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# Mg–Cu–Y–Ag bulk metallic glasses with enhanced compressive strength and plasticity

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ABSTRACT

Novel Mg–Cu–Y–Ag bulk metallic glasses (BMGs) were prepared by water cooled copper mold casting. The compressive test shows that, by partial substitution of Mg with Ag, the compressive fracture stress, plastic strain, and Young's modulus of $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMG alloy reach 1330 MPa, ~0.2% and 74.8 GPa, respectively. The compressive strength of this BMG is the highest among those of Mg-based BMGs and crystalline alloys reported to date. Fine vein patterns and dimples are observed on the fracture surface of these BMGs. It is suggested that the improvement in the mechanical properties of Mg–Cu–Y–Ag BMG alloys is mainly attributed to the high moduli and Poisson's ratio of Ag.



## 1. Introduction

Mg-based bulk metallic glasses (BMGs) have many advantages such as low cost, high specific strength and environmental friendship over other BMG systems. In the last decade, a series of Mg–Cu–RE–Ag (RE = Y, Gd) based alloys, *e.g.*, $Mg_{65}Cu_{20}Ag_5Gd_{10}$ [1,2], $Mg_{56}Cu_{29.7}Ag_{3.3}Y_{11}$ [3], $Mg_{54}Cu_{28}Ag_7Y_{11}$ [3,4], $Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$ [4], $Mg_{65}Cu_{7.5}Ni_{7.5}Ag_5Zn_5Y_5Gd_5$ [5] and $Mg_{65}Cu_{20}Ag_5Gd_{10}$ [6] *etc.*, have been prepared with critical diameter in centimeter scale. Compared the glass forming ability, however, the mechanical properties of these Mg-based BMGs has become one of the most important issues hindering their engineering application. Most of these Mg-based BMG alloys have the strength lower than 1000 MPa and little plasticity. Therefore, it is imperious to seek a liable method to improve the mechanical properties of this kind of Mg-based BMG alloys.

As previously reported [7–9], there is a linear correlation between the Young's modulus, *E*, and the fracture strength in BMG alloys. The ratio of $G/B$ (shear modulus, *G*, bulk modulus, *B*) and Poisson's ratio, $\nu$, have correlations with the toughness of some BMG materials. Therefore, one can get a material with higher strength and larger plasticity by increasing the values of *E* and $\nu$ of a BMG alloy. It is known that, for most of BMG alloys, the elastic constants of BMGs can be calculated as the formula of $M^{-1} = \sum f_i M_i^{-1}(1/2)$ (where *M* is an elastic constant and $f_i$ the atomic percentage of a component) [10]. By employing this routine, we have investigated the effect of Be, Nb and rare earth elements on the mechanical properties of Mg-based BMG alloys, and found that the addition of proper elements with larger *E* and $\nu$ can obviously increase the fracture strength and toughness of BMG alloys [11–14]. Considering that Ag has larger *E* and $\nu$ and lower $G/B$ than Mg [15], the mechanical properties of Mg-based BMGs can be expected to be improved by the substitution of Mg with Ag. In this paper, we investigate the effect of Ag on the mechanical properties of Mg–Cu–Y glassy alloys. It is found that high fracture strength and plasticity can be obtained in Mg–Cu–Y–Ag metallic glasses by partial substitution of Mg with Ag.

## 2. Experimental method

The alloy compositions investigated in the present work are $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) (in atomic percentage). The raw materials for these bulk metallic glasses are elemental pieces with the purity higher than 99.9%. Cu–Y intermediate alloys were firstly prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper mould. These intermediate alloys were then melted together with Mg and Ag pieces by induction melting under argon atmosphere. Then the master alloys were remelted in a quartz tube using induction melting. Rods with a diameter of 2 or 3 mm for $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) and $Mg_{65}Cu_{25}Y_{10}$, respectively, were finally injected into a water-cooled copper mold.

