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LETTER

# Glass forming ability of $Gd_{55}Al_{15}Ni_{30}$ ternary alloy

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## Introduction

Recently, some of the rare earth (RE) metals and RE-based alloys, such as Gd, Gd(Dy)–Al, Gd(Dy)–Ni, Gd(Dy)–Ni–Al, Gd–Si–Ge and so on, have attracted increasing interests due to their magnetocaloric effect (MCE) [1–8]. The alloys with giant MCE (especially at room temperature) could be applied as functional materials because magnetic refrigeration technology based on MCE is regarded as an environment-safe technology and a promising alternative to conventional vapor-cycle refrigeration [1, 7]. For this application, several features of these materials, such as large total angular momentum number, small fraction of lattice entropy, large electric resistance and fine molding and processing behaviors, are required. Hence, many urgent problems including easy oxidation and hard preparation should be solved before they are employed in magnetic refrigeration [7]. Amorphous materials with high glass forming ability (GFA) and MCE, which have unique properties such as high corrosion resistance and electric resistivity, can be easily prepared into bulk samples by copper mold casting and could be attractive for application as magnetic refrigerants [8–10]. Si et al. [11] have studied the magnetic properties of Gd–Al–Ni amorphous ribbons and found they had a high MCE indicating the possible application of these alloys as magnetic refrigerant. On the other hand, Gao [8] and Zhu et al. [12] studied the GFA of Al–Gd–TM alloys in their Al riched corner and obtained amorphous ribbons as a strong and flexible glass. However, no bulk amorphous samples were reported until now. It should be noted that many RE–transition metal (TM)–Al bulk metallic glasses (BMGs) with excellent GFA, such as Nd(Pr)–Fe(Co)–Al, Nd(Pr)–Ni(Cu)–Al and La–Ni(Cu)–Al, were developed from the investigation of GFA of Al–TM–RE alloys [13–15]. It was demonstrated that the RE-rich part of RE–TM–Al alloys have superior GFA and the replacement of some of the transition metal by one or more transition metal elements could drastically enhanced the GFA of the alloys [14–15]. Therefore, similar to the case of other Al–TM–RE alloys, Gd–Al–Ni alloys could have much higher GFA in their Gd-rich corner than in their Al-rich corner and could be prepared into Gd-rich bulk metallic glasses (BMGs).

More recently, we studied the glass forming ability of Gd-rich Gd–Al–Ni alloys systematically and found that some of the Gd–Al–Ni ternary alloys can be prepared into fully glassy rods by a conventional copper-mold casting method. In this work, we reported $Gd_{55}Al_{15}Ni_{30}$ BMG prepared by suction casting in the shape of rod 2 mm in diameter. The rod exhibit typical amorphous characters in XRD patterns, distinct glass transition in DSC traces and paramagnetic property at room temperature. The glass forming ability of the alloy were investigated by means of the reduced glass transition temperature $T_{rg}$, parameter $\gamma$ and the fragility parameter m obtained from the VFT dependence of glass transition temperature ($T_g$) on In $\phi$ ($\phi$ is the heating rate).

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Ingot with nominal composition of $Gd_{55}Al_{15}Ni_{30}$ was prepared by arc-melting of 99.9% (at.%) pure Gd, Al and Ni under a titanium–gettered argon atmosphere. Cylinders of the alloy were prepared in the shape of rods 1 mm in diameter by suction casting under an argon atmosphere. The structure of the samples was characterized by XRD on a Rigaku $D_{max}$-2550 diffractometer using Cu $K_\alpha$ radiation. The magnetic properties of the rods were measured by a vibrating sample magnetometer (VSM) at room temperature. The field applied was 1,592 kA/m. DSC measurements were carried out under a purified argon atmosphere in a Perkin Elmer DSC-7 at the heating rates ranging from 5 K/min to 120 K/min. The calorimeter was calibrated for temperature and energy at various heating rates with high purity indium and zinc. In order to obtain the melting and liquidus temperature of the alloys, high-temperature DSC curve was measured in a Netzsch DSC-404 under an argon atmosphere.

Figure 1 shows the XRD pattern of $Gd_{55}Al_{15}Ni_{30}$ as-cast rod 1 mm in diameter. The typical broad diffraction maxima of amorphous phases for $Gd_{55}Al_{15}Ni_{30}$ as-cast rod illustrate the glassy characters of the alloy and no obvious crystalline peaks were found within the XRD detection limit. The hysteresis loop reveals the paramagnetic property of the rod at room temperature, as shown in the inset of Fig. 1.

