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Low-density Mg-rich metallic glasses with bending ductility

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Amorphous Mg–Cu–Ca(Y) alloys that contain more than 80 at.% magnesium and have a density as low as 1.8 g cm^{-3} have been prepared by melt spinning. Tension fracture strengths of ∼570 MPa are obtained for $Mg_{85}Cu_5Ca_{10}$ ribbons, resulting in a specific strength of 300 MPa cm^3 g^{-1}. Scanning electron microscopy studies reveal dense river patterns on the fracture surface. The high Mg content and the thermal transformation behavior of these amorphous light alloys invite comparison to the Al-based metallic glasses.

Keywords: Amorphous alloy; Magnesium alloy; Bending ductility; Mass density

To date, amorphous alloys based on light metals have been reported for Al–TM (transition metals)–RE (rate earths) [1–3], Al–Cu–Mg–Ni(Pd) [4], Mg–Cu(Ni)–RE [5–8], Mg–Zn–Ca [9], Ca–Cu–Mg [10], Ca–Al–Mg–(Cu, Zn) [11] and Ca–Mg–Zn–(Cu) [12]. Although these amorphous alloys are based on light metals, their mass densities are, in general, appreciably higher than those of the base metal solvent due to the presence of heavy solute elements. Several representative alloy compositions with their calculated mass densities are listed in Table 1. The Al- and Mg-based amorphous alloys have a higher mass density than commercial Al and Mg alloys. Ca-based alloys have a mass density close to or less than 2 g cm^{-3}. Besides the high mass densities, most of the Mg- and Ca-based amorphous alloys so far reported are also quite brittle.

In view of the Mg-based amorphous light alloy's potential as a new class of structural light metals, the possibility of improving their ductility by designing new compositions are explored. Considering the low mass density requirement, the alloys must contain a minimal amount of heavy solute elements. Furthermore, by taking advantage of the light element Ca, which also has a desirably large atomic size for glass formation [13], it is selected as one of the key alloying elements in constituting a new Mg-based amorphous alloy. In this paper, the result of a current investigation of glass-forming ability in some Mg-rich alloy systems is reported. Amorphous ribbons with a mass density of less than 2 g cm^{-3} and bending ductility are produced.

The purities of the alloying elements used in this work are at least 99.9 at.%. Alloy precursors such as Y_2Cu and Y_2Ni were prepared by using arc-melting under an argon partial pressure. The final melting of the alloys was carried out in an induction furnace under a flowing argon atmosphere. Boron nitride-coated graphite crucibles were used as the melting boats for induction melting. Melt spinning was done under a helium partial pressure, using a circumferential wheel speed of 25 m s^{-1} unless otherwise specified. The ribbon thickness prepared at 25 m s^{-1} is about 40 μm (as shown later in Fig. 5a). The amorphous nature of the ribbon samples was examined using X-ray diffraction (XRD) equipped with Cu Kα radiation. Thermal analysis was carried out using differential scanning calorimetry (DSC) at a heating rate of 20 °C min^{-1}. The ductility of the as-spun ribbon samples was examined by a simple bending and pinching method which will be described later. Mechanical strength was measured for as-spun ribbons. A testing machine with a screw-driven frame was used with a strain rate of 10^{-4} s^{-1} under the tension mode. Fracture surface observation was carried out using scanning electron microscopy (SEM).

Starting with Mg–Ca binary alloys near the Mg-rich eutectic composition ($Mg_{89.5}Ca_{10.5}$) [14], it is found that fully amorphous phase ribbons cannot be formed even at a wheel speed of 30 m s^{-1}. From Figure 1, both crystalline diffraction peaks (indexed as hexagonal close-packed magnesium) and an amorphous diffuse background appear in the diffraction pattern for as-spun

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Table 1. Glass-forming ability (in mm of the as-made amorphous rod) and mass density (in the unit of g cm^{-3}) of several representative amorphous alloys based on light metals Al, Mg and Ca[a]

Composition (at.%)	Glass-forming ability	Mass density	References
$Al_{87}Ni_7Gd_6$	Ribbon	3.576	[2,3]
$Al_{85}Ni_5Co(Fe)_2Gd(Y)_8$	Ribbon	3.190	[1,2]
$Mg_{85}Cu_5Y_{10}$	Ribbon	2.302	[8]
$Mg_{65}Cu_{25}Y_{10}$	4	3.160	[5]
$Mg_{65}Cu_{7.5}Ni_{7.5}Ag_5Zn_5Y_5Gd_5$	14	3.515	[6]
$Mg_{56}Cu_{26.5}Ag_{8.5}Gd_{11}$	25	4.518	[7]
$Ca_{57}Cu_{24}Mg_{19}$	4	2.237	[10]
$Ca_{60}Mg_{20}Al_{20}$	1.5	1.689	[11]
$Ca_{55}Al_{10}Mg_{15}Zn_{15}Cu_5$	8	2.172	[9]
$Ca_{62.5}Mg_{17.5}Zn_{20}$	10	2.074	[12]

[a] Mass densities of pure Al, Mg and Ca are 2.70, 1.74 and 1.55 g cm^{-3}, respectively.