The structural characteristics of the as-cast rods were analyzed by Rigaku D/max-3B X-ray diffractionmeter (XRD) using a

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monochromatic Cu $K_\alpha$ radiation and ZEISS SUPRA55 scanning electric microscopy (SEM). Thermal stabilities associated with glass transition temperature, crystallization temperature and supercooled liquid region were examined by STA449C type of differential scanning calorimeter (DSC). To investigate the thermal stability of these BMGs, the DSC tests were performed on $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMGs with the heating rates of 5, 10, 20, 30 and 40 K/min, respectively. Uniaxial compression tests at room temperature were performed on a CMT4305 universal testing machine at a strain rate of $1 \times 10^{-4}\,s^{-1}$. The size of compression test samples is 4 and 6 mm in height for $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) and $Mg_{65}Cu_{25}Y_{10}$, respectively. By using SEM, the fracture surfaces of these metallic glasses were examined.

## 3. Results and discussion

The XRD patterns of as-cast $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) alloys rods with different diameters are shown in Fig. 1. The XRD patterns reveal that there are only broad peaks and no diffraction peaks corresponding to crystalline phases in these samples except for the peaks of $Y_2O_3$, indicating the formation of glassy phase within XRD resolution.

To further examine the microstructure of these alloys, we performed the scanning electronic microscopic examination. Fig. 2 shows the SEM backscattered electron images of $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) alloys with a diameter of 2 mm. It is shown that there is no other phase in the micrograph except for a few white particles. To identify these white particles, we conducted electron diffraction scanning (EDS) analysis. It is determined that the white phase contains 42.42% O and 57.58% Y for $Mg_{60}Cu_{25}Y_{10}Ag_5$ and 38.68% O and 61.32% Y for $Mg_{58}Cu_{25}Y_{10}Ag_7$ alloy. From the contents of O and Y in the white phase and the X-ray diffraction curves as shown in Fig. 1, it can be deduced that this white phase is $Y_2O_3$.

The DSC traces of Mg–Cu–Y–Ag BMG alloys are shown in Fig. 3. It is shown that these specimens exhibit obvious glass transition followed by a large supercooled liquid region, $\Delta T_X$ (=$T_x - T_g$), and exothermic reaction corresponding to the crystallization. The distinct glass transition observed in these DSC traces further proves the glassy nature of these metallic glasses. It is also seen that glass transition temperature, $T_g$, and crystallization temperature, $T_x$, for $Mg_{58}Cu_{25}Y_{10}Ag_7$ are higher than those of $Mg_{65}Cu_{25}Y_{10}$ alloy. When heated at 20 K/min, the $T_g$ and $T_x$ are increased from 418 K and 473 K for $Mg_{65}Cu_{25}Y_{10}$ to 430 K and 482 K for $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMG alloy, respectively. It has been verified that the Young's modulus

