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A paramagnetic $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ alloy with high glass-forming ability

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Abstract
A new rare-earth Nd-based bulk metallic glass (BMG) $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ was prepared in the shape of a rod up to 5 mm in diameter by suction casting. In contrast to the previously reported hard magnetic $Nd_{60}Fe_{20}Co_{10}Al_{10}$ BMG, the present BMG exhibits a distinct glass transition (GT) with low transition temperature, a stable supercooled liquid region, obvious multi-crystallization, near eutectic melting, a high reduced GT temperature and paramagnetic property.

1. Introduction

Rare-earth–transition metal (RE–TM) based bulk metallic glasses (BMGs) have been studied widely in recent years because of their high glass-forming ability (GFA) and magnetic properties [1, 2]. There have been considerable efforts made to understand the atomic and electric structures, mechanical, magnetic and chemical properties of the metallic glasses [3]. For NdAlFe alloys it was reported that bulk amorphous rods, 12 mm in diameter, can be obtained by suction casting into a copper mould [4, 5]. The high GFA of these alloys was related to a very highly reduced crystallization temperature $T_r = T_x/T_m$ (T_x, crystallization temperature; T_m, melting temperature). Although the glassy samples with large diameter and high GFA can be prepared, the RE–TM BMGs have neither distinct glass transition (GT) nor undercooled liquid region in their differential scanning calorimetry (DSC) traces which are common features for BMGs. The BMGs are hard magnets while ribbons with the same composition are soft magnets [6, 7]. Recently, a novel $Pr_{60}Cu_{20}Ni_{10}Al_{10}$ BMG was obtained in the shape of a rod up to 5 mm in diameter by die casting. The BMG exhibits a distinct GT with the lowest GT temperature, $T_g = 409$ K among the known BMGs and a large and stable supercooled liquid region and paramagnetic property [8]. In this work, a new highly glass forming $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ alloy, which has completely different properties as compared with the previously reported Nd-based BMG forming alloys, has been developed. The alloy has excellent GFA, a distinct GT with low T_g, obvious crystallization behaviours, and paramagnetic property. The composition of the alloy is near eutectic melting point. The features of the BMG could make it an ideal alloy to investigate the nature of GT as well as the relaxation and nucleation in metallic alloys at low temperatures, and it also offers a suitable matrix material for the preparation of various composites.

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2. Experiments

Ingots of $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ alloy were prepared by melting 99.9 at% pure Nd, Cu, Ni and Al in an arc-melting furnace under argon atmosphere. As-cast rod samples with 3 and 5 mm diameters and 80 mm length were produced by suction of the melt into a copper mould. The amorphous samples were characterized by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu K_α radiation. DSC measurements were carried out in a Perkin Elmer DSC-7 with the temperature scanning rate 20 K min^{-1}. Magnetic and transport properties were carried out on the Physical Properties Measurement System (PPMS, Quantum Design Inc., USA).

3. Results and discussions

Figure 1 shows the XRD patterns of as-cast $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ and $Nd_{60}Fe_{20}Co_{10}Al_{10}$ BMGs. Both samples exhibit a broad diffraction maxima characteristic of metallic glasses

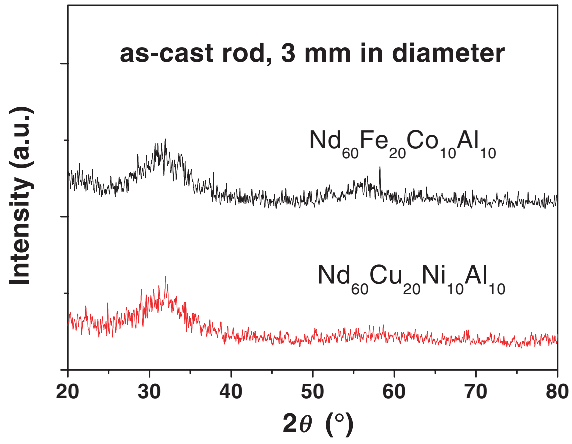

Figure 1. XRD patterns for the as-cast $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ and $Nd_{60}Fe_{20}Co_{10}Al_{10}$ rods with 3 mm diameter.