Figure 2 shows the continuous DSC trace of $Gd_{55}Al_{15}Ni_{30}$ as-cast rod at a heating rate of 20 K/min. A marked endothermic behavior before crystallization demonstrates a distinct glass transition with the onset temperature ($T^{onset}{}_g$) at about 566 K. A sharp exothermic reaction occurs after the glass transition associated with the transformations from supercooled liquid state to the equilibrium crystalline phases. The onset and peak temperatures for crystallization ($T^{onset}{}_x$ and $T^{peak}{}_x$) are about 615 K and 624 K, respectively. The melting and liquidus temperatures ($T_m$ and $T_l$) of the alloy obtained from the high-temperature DSC curve are about 916 K and 960 K, as shown in the inset of Fig. 2. Thus, the supercooled liquid region $\Delta T_x$ ($=T_x$–$T_g$) and the reduced glass transition temperature $T_{rg}$ ($=T_g/T_l$) [16] of the rod are about 49 K and 0.59, respectively. The parameter $\gamma$ ( $=\frac{T_x}{T_g+T_l}$), which is confirmed and validated in various glass-forming systems [17–18], is also employed for the evaluation of GFA and for $Gd_{55}Al_{15}Ni_{30}$ BMG is about 0.4. Thus the critical cooling rate ( $R_c = C_1 \exp[(-\ln C_1/\gamma_0)\gamma]$ where $C_1$ and $\gamma_0$ are constants) and section thickness ($Z_c = 2.80 \times 10^{-7} \exp(41.70\gamma)$) of the BMG can be predicted to be about 22 K/s and 4.9 mm, respectively. Therefore, both $T_{rg}$ and parameter $\gamma$ predict the excellent glass forming ability of $Gd_{55}Al_{15}Ni_{30}$ ternary alloy.

To understand the glass forming ability of $Gd_{55}Al_{15}Ni_{30}$ ternary alloy in more detail, the liquid behavior of the alloy was investigated in terms of the Angell's fragility concept [19]. Figure 3 shows the details of glass transition and the crystallization behaviors on the DSC traces of $Gd_{55}Al_{15}Ni_{30}$ amorphous rod at the heating rates ($\phi$) of 5 K/min, 10 K/min, 20 K/min, 40 K/min, 80 K/min and 120 K/min, respectively. $T^{onset}{}_g$ and $T^{peak}{}_x$ shift to higher values with increasing heating rates indicating the marked kinetic characters. Some authors have observed the linear increase of $\ln(T^2/\phi)$ with $1/T$ ($T$ is the transition temperature including $T^{onset}{}_g$ and $T^{peak}{}_x$) according to the Kissinger equation and the linear relationship between $T$ and In φ according to the Lasoka's equation [20–22]. However, we can not found Kissinger's linear relationship between $\ln(T^2/\phi)$ and $1/T$ for glass transition and crystallization of $Gd_{55}Al_{15}Ni_{30}$ as-cast rod , as shown in the inset of Fig. 3. The non-linear dependence of the glass transition temperature (Fig. 4(a)) and the crystallization temperature (Fig. 4(b)) on heating rates ranging from 5 K/min to 120 K/min follows the VFT equation:

$$\ln \phi = \ln B - D^* T_g^0 / \left( T_g - T_g^0 \right) \quad (1)$$

where $B$ is a constant, $T_g^0$ the hypothetical value of glass transition temperature at the limit of infinitely slow cooling and heating rate (the Vogel–Fulcher temperature), and $D$ the strength parameter used to describe how closely the system obeys the Arrhenius law [23–26]. The values of $T_g^0$, $D^*$ and constant B are found to be about 530 K, 0.29, 1,423 for glass transition and 558 K, 0.6, 3,106 for crystallization respectively. Therefore, the fragility parameter $m$ can be evaluated from equation as follow [19,27]:

$$m = (D^*/\ln 10) \times \left( T_g^0/T_g \right) \times \left( 1 - T_g^0/T_g \right)^{-2} \quad (2)$$

Parameter $m$ of $Gd_{55}Al_{15}Ni_{30}$ BMG calculated accordingly at a heating rate of 20 K/min is about 29 and is roughly in accordance with other multicomponent BMGs with excellent GFA [25, 28, 29]. The value of $m$, which is much closer to the strong limit than to the fragile limit, classifies the $Gd_{55}Al_{15}Ni_{30}$ alloy into the intermediate category according to Angell's classification [19]. Furthermore, the alloys with small value of parameter $m$ are usually considered to be better glass former because their metastable equilibrium

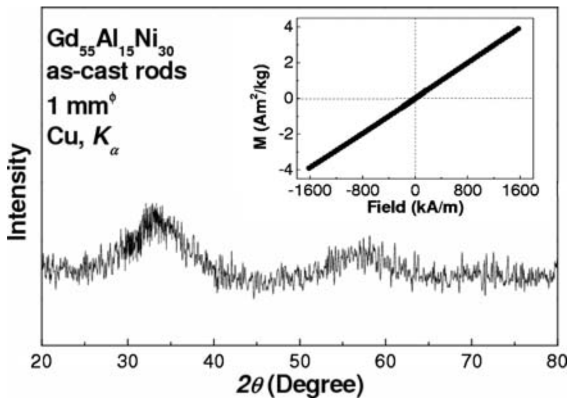


**Fig. 1** X-ray diffraction pattern of $Gd_{55}Al_{15}Ni_{30}$ as-cast rod. The inset is the hysteresis loop of the rod at room temperature

