

Improvement of corrosion resistance in NaOH solution and glass forming ability of as-cast Mg-based bulk metallic glasses by microalloying

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Abstract: The influences of the addition of Ag on the glass forming ability (GFA) and corrosion behavior were investigated in the Mg-Ni-based alloy system by X-ray diffraction (XRD) and electrochemical polarization in 0.1 mol/L NaOH solution. Results shows that the GFA of the Mg-Ni-based BMGs can be improved dramatically by the addition of an appropriate amount of Ag; and the addition element Ag can improve the corrosion resistance of Mg-Ni-based bulk metallic glass. The large difference in atomic size and large negative mixing enthalpy in alloy system can contribute to the high GFA. The addition element Ag improves the forming speed and the stability of the passive film, which is helpful to decrease the passivation current density and to improve the corrosion resistance of Mg-Ni-based bulk metallic glass.

Key words: Mg-Ni-based alloy; glass forming ability; corrosion resistance

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During recent years, bulk metallic glasses (BMGs) have been a subject of great interest in the field of materials science and engineering because of their unique properties. Among a large number of BMGs, Mg-based BMGs have attracted considerable attention because of their low cost and low density. To date, Mg-Cu-TM-RE (TM = transition metal; RE = rare earth) alloy systems have been reported to be of high GFA and most researches have focused on Mg-Cu-based BMGs^[1-8]. Compared with Mg-Cu-based BMGs, Mg-Ni-based BMGs have been studied because of their excellent hydrogen storage properties and high thermal stability^[9-12]. However, the low GFA of Mg-Ni-based BMGs limits their applications for metallic glasses. Moreover, enhancing anti-corrosion performance of the Mg-Ni-based electrode in alkali solutions is also an important method to improve the cycling stability of electrochemical hydrogen storage^[13].

Recently, Mg-Ni-Pr and Mg-Ni-Gd alloy systems have been studied^[9, 11]. In the present study, Ag was selected as the fourth alloying element and its effect on glass formation and corrosion resistance of Mg-Ni-Pr (Gd) -Ag alloys was studied.

1 Experimental methods

Ni-Pr (Gd) and Ni-Pr (Gd)-Ag intermediate alloys were prepared by arc melting Ni, Pr (Gd) and Ag (purity higher than 99.99 %) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The intermediate alloys were then melted with Mg (purity higher than 99.9 %) using an induction furnace to obtain master alloys with the nominal composition. After that, the master alloys were re-melted in quartz tubes and injected into cylinder-shaped copper molds in inert atmosphere in an evacuated chamber. Sample rods with diameters of 3–7 mm were prepared. The cross-sectional surfaces of the as-cast rods were analyzed using X-ray diffraction (XRD) using a Japanese Rigaku D/max-RB X-ray diffractometer with monochromatic Cu K_α radiation. The maximum diameter of the rods obtained with a fully glassy phase was taken as the critical glassy diameter (D_c). The glass transition temperature (T_g), the onset temperature of the first crystallization event (T_x), the melting temperature (T_m), and the liquidus temperature (T_l) were investigated using a Shimadzu DSC-60 differential scanning calorimeter (DSC) under the protection of N₂ gas (flow rate: 50 mL/min). The instrument was calibrated with In and Zn standard specimens. The corrosion behavior of BMGs was investigated by electrochemical polarization in 0.1 mol/L NaOH solution. Potentio-dynamic polarization was performed on samples at room temperature in a three-electrode cell with platinum net counter-electrode and saturated calomel electrode

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(SCE) with U (SHE) = 240 mV. The working electrode was made by attaching a Cu wire to one end of the sample that was closely sealed with epoxy resin. Potentio-dynamic polarization curves were recorded at a potential sweep rate of 1 mV/s after immersing the specimens for about 15 minutes, when the open circuit potentials became almost steady.

2 Results and discussion

2.1 The effect of the addition of Ag on the GFA

The XRD patterns of the as-cast Mg-Ni-based alloys with different contents of Ag are shown in Fig. 1. All the XRD patterns consist only of characteristic amorphous broad

