

Formation of MgNiPr bulk metallic glasses in air

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Abstract

The Mg–Ni–Pr bulk metallic glasses (BMGs) can be easily cast into glassy rods up to 3 mm in diameter in argon and air atmosphere. The underlying mechanism for the unusual oxygen resistance during the preparation process and high glass forming ability of the alloy are investigated and discussed.

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Bulk metallic glasses (BMGs) have attracted increasing interest during the last decade because of their fundamental scientific interest and promising potential for engineering applications [1]. Extensive research is also being actively carried out to design new alloy systems exhibiting good glass-forming ability (GFA) and a low critical cooling rate. Among the large number of amorphous alloys, Mg-based alloys are of high interest due to their high strength to weight ratio and relatively low price. In addition, because the Mg-based alloys have the possibility of high endurance limit against pulverization due to the small volume expansion during hydrogen absorption, Mg-based BMGs are potential candidate for a hydrogen-storage material with light weight and low cost. Mg–Cu–RE (RE: rare earth metals) alloys have been reported to show a large super-cooled liquid region and high GFA [1–6]. Generally, high purity starting materials and high vacuum are key factors for the formation of BMGs. Recently, a Mg₆₅Cu₂₅RE₁₀ BMG was reported to be successfully fabricated by a conventional Cu-mold casting method in air instead of in argon atmosphere or in vacuum [4,5]. This progress can dramatically reduce the cost of the BMG materials and extend their application in industry.

Ni is an element adjacent to Cu in periodic table, and from an alloy chemistry point of view, Ni and Cu and Pr and Gd are quite similar to each other [7]. The negative heat of mixing in liquid and the difference of atomic size between component elements in the MgCuGd and MgNiPr systems are nearly the same [7]. According to the empirical rules for BMG formation [1], the Mg–Ni–RE alloys should also have high GFA as Mg–Cu–RE alloys do. Mg–Ni-based alloys also have higher potential for hydrogen-storage application. Therefore, the formation of MgNiRE BMGs is of significance both for understanding the universal features and underlying mechanism of the high oxygen resistance and GFA in BMGs and for future applications. In this paper, we prepare Mg–Ni–Pr BMGs in both argon and air atmospheres. The objective is to examine the possibility of manufacturing bulk Mg–Ni-based glass materials in air and study their GFA and formation mechanism.

NiPr master alloy was prepared by arc melting Ni (99.8%) and Pr (99.9%) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. Each ingot was remelted at least five times in an arc furnace to guarantee the chemical homogeneity. In order to prevent the evaporation of Mg, the master alloy was then alloyed with Mg (99.99%) in a quartz tube in argon atmosphere using an induction furnace. After completely melting, the liquid alloy was poured into a Cu-mold without water cooling. For a

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comparison, a $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ sample with a 3 mm diameter was also prepared in air in an induction furnace. The transverse cross-sections of all bulk samples were analyzed by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu K radiation. The glass transition and crystallization behaviors of all samples were examined with a differential scanning calorimeter performed on a Perkin-Elmer DSC under flowing purified argon at a heating rate of 20 K/min.

Fig. 1 shows the XRD patterns taken from the cross-section of the as-cast 3-mm MgNiPr rods with different compositions. The XRD patterns exhibit a broad characteristic diffraction peak of metallic glasses with no obvious crystalline peaks within detectable limitation. This demonstrates that Mg–Ni-based BMGs can be formed without strict casting atmosphere. It is difficult or impossible for the formation of other BMGs in air so far.

Fig. 2 presents the DSC traces obtained from different Mg–Ni–Pr alloys during heating with a heating rate of 20 K/min. Each of the traces exhibits an endothermic event characteristic of the glass transition and a distinct under-cooled liquid region, followed by one or two exothermic events characteristic of crystallization processes. Fig. 3 shows the DSC curves of $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ BMG obtained in air and argon atmosphere. The distinct glass transition and the sharp crystallization further confirm the glassy structure and the high GFA of the alloys. The crystallization enthalpy (ΔH_x) of the $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ alloy cast in argon atmosphere and air are 83 and 80 J/g, respectively. The similar crystallization enthalpy of the alloys cast in different atmospheres confirms that the alloy cast in air consists mainly of amorphous phase.