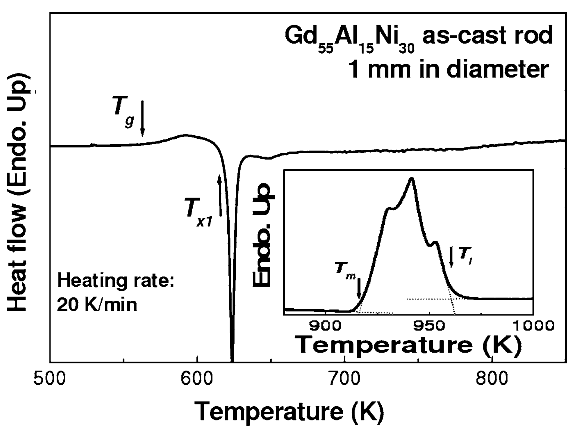


**Fig. 2** DSC trace of $Gd_{55}Al_{15}Ni_{30}$ BMG at a heating rate of 20 K/min. The inset is the high temperature DSC curve (melting behavior) of $Gd_{55}Al_{15}Ni_{30}$ BMG at a heating rate of 20 K/min

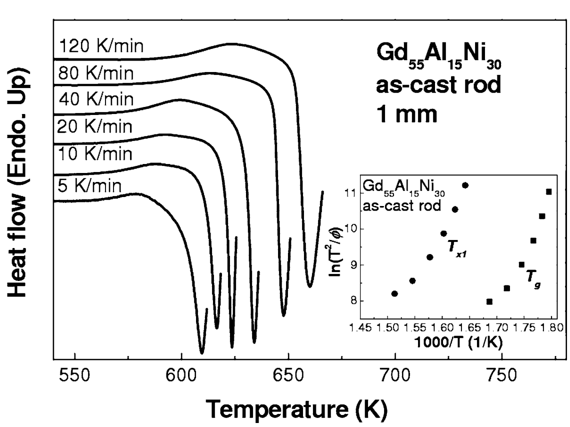


**Fig. 3** Details of glass transition and primary crystallization of $Gd_{55}Al_{15}Ni_{30}$ BMG in DSC traces at the heating rates of 5 K/min, 10 K/min, 20 K/min, 40 K/min, 80 K/min and 120 K/min. The inset is the Kissinger plots for the onset temperature of glass transition $T^{onset}{}_{g}$ and the peak temperature of crystallization $T^{peak}{}_{x}$

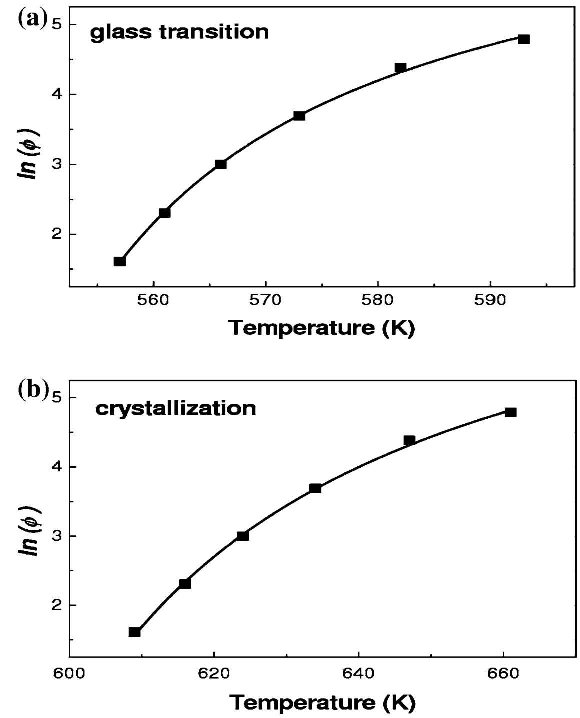


**Fig. 4** VFT dependence of (**a**) $T^{onset}{}_{g}$ and (**b**) $T^{peak}{}_{x}$ on In ( of $Gd_{55}Al_{15}Ni_{30}$ BMG

supercooled liquid is fairly stable and the small value of *m* is considered as one of the empirical rules for designing BMGs. Therefore, the value of parameter *m* of $Gd_{55}Al_{15}Ni_{30}$ BMG, which is similar to those of other BMGs, indicates a better GFA of the alloy.

In summary, we reported a new ternary $Gd_{55}Al_{15}Ni_{30}$ BMG prepared by suction casting. The glass forming ability of $Gd_{55}Al_{15}Ni_{30}$ ternary alloy has been studied. The reduced glass transition temperatures ($T_{rg}$ = 0.59), the parameter $\gamma$ (=0.4) and the predicted critical section thickness ($Z_c$ = 4.9 mm) as well as the critical cooling rate ($R_c$ = 222 K/s) indicate the excellent GFA of the BMG. The fragility parameter *m* obtained from the VFT dependence of $T_g$ on In $\phi$ classified the BMG into the intermediate category according to the Angell's classification.

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