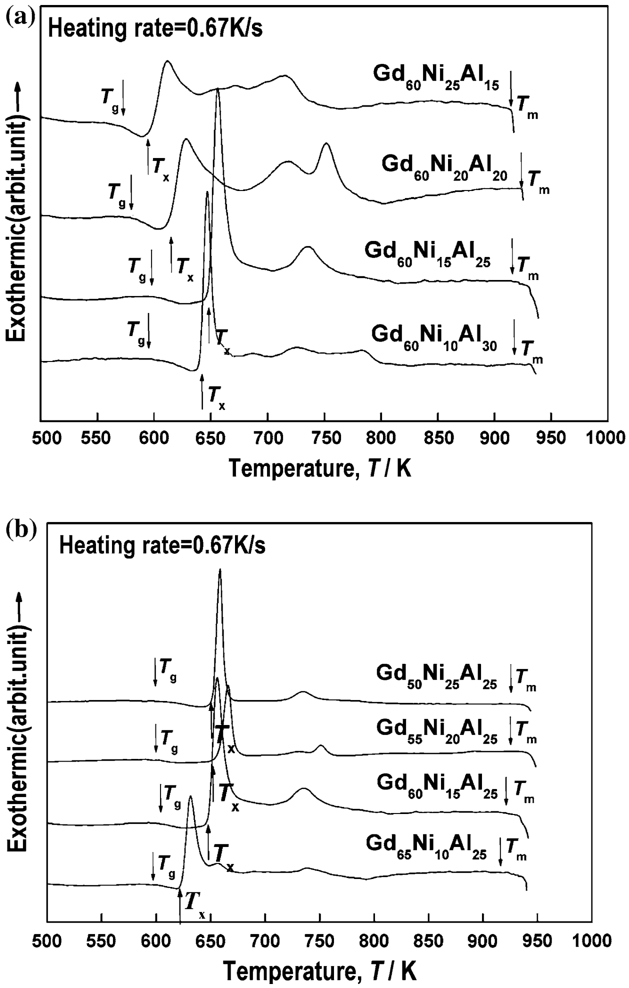

Fig. 2 DSC curves of the as-cast Gd–Ni–Al bulk metallic glasses cylinders with the diameter of 1 mm. (**a**) $Gd_{60}Ni_{40-x}Al_x$ (x = 20, 25 and 30), (**b**) $Gd_{75-x}Ni_xAl_{25}$ (x = 25, 20 and 15)

those of and Gd–Ni–Al alloy systems. On the other hand, atomic radius of Fe atom is larger than that of Ni atom, but smaller than those of Gd and Al atoms. Hence, the different in the atomic radius of the Gd–Fe–Al alloy system is smaller than that of the Gd–Ni–Al alloy system. Thus, it is easy to conclude that the Gd–Fe–Al alloy system has the minimum glass-forming ability for its smaller values of negative mixing heat and difference of atomic radius.

Figure 3 shows the strain–stress curves of the Gd–Ni–Al bulk metallic glasses with a diameter of 2 mm subjected to the compressive test. The data of the mechanical properties of these Gd–Ni–Al BMG$_S$ are summarized in Table 3. As shown in Fig. 3 and Table 3, the compressive fracture strength of the $Gd_{60}Ni_{40-x}Al_x$ bulk metallic glasses increases from 1,240 to 1,330 MPa with increasing Al content form 20 to 30 at.% while it increases from 1,280 to 1,320 MPa with increasing Ni content from 15 to 25 at. % for $Gd_{75-x}Ni_xAl_{25}$ alloys. And the Young's moduli (E) of Gd–Ni–Al BMGs have the same change tendency. It should be noted that the increase of the compressive fracture strength with Al content in the Gd–Ni–Al bulk metallic glassy systems is consistent with those in Ln–Ni–Al and Ln–Cu–Al bulk metallic glasses systems [4, 5]. In addition, it is noted that the Gd-based BMGs exhibit the highest fracture strength among the RE (rare-earth)-based bulk metallic glasses published to date, but the previous data show lower fracture strength below 1,000 MPa [4, 5, 23, 24]. Furthermore, the mechanical properties of Gd-based BMG could be further improved by adding some other elements.

Figure 4a is the hysteresis *J–H* loops of the as-cast $Gd_{60}Ni_{15}Al_{25}$ bulk metallic glasses with the diameter of 1 mm at room temperature. The data of the melt-spun ribbons are also shown for comparison. It shows that this bulk metallic glasses exhibit paramagnetism at room temperature. On the contrary, *J–H* loops at low temperature ranging from 77 to 173 K shown in Fig. 4b is different. At lower temperatures, the *J–H* loops show superparamagnetism-like behavior, which is also confirmed for Gd–Fe–Al bulk amorphous alloys in Ref. [17].

