Mg–Cu–(Y, Nd) pseudo-ternary bulk metallic glasses: The effects of Nd on glass-forming ability and plasticity

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We report the improvement of glass-forming ability by using Nd to substitute Y in the Mg–Cu–Y bulk metallic glass (BMG). A search in the Mg–Cu–(Y,Nd) pseudo-ternary system located the best glass former at the Mg 57Cu31Y6.6Nd5.4 composition, where the critical size for BMG formation (diameter \( D_c \) for copper mold casting) reached at least 14 mm. In comparison with the ternary Mg–Cu–Y glass, the Nd-containing BMG, without a significant change in Poisson’s ratio, exhibits higher strength and improved compressive plasticity.

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As a new family of engineering alloys, bulk metallic glasses (BMGs) have attracted considerable attention in recent years. Among them, Mg-based BMGs are particularly interesting due to their high (specific) strength and low cost. Ever since the first search that discovered a Mg–BMG in the ternary Mg–Cu–Y system [1], a great deal of effort has been devoted to developing Mg-based BMGs in different systems [2–4]. Recently, the best BMG former in the Mg–Cu–Y system was found to be located at the off-eutectic composition, \( \text{Mg}_{58.5}\text{Cu}_{30.5}\text{Y}_{11} \), with a critical size (diameter \( D_c \) for copper mold casting) of 9 mm [5]. Furthermore, our group successfully developed the first inch-diameter Mg-based BMG using a three-dimensional (3D) search method in the Mg–Cu–Ag–Gd system [6,7].

A challenging problem for the monolithic Mg-based BMGs is their brittleness. The Mg–Cu–Y BMGs, for example, fail in a catastrophic manner due to highly localized shear bands, without obvious macroscopic plasticity. Recently, it has been proposed that the intrinsic ductility of metallic glasses correlates with their Poisson’s ratio, \( \nu \) [8,9], or equivalently a ratio of the elastic shear modulus \( \mu \) to the bulk modulus \( B \), \( \mu/B \) [10]. This suggests that Mg-based BMGs are probably intrinsically brittle due to their low \( \nu \) (or high \( \mu/B \)) and that one should select alloying elements with relatively high \( \nu \) to improve their ductility.

Almost all of the previous studies on Mg-based BMGs have focused on Mg–Cu–RE (RE stands for rare-earth metals such as Y, Gd) alloy systems. The late transition metals such as Ni, Cu, Zn, Ag, Pd were selected to substitute for Cu to improve the glass-forming ability (GFA) [7,11–14]. In this work, we selected Nd as an example of an alloying element, to study the effects of rare-earth substitution on GFA. With \( \nu = 0.28 \) [15], Nd has the largest Poisson’s ratio among the most commonly used rare earth metals (such as Y and Gd, for which \( \nu = 0.24 \) and 0.26, respectively) in Mg-based BMGs. We start from the \( \text{Mg}_{58.5}\text{Cu}_{30.5}\text{Y}_{11} \) alloy (\( D_c = 9 \) mm), which is the best glass former in the Mg–Cu–Y ternary system. Nd is introduced to substitute for Y to form the Mg–Cu–(Y,Nd) pseudo-ternary system. As the atomic radius of Nd (\( r_{\text{Nd}} = 0.164 \) nm) is slightly smaller than that of Y (\( r_{\text{Y}} = 0.180 \) nm) and Y–Nd binary system has a near-zero heat of mixing, the two elements form continuous solid solutions. In the following, we demonstrate the effects of Nd in improving both the GFA and the ductility.

Elemental pieces of better than 99.9% purity were used as starting materials. Cu–Y (or Y,Nd) ingots as
an intermediate alloy were prepared by arc melting under a Ti-gettered argon atmosphere. This alloy was then melted with Mg pieces by induction melting under an inert gas atmosphere to obtain a master alloy with the nominal composition (in atomic percentage). The master alloy was re-melted in a purified inert atmosphere using induction melting, then injected into the copper mold with internal rod-shaped cavities or cast into the copper mold in a tilting furnace (if diameter >10 mm).