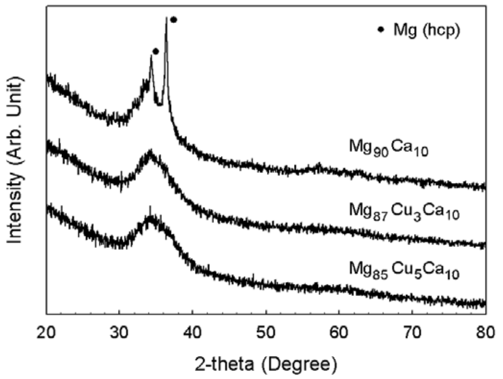

Figure 1. XRD patterns of Mg–Ca and Mg–Ca–Cu as-spun ribbons at a circumferential wheel speed of 25 m s^{-1}.

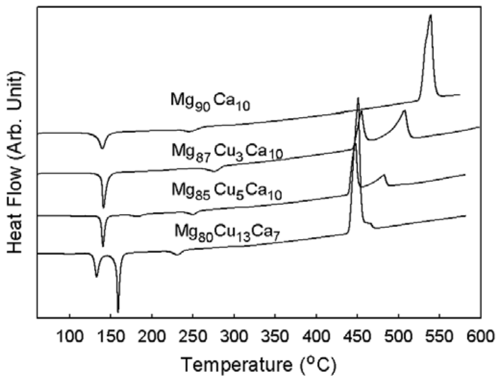

Figure 2. DSC curves of Mg–Ca and Mg–Ca–Cu as-spun ribbons at a heating rate of 20 °C min^{-1}.

$Mg_{90}Ca_{10}$ ribbons. Replacing as little as 3 at.% Mg with Cu, an almost fully amorphous structure is obtained at 25 m s^{-1} with barely visible magnesium crystalline diffraction peaks. With further introduction of Cu, replacing up to 20 at.% Mg, while keeping the Ca content the same, a fully amorphous phase can be readily obtained. The X-ray pattern of the ribbon with 5 at.% Cu addition is shown in Figure 1 as a representative. Because of the higher mass density of Cu, the alloys with more than 10% of Cu have a density greater than 2 g cm^{-3}. Besides the higher mass density, amorphous ribbons made from alloys with more than 10 at.% Cu also tend to be brittle.

Thermal analysis of the Mg–Ca–(Cu) amorphous alloys is shown in Figure 2, where the DSC curves were obtained at a heating rate of 20 °C min^{-1}. The addition of Cu to replace Mg does not change the thermal stability of the amorphous alloys, and the crystallization peaks are now near 130 °C. On the other hand, the melting temperature decreased significantly with Cu additions. The binary $Mg_{90}Ca_{10}$ alloy exhibits a near-eutectic melting, with the melting temperature (onset of the melting peak) at 517 °C. Introduction of 3 at.% Cu leads to a non-eutectic melting of $Mg_{87}Cu_3Ca_{10}$, with the initial and final melting temperatures at 437 and 480 °C, respectively. For $Mg_{85}Cu_5Ca_{10}$, the initial and final melting points are further decreased to 430 and 455 °C, respectively. Considering the unchanged thermal stability of the amorphous alloys and the decreased melting temperature, it would be expected that the alloys with Cu additions show an improved glass-forming ability. However, bulk amorphous rods of 1 mm in diameter could not be formed by injection casting.

It is known that alloys with a near-eutectic composition usually exhibit a better glass-forming ability. Hence an effort was made to locate the eutectic composition for the Mg–Ca–Cu ternary alloys. The eutectic is quite close to $Mg_{80}Cu_{13}Ca_7$, with a melting temperature of 431 °C (DSC curve, Fig. 2). However, this alloy does not show any improvement in glass-forming ability, perhaps because of the lower thermal stability of the amorphous phase (crystallization temperature is at 120 °C). Injection casting of a 1 mm diameter rod also failed to form an amorphous structure. Obviously, other components need to be introduced to Mg–Ca–Cu ternary alloys in order to improve the glass-forming ability of the alloys.

Mg-based bulk amorphous alloys were first reported by Inoue et al. group in the 1990s [5]. By injection casting into a water-cooled copper mold, Mg–Cu–Y alloys with 65 at.% Mg were found to form 4 mm amorphous rods. Later, modified chemistries doubled the thickness of the amorphous samples at the off-eutectic compositions [15]. More recently, centimeter-to-inch-sized Mg amorphous alloys have been reported by introducing Ag, Ni, Zn, Pd, Gd, etc. [6,7]. However, due to the introduction of heavy solute components, all these alloys have a density of more than 3 g cm^{-3}, which is more than 50% higher than that of commercial crystalline Mg alloys. In view of the positive effect of Y on the glass-forming ability of Mg alloys, Y is added to the