The bulk Gd–Ni–Al bulk metallic glass which exhibit superparamgneticsm-like behavior in the certain temperature range below room temperature is interesting, because it is of technological importance for a large magnetocaloric effect, which have potential application for magnetic

Table 1 Thermal stability of the as-cast Gd–Ni–Al cylinders with a diameter of 1 mm

Alloys	T_g / K	T_x / K	T_m / K	T_x / T_m	ΔT/ K	d_{max} / mm
$Gd_{50}Ni_{25}Al_{25}$	598	645	942	0.634	47	2
$Gd_{55}Ni_{20}Al_{25}$	598	650	940	0.636	50	2.5
$Gd_{60}Ni_{25}Al_{15}$	573	598	913	0.628	26	1
$Gd_{60}Ni_{20}Al_{20}$	587	621	926	0.634	34	2
$Gd_{60}Ni_{15}Al_{25}$	603	648	931	0.648	45	4
$Gd_{60}Ni_{10}Al_{30}$	596	638	932	0.639	42	2.5
$Gd_{65}Ni_{10}Al_{25}$	598	624	942	0.634	26	1

T_x, crystallization temperature; T_m, melting temperature; T_g, glass transition temperature; T_g/T_m, reduced glass transition temperature, $\Delta T = T_x - T_g$; d_{max}, maximum diameter

Table 2 Heat of mixing and atomic radius of the Gd–Al–TM (TM = Fe and Ni) alloy systems

Heat of mixing/KJ·mol^{-1}				
Element	Gd	Al	Fe	Ni
Gd	_	–38	–1	–31
Al	–38	_	–11	–22
Atomic radius (Å) and Their ratios versus Gd				
	Gd	Al	Fe	Ni
Atomic radius(Å)	1.80	1.43	1.27	1.24
Their ratios versus Gd	_	0.79	0.71	0.69

Table 3 Mechanical properties of the bulk Gd–Ni–Al amorphous alloys with a diameter of 2 mm

Alloys	Compressive fracture strength σ_f/MPa	Compressive fracture stain ε_f	Young's modulus *E*/Gpa
$Gd_{50}Ni_{25}Al_{25}$	1,320	0.0201	66
$Gd_{55}Ni_{20}Al_{25}$	1,300	0.0200	65
$Gd_{60}Ni_{20}Al_{20}$	1,240	0.0197	63
$Gd_{60}Ni_{15}Al_{25}$	1,280	0.0201	64
$Gd_{60}Ni_{10}Al_{30}$	1,330	0.0199	67

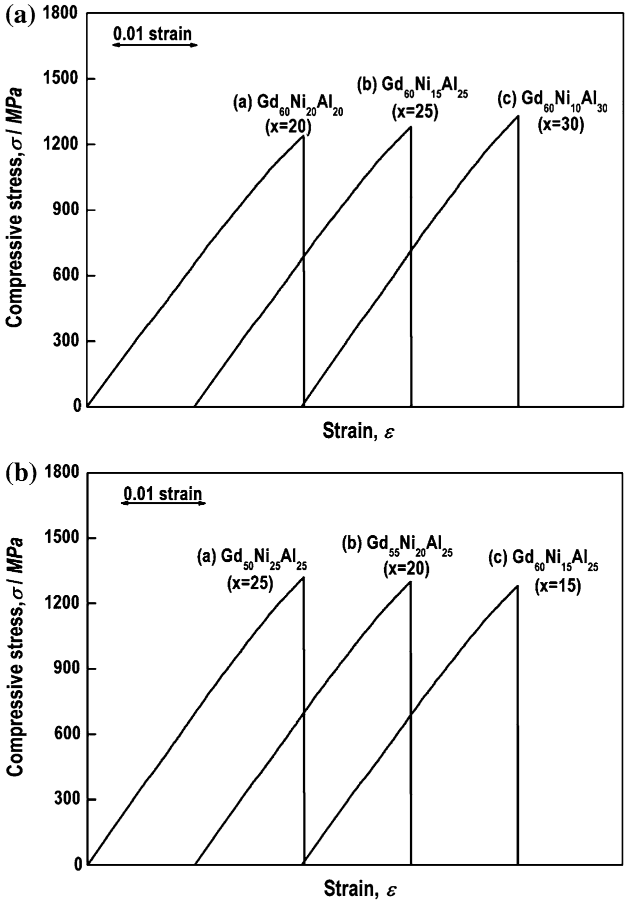

Fig. 3 Compressive stress–strain curves of the bulk Gd–Ni–Al metallic glasses with the diameter of 2 mm. (**a**) $Gd_{60}Ni_{40-x}Al_x$ (x = 15, 20, 25 and 30), (**b**) $Gd_{75-x}Ni_xAl_{25}$ (x = 10, 15, 20 and 25)