The cross-sectional surfaces of the as-cast rods were analyzed by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer with monochromated Cu $K_\alpha$ radiation. The glass transition, crystallization and melting behavior of the cast samples were investigated in a Perkin-Elmer differential scanning calorimeter (DSC-diamond) under flowing purified argon. The samples were contained in graphite pans. A heating rate of 20 K min$^{-1}$ was employed. All measurements for the glass transition temperature, $T_g$, and the onset temperature of the first crystallization event, $T_x$, were reproducible within the accuracy of ±1 K. The heat of crystallization $\Delta H_x$ for the glassy phase was determined by integrating the area under the DSC curve.

The compression test samples 2 mm in height were cut from the as-cast rods of 1 mm in diameter, prepared by suction casting. The loading surfaces were polished to be parallel to an accuracy of less than 10 $\mu$m. Uniaxial compression tests at room temperature were conducted using a constant strain rate of 1 $\times$ 10$^{-4}$ s$^{-1}$. At least five samples were measured to ensure that the results were reproducible. The strain was determined from the platen displacement after correction for machine compliance.

The elastic constants (e.g., bulk modulus $B$, Young’s modulus $E$, shear modulus $\mu$, and Poisson’s ratio $\nu$) and the Debye temperature, $\Theta_D$, of the BMGs were determined from the acoustic velocities and density, $\rho$. The acoustic velocities were measured at room temperature by using a pulse echo overlap method [16–18]. Densities of the as-cast glassy rod were measured at room temperature by the Archimedes principle.

To locate the best BMG former in the Mg–Cu–(Y,Nd) pseudo-ternary system, we adopted our previously-published search strategy (protocol) in 3D composition space [6,7]. The BMG formation was investigated on a few consecutive compositional planes, each with a fixed Nd to Y ratio, expressed as Y$_{1-x}$Nd$_x$ ($x = 0.2, 0.3, 0.45$), as shown in Figure 1(a). Tests at various compositions to pinpoint the best GFA on each plane were then performed. Figure 1(b) through Figure 1(d) display the composition maps for glass formation on several representative composition planes. The contours are for different critical sizes, $D_c$, for BMG formation in the cast samples. For the $x = 0.2$ plane as shown in Figure 1(b), Mg$_{57}$Cu$_{31.5}$Y$_{9.2}$Nd$_{2.3}$ alloy exhibits the best GFA. The $D_c$ increased to 10 mm, over the composition range of 56–58% Mg, 31–32% Cu, and 11–12% Nd$_{0.2}$–Y$_{0.8}$. On further increasing the Nd content to $x = 0.3$ (see Fig. 1(c)), Mg$_{57}$Cu$_{31.3}$Y$_{8.3}$Nd$_{1.5}$ alloy exhibits the best GFA. The $D_c$ increased to 12 mm, and fully glassy rods can be obtained at this diameter for a small composition range (56–58% Mg, 31–32% Cu, and 11–12% Nd$_{0.3}$Y$_{0.7}$). Moving the Nd to Y ratio to $x = 0.45$, only one composition gave a $D_c$ of 14 mm. As such, the highest GFA in the Mg–Cu–(Y,Nd) pseudo-ternary system was located at Mg$_{57}$Cu$_{31}$Y$_{6.6}$Nd$_{5.4}$ (total Y + Nd content at 12%), as

![Figure 1](https://example.com/figure1.png)

Figure 1: (a) The tetrahedron shows the three composition planes examined in the Mg–Cu–(Y$_{1-x}$Nd$_x$) system. The three panels, (b)–(d), show the composition maps for the formation of BMGs with several different diameters, at several ratios of Y$_{1-x}$Nd$_x$: (b) $x = 0.2$, 10 mm, (c) $x = 0.3$, 12 mm and (d) $x = 0.45$, 14 mm. The full and half open symbols represent the formation of fully and partially glassy rods, respectively. The alloy with the best GFA on each plane is marked as a red full symbol in (b) and (c). The alloy with a $D_{c\text{max}} = 14$ mm is marked as a star in (d).
marked with a star in Figure 1(d). Apparently, Nd as the element substituting for Y improves the GFA of the Mg–Cu–Y base alloy.