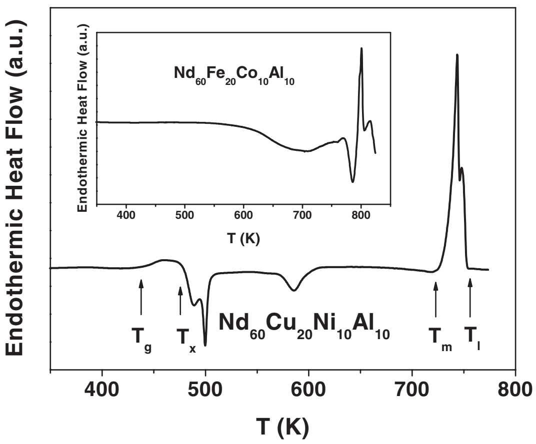

Figure 2. The DSC trace of the $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ sample showing the GT, crystallization and the melting process. The inset is the DSC trace of the $Nd_{60}Fe_{20}Co_{10}Al_{10}$ sample. The scanning rate is 20 K min^{-1}.

characterizing of amorphous structure of alloys with the limitation of the XRD. From the XRD patterns, no significant difference between the two alloys can be found. Figure 2 shows the GT, the crystallization and the melting process of the samples by DSC at heating rate of 20 K min^{-1}. Unlike other RE-based BMGs represented by $Nd_{60}Fe_{20}Co_{10}Al_{10}$ BMG also shown in figure 2, the remarkable features of the DSC trace for the $Nd_{60}Al_{10}Ni_{10}Cu_{20}$ alloy shows an obvious endothermic characteristic before crystallization demonstrating a distinct GT with onset at $T_g = 438$ K. Following the GT, the $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ sample exhibits two exothermic heat release events associated with the transformations from undercooled liquid state to the equilibrium crystalline intermetallic phases. The first crystalline temperature T_{x1}, the second crystalline temperature T_{x2} and the undercooled liquid region $\Delta T_x (= T_{x1} - T_g)$ are 478 K, 572 K and 40 K, respectively. The multi-component alloy is very close to a eutectic point from the endothermal signal of the melting in the DSC trace. The melting temperature T_m is determined to be 728 K. The reduced GT temperature T_{rg}, which is a critical parameter in determining the GFA of an alloy, $T_{rg} = T_g/T_m$ is 0.60 indicating the excellent GFA of

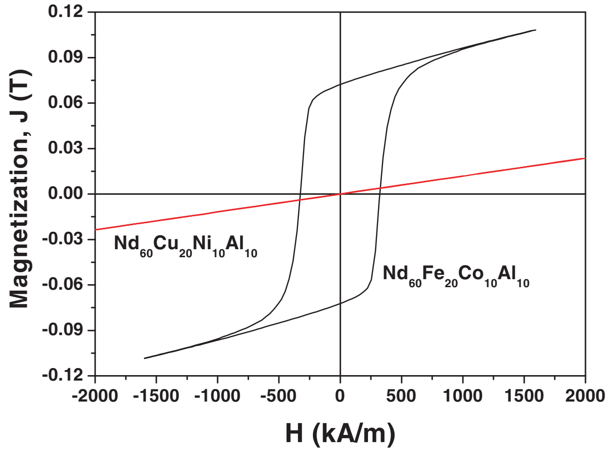

Figure 3. The hysteresis M–H loops of the as-cast rod $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ and $Nd_{60}Fe_{20}Co_{10}Al_{10}$.

the alloy according to the Turnbull criterion [9]. For the $Nd_{60}Fe_{20}Co_{10}Al_{10}$ alloy, however, no obvious GT and only a very broad exothermal peak corresponding to the growth of the nanocrystalline clusters [10] can be seen in the DSC trace. The high resolution transmission electron microscopy (HRTEM) result confirms that the so-called $Nd_{60}Al_{10}Fe_{20}Co_{10}$ glassy alloy mainly consists of heterogeneous and disoriented nano-ordered particles with the size smaller than 10 nm [11]. The features of the distinct GT, sharp crystallization events of the DSC trace for the Nd-based alloy are similar to other typical BMGs [12–14] and confirm the glassy state of the Nd-based BMG. The BMGs with an excellent GFA, stable supercooled liquid state and much lower T_g, which are comparable to a hard-sphere system and rather easily describable in contrast to inorganic, non-metallic glass formers and organic polymers [15], could give many possibilities to investigate the GT as well as relaxation and nucleation with a large experimentally accessible time and temperature window in a low temperature region [15–17]. The excellent GFA and low T_g and T_m, may make the BMG potential candidate for applications in areas such as phase change erasable optical storage [18]. It also is a suitable matrix material for the preparation of various composites with functional materials.

Figure 3 shows the room temperature M–H hysteresis loops measured at a maximum applied field of 2000 kA m^{-1} by the PPMS for $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ BMG. For comparison, the M–H hysteresis loop of $Nd_{60}Al_{10}Fe_{20}Co_{10}$ alloy is also displayed in figure 3. The as-cast $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ BMG exhibits paramagnetic property. But the as-cast rod of $Nd_{60}Al_{10}Fe_{20}Co_{10}$ BMG shows hard magnetic property, with a coercivity of 330 kA m^{-1}, a remanence of 0.072 T, and a saturation magnetization of 0.108 T at a maximum applied field of 1594 kA m^{-1}. The hard magnetic property of $Nd_{60}Al_{10}Fe_{20}Co_{10}$ BMG results from the nano-ordered clusters [19].