Several simple parameters have been introduced to reflect the relative GFA for various systems. Among them, the widely used one is the reduced glass transition temperature $T_{rg} = T_g/T_l$ [8]. Table 1 summarizes the glass transition temperature T_g , onset crystallization temperature T_x , onset

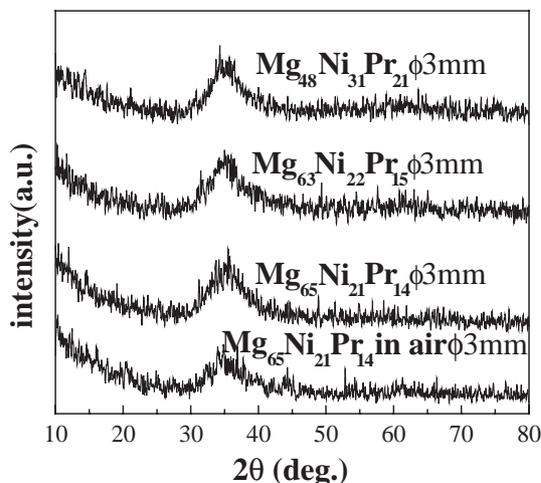


Fig. 1. X-ray diffraction patterns of the MgNiPr BMGs prepared in air and argon atmosphere.

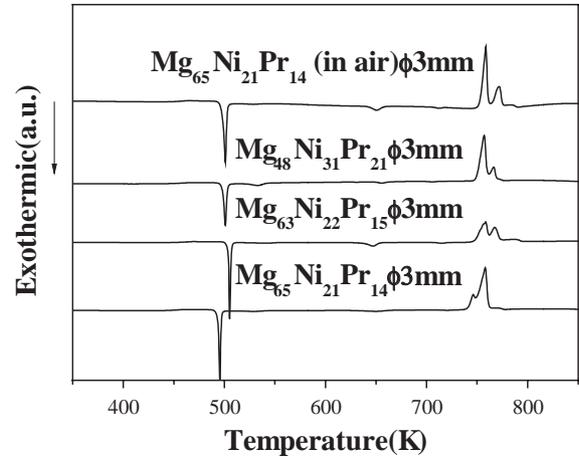


Fig. 2. DSC curves for the MgNiPr BMGs formed in air and argon atmosphere.

melting temperature T_m , liquidus temperature T_l , super-cooled liquid region ΔT ($\Delta T = T_x - T_g$), GFA parameter T_{rg} , and γ . From Table 1, it is noted that T_{rg} are almost of the same values for the $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ alloy produced under both air and argon conditions. These values are larger than that of ternary $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ glass (0.55) [9]. The value of ΔT_x and a newly defined parameter γ defined as $T_x/(T_g + T_l)$ [10] are also used to measure the GFA of the glass-forming alloys. The differences of ΔT_x and γ between the two samples cast in Ar and air are very small (see Table 1). All these data show that the oxygen does not play an adverse role in the glass formation of the Mg–Ni-based alloys as in other systems do [11]. The MgNiPr has high oxidation resistance ability, and can be easily prepared in air without significantly destroying the excellent GFA of the alloy.

From the heat of crystallization (ΔH_x) and the heat of fusion, ΔH_m , the order parameter, η , of an alloy in the solid state can be expressed as: $\eta = 1 - \Delta H_x / \Delta H_m$ [11]. $\eta = 1$ and $\eta = 0$, each corresponds to a fully ordered crystalline state and a fully disorder state, respectively [10]. From Table 1,

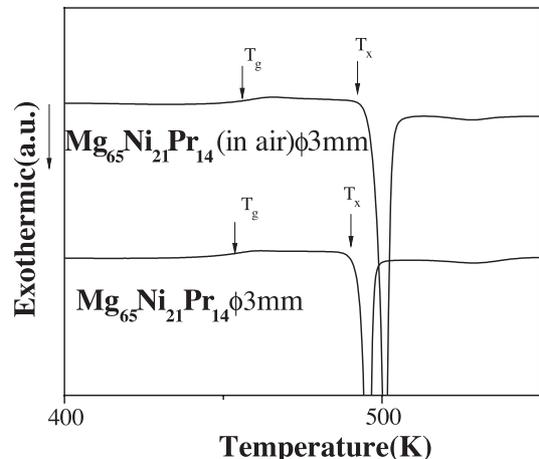


Fig. 3. DSC curves for the $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ BMG formed in air and argon atmosphere.