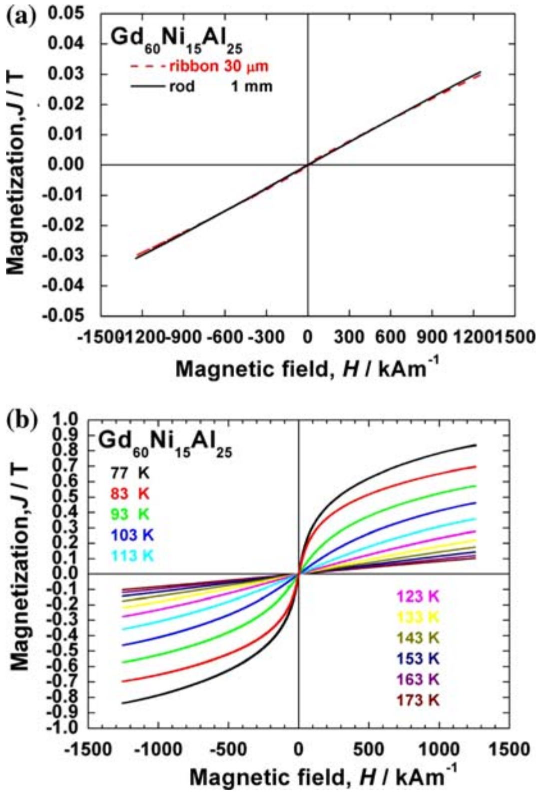

Fig. 4 (**a**) Hysteresis *J–H* loops of the as-cast $Gd_{60}Ni_{15}Al_{25}$ bulk amorphous alloy with a diameter of 1 mm at the room temperature. The data of melt-spun ribbon also were shown for comparison. (**b**) Hysteresis *J–H* loops of the as-cast $Gd_{60}Ni_{15}Al_{25}$ bulk amorphous alloy with a diameter of 1 mm at the low temperature (77–173 K)

refrigeration [25–28]. Hence, the Gd–Ni–Al bulk metallic glasses maybe have the potential to be used as a kind of magnetic refrigeration material, although the magnetocaloric effect of these bulk amorphous alloys is under investigation. First, they have the possibility of great magnetocaloric effect for Gd-base alloy component [25–30]. It is expected that the magnetic entropy change (ΔS_M) of these bulk amorphous alloys is reduced from those of Gd–Ni–Al crystalline and amorphous ribbon and powders [31–33]. Second, the Gd–Al–TM bulk amorphous alloy will have the advantage of great total magnetic entropy change for the volume effect, good temperature cycle-resistant ability for the relatively good thermal stability and breakage resistance for the relatively high compressive fracture strength as well as interesting properties for magnetic refrigeration for their amorphous nature [34, 35] (such as higher electrical resistivity, smaller eddy-current heating, improved corrosion resistance and large specific surface, etc.). Thus, it can be presumed that the high glass-forming ability and good mechanical properties of Gd-based BMG will offer the potential application as a new kind of function material and device.

Summary

With the aim of developing the new Gd-based BMG systems, a number of Gd–Ni–Al bulk metallic glasses with high glass forming ability were obtained. The thermal stabilities and mechanical properties were investigated. The results obtained are summarized as follows:

(1) The Gd–Ni–Al bulk metallic glasses were obtained by the copper mold casting method. The maximum diameter for $Gd_{60}Ni_{15}Al_{25}$ glass alloy is 4 mm.
(2) The Gd–Ni–Al bulk metallic glasses have high glass-forming ability and thermal stability. The reduce glass transformation temperature (T_g/T_m) and the distance of supercooling region ΔT_x are 0.648 and 45 K respectively for the $Gd_{60}Ni_{15}Al_{25}$ glassy alloys.
(3) The Gd–Ni–Al bulk metallic glasses exhibit good mechanical properties. The compressive fracture strength and Young's modulus of the Gd–Ni–Al bulk metallic glasses are 1,240–1,330 MPa and 63–67 GPa, respectively. Combined with the superparamgneticsm-like behavior in the certain temperature range below room temperature, the Gd–Ni–Al bulk metallic glasses exhibit the highest compressive fracture strength among the other available.

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