The GFA of metallic alloys generally follows three empirical rules [20]: multi-component systems consisting of more than three elements; significant difference in atomic size ratios above ∼12% among the main constituent elements and negative heat of mixing among the main constituent elements. In the Nd–Cu–Ni–Al and Nd–Fe–Co–Al systems, the atomic size sequence is of the order of Nd > Al > Ni > Cu and Nd > Al > Fe > Co and the atomic size ratios are 1.47 for Nd/Al, 1.12 for Al/Ni, 1.03 for Ni/Cu, 1.06 for Al/Fe and 1.03 for Fe/Co. The different elements in the two alloys do not significantly change the atomic size difference ratios among the main constituent elements. However, the basis element Nd has a positive heat of mixing with other main element Fe (+1 kJ mol^{-1}), while Nd–Cu has large negative heat of mixing (-156 kJ mol^{-1} for Nd–Cu, -42 kJ mol^{-1} for Nd–Ni) [21]. The $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ alloy perfectly satisfies the three empirical rules of glass formation [20]. However, in the $Nd_{60}Al_{10}Fe_{20}Co_{10}$ alloy, the positive heat of mixing between Nd and Fe leads to phase separation in the undercooled liquid [22]. The mutually repulsive interaction between Nd and Fe lead to phase separation and clustering in liquid state and is frozen into the alloy [23]. In addition, as shown in figure 2, the $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ alloy is close to eutectic point where precipitation of crystalline phase is difficult during solidification. Therefore, the $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ BMG has high GFA and can be obtained in full bulk amorphous state. The hard magnetic properties of the Nd-based alloys can be correlated to the pre-existence of nano-crystalline clusters with approximate composition of Fe_3RE (A_1 phase), whose size is so small that they cannot be detected by XRD [22, 24]. The magnetic exchange coupling interaction among the magnetic clusters with large random anisotropy causes the high coercivity of the Fe-rich RE-based alloys [22, 24].

4. Conclusion

The $Nd_{60}Cu_{20}Ni_{10}Al_{10}$ BMG with a high GFA is obtained in full bulk amorphous state. The gain of full bulk RE-based metallic glass with paramagnetic property is also useful for understanding the origin of the observed hard magnetic behaviour in Fe-rich RE-based alloys. The features of the BMG could also make it an ideal alloy to investigate the nature of GT as well as the relaxation and nucleation in metallic alloys at low temperatures, and it also offers a suitable matrix material for the preparation of various composites.

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References

[1] He Y, Price C E and Poon S J 1994 *Phil. Mag. Lett.* **70** 371
[2] Inoue A, Zhang T and Takeuchi A 1996 *Mater. Trans. JIM* **37** 1731
[3] Inoue A 2000 *Acta Mater.* **48** 277
[4] Inoue A, Zhang T, Takeuchi A and Zhang W 1996 *Mater. Trans. JIM* **37** 636
[5] Inoue A, Zhang T, Wang W and Takeuchi A 1996 *Mater. Trans. JIM* **37** 99
[6] Inoue A, Takeuchi A and Zhang T 1998 *Metall. Mater. Trans.* A **29** 1779
[7] Xing L Q, Eckert J, Löser W, Roth S and Schultz L 2000 *J. Appl. Phys.* **88** 3565
[8] Zhao Z F, Pan M X, Zhao D Q, Wang W H and Wang W L 2003 *Appl. Phys. Lett.* **82** 4699
[9] Turnbull D 1969 *Contemp. Phys.* **10** 473
[10] Fecht H J 1995 *Mater. Trans. JIM* **36** 777
[11] Zhang Z, Zhao D Q, Pan M X and Wang W H 2002 *Appl. Phys. Lett.* **81** 4371
[12] Johnson W L 1999 *MRS Bull.* **24** 42
[13] Wang W H, Bai H Y and Wei Q 1997 *Appl. Phys. Lett.* **71** 58
[14] Wang W H and Wang R J 1999 *Appl. Phys. Lett.* **74** 1803
[15] Angell A C 2000 *J. Appl. Phys.* **88** 3113
[16] Debenedetti P G and Stillinger F H 2001 *Nature* **410** 259
[17] Angell C A 1995 *Science* **267** 1924
[18] Libera M and Chen M 1990 *MRS Bull.* **15** 40
[19] Xia L, Wei B C, Zhang Z and Wang W H 2003 *J. Phys. D: Appl. Phys.* **36** 775
[20] Inoue A 1997 *Mater. Sci. Eng.* A **226–228** 357
[21] De Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1988 *Cohesion in Metals* (Amsterdam: North-Holland)
[22] Wei B C, Löser W, Xia L, Roth S, Pan M X, Wang W H and Eckert J 2002 *Acta Mater.* **50** 4357
[23] Delamare J, Lemarchand D and Vigier P J 1994 *Alloys Comp.* **216** 273
[24] Wei B C, Wang W H, Pan M X and Han B S 2001 *Phys. Rev.* B **64** 012406