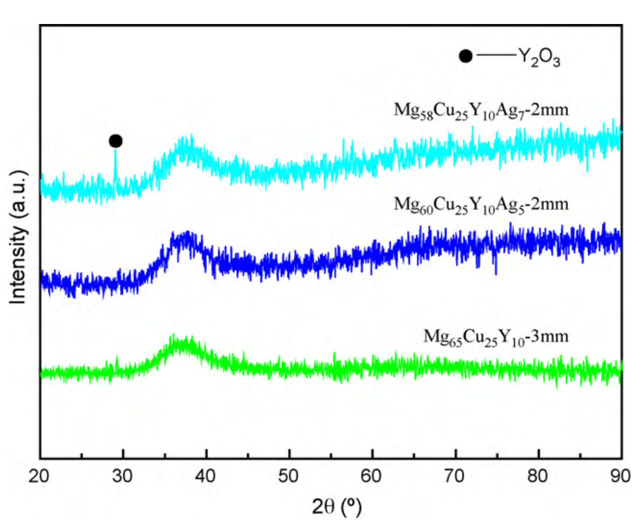


**Fig. 1.** XRD patterns of as-cast $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) alloys.

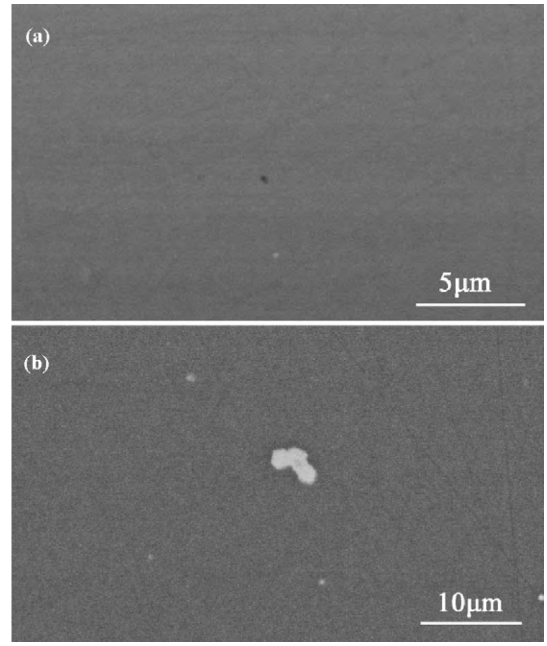


**Fig. 2.** SEM backscattered electron images of (a) $Mg_{60}Cu_{25}Y_{10}Ag_5$ alloy; (b) $Mg_{58}Cu_{25}Y_{10}Ag_7$ alloys with 2 mm in diameter.

has a good linear relation with its glass transition temperature in the ratio: $|T_g| \propto |2.5E|$ [16,17]. Therefore, the high elastic properties or facture strength may be expected for the Ag bearing Mg-based BMG alloys. As for thermal stability, the $\Delta T_X$ of $Mg_{58}Cu_{25}Y_{10}Ag_7$ alloy is 52 K at the heating rate of 20 K/min, little lower than that of $Mg_{65}Cu_{25}Y_{10}$. This result is same as that reported by Madge et al. [18], who found that the addition of Ag to Mg–Cu–Y decreases the thermal stability of the Mg–Cu–Y alloy.

We further performed the kinetic analyses of the glass transition and crystallization of these BMG alloys by using Kissinger's equation [19]

$$\ln\left(\frac{T^2}{\phi}\right) = \ln\left(\frac{E_a}{k_B K_0}\right) + \frac{E_a}{k_B T} \qquad (1)$$

where $\phi$ is the heating rate, $k_B$ is the Boltzman constant, $K_0$ is the frequency factor, and $E_a$ is the apparent activation energy. The activation energy for glass transition ($E_g$) and crystallization ($E_x$) can be obtained for these BMGs. As shown in Fig. 3(c) and (d), the calculated activation energy for glass transition and crystallization of these Mg–Cu–Y and BMGs. It is seen that with the addition of Ag into Mg–Cu–Y BMGs, both glass transition activation energy and crystallization activation energy are decreased, indicating that it is easier for glass transition and crystallization to take place.

In Mg–Cu–Y–Ag system, Ag has largest Poisson's ratio among all the components, and larger bulk modulus and Young's modulus than Mg and Y. Therefore, the elastic moduli and the Poisson's ratio of Mg–Cu–Y bulk metallic alloys are expected to be improved when Mg is partially substituted by Ag. Fig. 4 shows the compressive stress–strain curves for as-cast Mg–Cu–Y and Mg–Cu–Y–Ag BMG alloys. It is shown that with the increase of Ag, the fracture strength and plasticity are greatly increased. The fracture stress of $Mg_{65}Cu_{25}Y_{10}$ BMG is 729 MPa. And the fracture stresses for $Mg_{60}Cu_{25}Y_{10}Ag_5$ and $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMGs reach 990 and 1330 MPa, respectively. To compare the fracture strength with that of other Mg-based metallic glasses, we list the mechanical properties of some Mg-based metallic glasses in Table 1. It is seen that the $Mg_{58}Cu_{25}Y_{10}Ag_7$ metallic glass exhibits largest fracture strength among the Mg-based metallic glasses reported to date. It is also noted from Fig. 4 that $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) BMG alloys