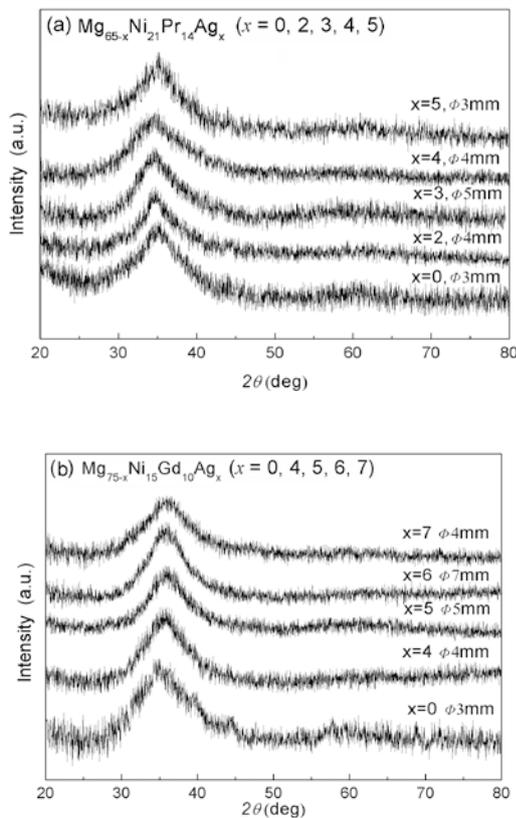


Fig. 1: XRD patterns obtained from the transverse cross-sections of the as-cast BMGs

diffraction peaks located at $2\theta \approx 35^\circ$, indicating the formation of fully glassy phase within XRD resolution. For the $Mg_{65-x}Ni_{21}Pr_{14}Ag_x$ ($x = 0, 2, 3, 4, 5$) alloys, the D_c increases up to 5 mm at $x = 3$. For the $Mg_{75-x}Ni_{15}Gd_{10}Ag_x$ ($x = 0, 4, 5, 6, 7$) alloy system, the maximum D_c is 7 mm at $x = 6$. The results clearly indicate that the GFA can be improved by partial substitution of Ag for Mg, see Table 1.

Figure 2 shows DSC curves of the Mg-Ni-based glassy alloys. All the DSC curves were obtained at a heating rate of 20 K/min. It is seen that all the specimens exhibit distinct glass transition, followed by a broad super-cooled liquid region, and then exothermic reactions due to crystallization. T_g , T_x , T_m and T_i are marked by arrows in the DSC traces and listed in Table 1.

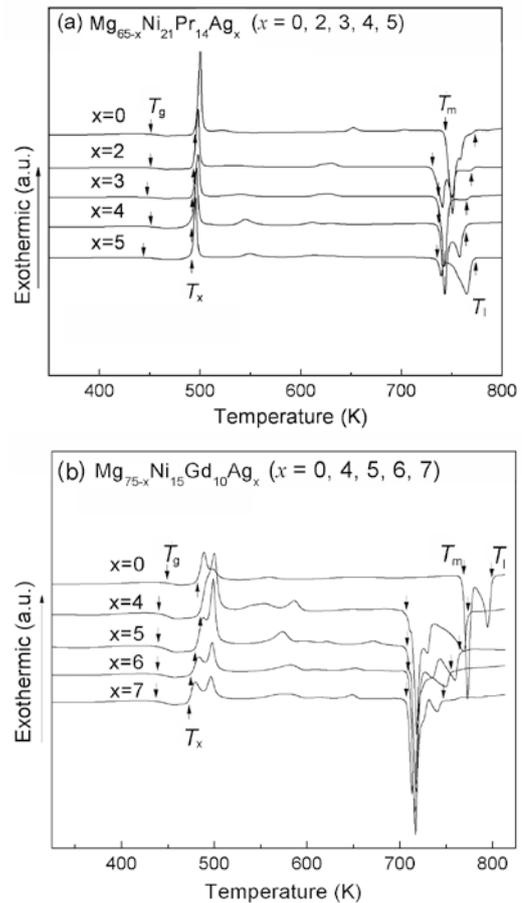


Fig. 2: DSC curves of BMGs

Table 1: The results of thermal analysis for $Mg_{65-x}Ni_{21}Pr_{14}Ag_x$ ($x = 0, 2, 3, 4, 5$) (a) and $Mg_{75-x}Ni_{15}Gd_{10}Ag_x$ ($x = 0, 4, 5, 6, 7$) (b) BMGs

Alloys (a)	T_g (K)	T_x (K)	T_m (K)	T_i (K)	D_c (mm)	Alloys (b)	T_g (K)	T_x (K)	T_m (K)	T_i (K)	D_c (mm)
$Mg_{65}Ni_{21}Pr_{14}$	451.0	494.8	743.8	773.5	3	$Mg_{75}Ni_{15}Gd_{10}$	449.0	482.0	769.0	799.1	3
$Mg_{63}Ni_{21}Pr_{14}Ag_2$	450.7	493.3	730.4	769.2	4	$Mg_{71}Ni_{15}Gd_{10}Ag_4$	440.3	485.0	706.9	773.5	4
$Mg_{62}Ni_{21}Pr_{14}Ag_3$	447.7	492.0	733.5	764.3	5	$Mg_{70}Ni_{15}Gd_{10}Ag_5$	449.6	479.1	707.8	764.2	5
$Mg_{61}Ni_{21}Pr_{14}Ag_4$	450.9	491.9	736.8	762.8	4	$Mg_{68}Ni_{15}Gd_{10}Ag_6$	439.2	474.5	710.0	756.9	7
$Mg_{60}Ni_{21}Pr_{14}Ag_5$	443.9	491.4	735.4	773.5	3	$Mg_{68}Ni_{15}Gd_{10}Ag_7$	437.3	472.8	706.7	746.9	4