Figure 2 shows the XRD patterns taken from the cross-sectional surface of the as-cast rods with the largest $D_c$ on each plane. It is seen that at diameters of 9, 10, 12, and 14 mm, respectively, these alloys exhibited broad diffraction peaks in the $2\theta$ range of 30–45°, which is characteristic of an amorphous structure with no evidence of any crystalline peaks within XRD resolution.

Figure 3 (a) shows the DSC curves for the as-cast BMG rods with the largest $D_c$ on each composition plane. In all cases, a clear endothermic event associated with the glass transition and a sharp exothermic crystallization peak are observed. The $T_g$, $T_x$, $\Delta T_x$ ($\Delta T_x = T_x - T_g$) and $\Delta H_x$ values are listed in Table 1. The Mg$_{57}$Cu$_{31.5}$Y$_9$Nd$_{3.5}$ glass at the $x = 0.3$ plane exhibits the largest $\Delta T_x$, 75 K. It is larger than that of the 14 mm Mg$_{57}$Cu$_{31}$Y$_{6.6}$Nd$_{5.4}$ (64 K). Increasing the Nd content in the glasses does not yield a significant change in $T_g$ and $T_x$. In all cases, either the Nd-containing or the Nd-free glasses, the crystallization of the glassy phase is completed in two steps.

Figure 3(b) shows the DSC traces at the temperature range of melting events for the as-cast rods with the largest $D_c$ on each plane. The onset and end temperatures of the endothermic signals in the curves caused by melting are designated by $T_m$ and $T_L$, respectively, and are summarized in Table 1. These curves show at least two events, indicating that these alloys are at off-eutectic compositions. It is noteworthy that with increasing Nd content, the $T_m$ decreased slightly, by 16–22 K, as seen in Figure 3(b), suggesting that the liquid is stabilized, thereby enhancing the GFA. The calculated reduced glass transition temperature $T_{rg}$ ($T_{rg} = T_g / T_L$) of these alloys are listed in Table 1 as well. The $T_{rg}$ values are all around 0.55, reflecting that this parameter is not sufficiently sensitive to tell apart their differences in GFA.

Figure 4 shows the compressive stress–strain curves for the as-cast Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ and Mg$_{57}$Cu$_{31}$Y$_{6.6}$Nd$_{5.4}$ BMG samples. In each case, the samples were tested to failure. From the stress–strain curve, the yield stress $\sigma_y$, fracture stress $\sigma_f$, elastic strain $\varepsilon_e$, plastic strain $\varepsilon_p$ for these two glasses were determined, as listed in Table 2. For comparison, the compressive properties of several typical Mg-based BMGs in literature [12–14] are also listed in Table 2. It is shown that the fracture strength of the Mg$_{57}$Cu$_{31}$Y$_{6.6}$Nd$_{5.4}$ glass is about 160 MPa higher than that of Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ glass, and also higher than that of Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ ternary alloy for comparison.

**Figure 2.** XRD patterns of as-cast rods at the compositions with the maximum $D_c$ for the three ratios of Y$_{1-x}$Nd$_x$ ($x = 0.2, 0.3, 0.45$), together with Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ ternary alloy for comparison.

**Figure 3.** DSC scans of (a) as-cast rods at the compositions with the maximum $D_c$ for the three ratios of Y$_{1-x}$Nd$_x$ ($x = 0.2, 0.3, 0.45$), together with Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ ternary alloy for comparison and (b) DSC traces of the alloys in (a) near their melting temperatures.

**Figure 4.** Stress–strain curves obtained from the uniaxial compression test of the Mg$_{58.5}$Cu$_{30.5}$Y$_{11}$ and Mg$_{57}$Cu$_{31}$Y$_{6.6}$Nd$_{5.4}$ BMG samples. The curves are shifted relative to each other for clarity.