Table 1

Thermal parameters (heating rate: 20 K/min) of T_g , T_x , ΔT_x , T_m , T_l , T_{rg} , γ , ΔH_x , and ΔH_m for the Mg–Ni–Pr BMGs with different compositions

Alloy system	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ	ΔH_x (J/g)	ΔH_m (J/g)
Mg ₄₈ Ni ₃₁ Pr ₂₁	446	493	741	776	47	0.57	0.403	69	185
Mg ₆₃ Ni ₂₂ Pr ₁₅	446	498	752	776	52	0.57	0.408	68	103
Mg ₆₅ Ni ₂₁ Pr ₁₄	452	494	748	794	42	0.57	0.396	83	109
Mg ₆₅ Ni ₂₁ Pr ₁₄ (in air)	454	495	753	790	41	0.57	0.398	80	118

one can get that the η is 0.24 for the Mg₆₅Ni₂₁Pr₁₄ glass formed in argon and 0.32 for the alloy formed in air. In this η range, the alloy can be approximately regarded as amorphous materials [11]. So, to some extent, the preparation of the BMG in air does not reduce its degree of disorder either.

Based on above results, the underlying mechanisms of the unusual high manufacturability and high oxygen resistance of the alloys can be twofold: Firstly, the system satisfies the three empirical rules for high GFA in metallic alloys [1]. The atomic radius of Pr (0.183 nm) is much larger than that of Mg and Ni whose radii are 0.160 nm and 0.124 nm, respectively [7]. Furthermore, Pr brings a large negative heat when mixed with Mg and Ni [12]. This leads to the high GFA of the Mg–Ni–Pr alloy. Secondly, the RE elements do indeed have been found to play a dominant role in oxygen resistance during the glass formation process [13–17]. From a thermodynamic point of view, RE elements have a stronger affinity with the oxygen compared with that of Mg and Ni in the alloy. The enthalpy of formation of RE oxide is about 1800–2000 kJ/mol, and much higher than that of the oxides of other constituent elements (e.g. MgO, 601.6 kJ/mol) [11]. The reaction between RE and oxygen is thermodynamically favored compared with other oxidation reactions in the alloy. Therefore, in the molten liquid, the RE element can prohibit the reaction between Mg and oxygen during melting and casting processes. The Mg oxide and Laves phase are similar in crystalline structure [18]. The formation of the Laves phase, which can act as a heterogeneous nucleus sites and makes the alloy lose its excellent GFA [1], will be triggered by Mg oxide nuclei. This is the main reason why the glass-forming alloys is so sensitive to the oxygen content. However, the RE oxide nucleus sites with larger microstructural difference compared with that of MgO cannot induce the formation of the Laves phases. The small RE oxide particles attract the most of oxygen in the alloy and uniformly distribute in the glassy matrix [16]. Thus, the excellent GFA of remaining liquid was maintained because of the alleviation of the harmful effect of oxygen. The high oxygen resistance may also result from the protective role of oxidized film during melting process. When heating in air, an oxide film forms immediately on the surface of the alloy and prevents further oxidation. It is found that even above T_m , an oxidized film still exists. In addition, RE may play a purification role during the alloying process [19]. RE has high affinity with other impurities such as H, S, and C which also have harmful effect on the GFA [11], and can improve the

manufacturability by scavenging these impurities from the melting alloy via the formation of innocuous RE compounds [19].

In conclusion, bulk metallic glasses of Mg–Ni–Pr system are produced by the conventional copper mold casting method. Especially, the ternary Mg₆₅Ni₂₁Pr₁₄ BMG with a diameter of 3 mm is successfully fabricated by conventional Cu-mold casting method in air. The addition of Pr significantly improves the GFA and the oxidation resistance of the alloys. This result may make the mass-production of BMGs in industry easier. More work in this direction is underway.

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