Three empirical rules have been suggested to achieve a high GFA for an alloy system [14, 15]: (1) multi-component system with more than three components; (2) large difference in atomic size between the constituent elements; (3) a large

negative mixing enthalpy in the alloy system. The increase of the GFA by the partial replacement of Mg by Ag in Mg-Ni-based alloys may be explained by the large difference in atomic size between Ag and the other constituent elements;

and by the large mixing enthalpy in Ag-Pr (Gd). The atomic size of Ag is 15.2% larger than that of Ni, and is smaller than those of Mg, Pr, Gd by 10.0%, 21.3% and 19.1%, respectively. The large atomic size difference between Ag and Mg, Ni, Pr (Gd) elements is favorable to increase the atomic packing density of the liquid structure. The mixing enthalpies for Ag-Gd, Ag-Pr, Mg-Gd and Mg-Pr are -29, -29, -6 and -6 kJ/mol, respectively [16]. When the mixing enthalpy of an alloy is negative, the larger the absolute value is, the more contribution to the GFA and the stabilization of the liquid phase the mixing enthalpy makes. So, the addition of Ag is helpful to the stabilization of the liquid phase by changing the local atomic structure. The highest GFA at $x = 3$ (for $\text{Mg}_{65-x}\text{Ni}_{21}\text{Pr}_{14}\text{Ag}_x$) and $x = 6$ (for $\text{Mg}_{75-x}\text{Ni}_{15}\text{Gd}_{10}\text{Ag}_x$) may be due to the more stable and densely packed liquid structure. As shown in Table 1, partial substitution of Ag for Mg decreases the melting temperature, which indicates that the liquid phase is stabilized with respect to competing crystalline phases. The stabilization of the liquid phase can be achieved by increasing the atomic packing density, and by forming short range compositional order in the liquid phase [17].

2.2 The effect of the addition of Ag on the corrosion resistance

Figure 3 shows the potentiodynamic polarization curves of $\text{Mg}_{65-x}\text{Ni}_{21}\text{Pr}_{14}\text{Ag}_x$ ($x = 0, 2, 3, 4, 5$) and $\text{Mg}_{75-x}\text{Ni}_{15}\text{Gd}_{10}\text{Ag}_x$ ($x = 0, 4, 5, 6, 7$) BMGs in 0.1 mol/L NaOH aqueous solution.

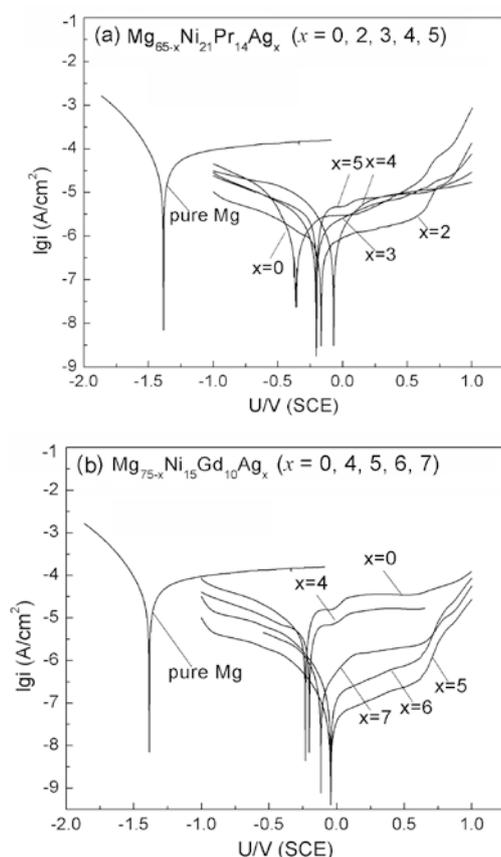


Fig. 3: Polarization curves of BMGs and pure Mg in 0.1 mol/L NaOH solution

For comparison, the electrochemical polarization behavior of pure Mg was also examined under the same conditions. Some corrosion data, including the passive potential (E_0) and passive current density (i_p) derived from the curves are summarized in Table 2. It is obvious that the addition of Ag can improve the corrosion resistance of Mg-Ni-Pr and Mg-Ni-Gd BMGs, as indicated by higher E_0 and lower i_p than those of $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ and $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$, respectively. These results indicate that the addition of appropriate amount of Ag can greatly enhance the corrosion resistance of the Mg-Ni-based BMG in alkaline solutions.