**Table 1.** Critical sizes and thermal properties (determined using DSC at a heating rate of 20 K min$^{-1}$) of Mg-based BMGs fabricated using copper mold casting

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$Y_{1-x}$Nd$_x$</th>
<th>$D_c$ (mm)</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$\Delta H_x$ (kJ/mol)</th>
<th>$T_m$ (K)</th>
<th>$T_L$ (K)</th>
<th>$T_{rg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{58.5}$Cu$</em>{30.5}$Y$_{11}$</td>
<td>$x = 0$</td>
<td>9</td>
<td>422</td>
<td>496</td>
<td>74</td>
<td>3.57</td>
<td>729</td>
<td>762</td>
<td>0.554</td>
</tr>
<tr>
<td>Mg$<em>{57}$Cu$</em>{31.5}$Y$<em>9$Nd$</em>{3.5}$</td>
<td>$x = 0.2$</td>
<td>10</td>
<td>428</td>
<td>502</td>
<td>74</td>
<td>3.61</td>
<td>713</td>
<td>777</td>
<td>0.551</td>
</tr>
<tr>
<td>Mg$<em>{57}$Cu$</em>{31.5}$Y$<em>8$Nd$</em>{3.5}$</td>
<td>$x = 0.3$</td>
<td>12</td>
<td>426</td>
<td>501</td>
<td>75</td>
<td>3.93</td>
<td>707</td>
<td>778</td>
<td>0.548</td>
</tr>
<tr>
<td>Mg$<em>{57}$Cu$</em>{31}$Y$<em>{6.6}$Nd$</em>{5.4}$</td>
<td>$x = 0.45$</td>
<td>14</td>
<td>427</td>
<td>491</td>
<td>64</td>
<td>4.19</td>
<td>707</td>
<td>778</td>
<td>0.549</td>
</tr>
</tbody>
</table>
of all previous Mg glasses. The macroscopic plastic strain of Mg58.5Cu30.5Y11 glass is nearly zero, but a plastic strain of about 1.2% appears in the Mg57Cu31Y6.6Nd5.4 glass, also larger than that of all the previous monolithic Mg glasses. Thus, the mechanical properties of the Mg57Cu31-Y6.6Nd5.4 BMG, in particular the plastic strain achievable in compression, are superior to previous Mg BMGs including the Mg58.5Cu30.5Y11 alloy.

The elastic constants, including $E$, $\mu$, $B$, and $\nu$ obtained from acoustic velocity measurements, density $\rho$ and Debye temperature $\Theta_D$ of the Mg58.5Cu30.5Y11 and Mg57Cu31Y6.6Nd5.4 BMGs are summarized in Table 3, together with data for other Mg-based BMGs from the literature for comparison. It can be seen that the $\nu$ value of Mg57Cu31Y6.6Nd5.4 glass is nearly the same as that of Nd-free Mg58.5Cu30.5Y11 glass within experimental accuracy. The $\nu$ value around 0.32 is comparable to the values of Mg65Cu25Gd10 and Mg65Cu25Tb10 glasses [10,17]. It indicates that the $\nu$ value is insensitive to the mutual substitution between RE elements. The $\mu/B$ ratio of Mg57Cu31Y6.6Nd5.4 is about 0.02, slightly larger than that of Mg58.5Cu30.5Y11. Even though there is no obvious difference between the Poisson’s ratios of Mg58.5Cu30.5Y11 and Mg57Cu31Y6.6Nd5.4, the change in plasticity is obvious. It has been demonstrated that $\nu = 0.32$ is the demarcation value that separates two groups of metallic glasses [10]. Those with $\nu > 0.32$ are more or less ductile, while those below tend to be brittle. Our alloys are possibly borderline cases.

In summary, a Mg57Cu31Y6.6Nd5.4 BMG of 14 mm in diameter has been successfully fabricated via conventional Cu-mold casting method. When compared with the GFA of the 9 mm Mg58.5Cu30.5Y11, this is a significant improvement of GFA due to the Nd effects. The new Mg57Cu31Y6.6Nd5.4 BMG exhibits obvious yielding and plastic strain during compressive loading; the ultimate fracture strength and plastic strain to failure reached 1188 ± 32 MPa and 1.2%, respectively. In comparison with Mg58.5Cu30.5Y11, this is a marked change in plasticity, even though their Poisson’s ratios are measured to be almost identical.

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