Table 2: The passive potential (E_0), passive current (i_p) in 0.1 mol/L NaOH solution for BMGs and pure Mg

(a) $\text{Mg}_{65-x}\text{Ni}_{21}\text{Pr}_{14}\text{Ag}_x$	Pure Mg	$x=0$	$x=2$	$x=3$	$x=4$	$x=5$
i_p (10^{-7} A/cm ²)	151	6.37	3.51	3.38	4.07	8.60
E_0 (mV)	-1,380	-364	-167	-205	-68	-197
(b) $\text{Mg}_{75-x}\text{Ni}_{15}\text{Gd}_{10}\text{Ag}_x$	Pure Mg	$x=0$	$x=4$	$x=5$	$x=6$	$x=7$
i_p (10^{-7} A/cm ²)	151	1.95	1.47	0.17	0.63	1.70
E_0 (mV)	-1,380	-233	-201	-42	-45	-114

In order to further understand the formation process of passive films of the Mg-based BMGs with different Ag contents, the kinetics of the formation of passive films was investigated by the galvanostatic step measurements. Figure 4 shows the potential-time ($E-t$) curves of the BMGs with different Ag contents in the alkaline solution. Usually, the

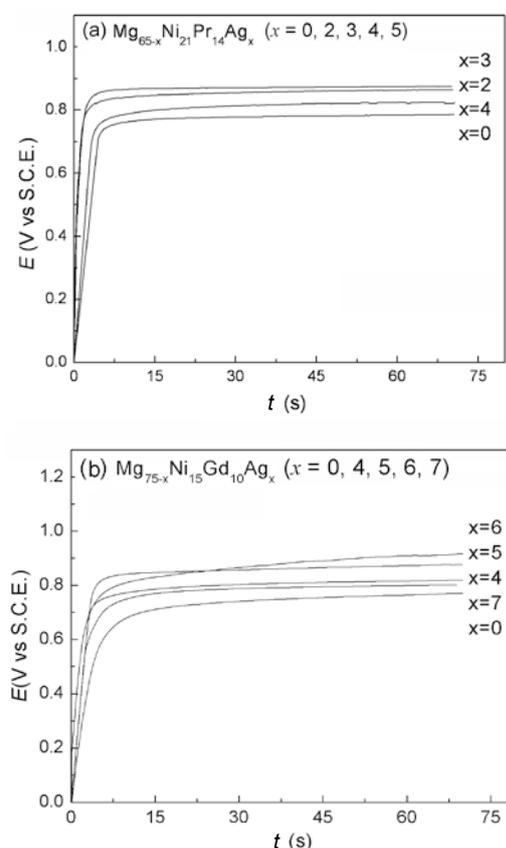


Fig. 4: The potential-time ($E-t$) curves of BMGs during anodizing at 2 mA/cm² in 0.1 mol/L NaOH solution

level of the plateau potential reflects the stabilization of the passive film, while the slope of the linear part in the $E-t$ curve indicates the rate for the formation of a passive film^[18]. The fact that the linear slope and the plateau potential increase with the increasing Ag content, as shown in Fig. 4, indicates that the addition of Ag speeds up the formation of passive film and simultaneously stabilizes the film in alkaline solution; and the film became denser. As a result, the passive film can be more protective.

3 Conclusions

In the present study, the influence of partial substitution of Ag for Mg on the GFA and corrosion behavior were investigated in the Mg-Ni-Pr (Gd)-Ag alloy system. The addition of an appropriate amount of Ag enhanced the GFA of the $Mg_{65}Ni_{21}Pr_{14}$ and $Mg_{75}Ni_{15}Gd_{10}$ alloys. $Mg_{62}Ni_{21}Pr_{14}Ag_3$ BMG with a diameter of 5 mm and $Mg_{69}Ni_{15}Gd_{10}Ag_6$ BMG with a diameter of 7 mm were successfully fabricated by conventional Cu-mold casting method. The addition of Ag also considerably improved the corrosion resistance of Mg-Ni-Pr (Gd) BMG in alkaline solutions. The improvement of corrosion resistance was achieved by the fast formation of a layer of uniform and dense passive film in alkaline solution, due to the addition of appropriate amount of Ag.

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