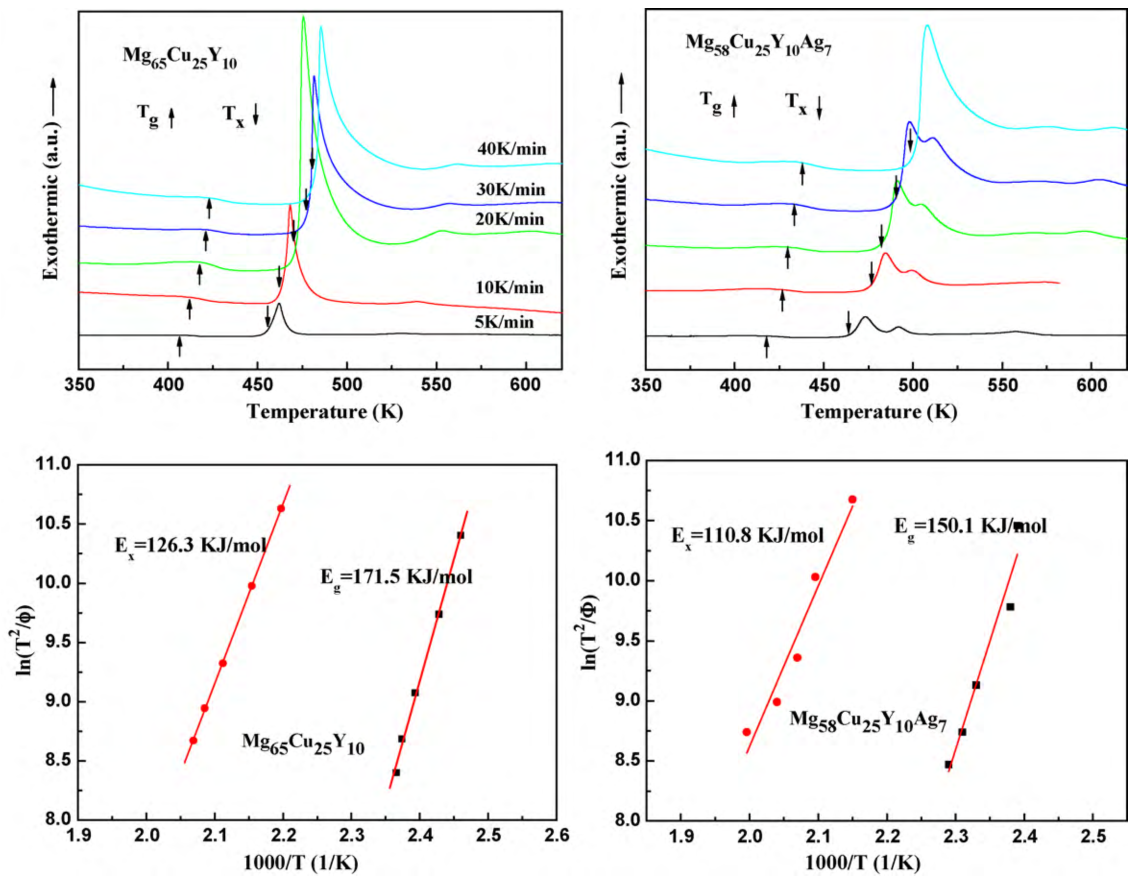


**Fig. 3.** DSC traces of and Kissinger plots of $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMG alloys measured at the heating rate of 5, 10, 20, 30 and 40 K/min.

exhibit certain plastic deformation. For $Mg_{58}Cu_{25}Y_{10}Ag_7$, the plastic strain reaches 0.18%. From Fig. 4, we fit the stress–strain curves linearly to obtain Young's modulus. It is obtained that the elastic moduli are 53.4, 59.7 and 74.8 GPa, respectively, for $Mg_{65}Cu_{25}Y_{10}$, $Mg_{60}Cu_{25}Y_{10}Ag_5$ and $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMGs.

Fig. 5 shows the SEM images of the fracture surface of the compressive specimens. It can be seen that the dominate morphology of $Mg_{65}Cu_{25}Y_{10}$ (Fig. 5a) is a typical featureless mirror surface, which exhibits the "brittle" nature of Mg-based bulk metallic glass. By increasing the resolution to nanometer scale (Fig. 5b), some periodic corrugations and dimple-like structure can be found. By the addition of Ag to $Mg_{65}Cu_{25}Y_{10}$, the fracture surface morphologies are obviously changed. Even in low magnification, the fracture morphologies are not featureless mirror surfaces, but exhibit a hackle appearance (Fig. 5c). Dimples and vein and river patterns can be easily observed. The difference between the morphologies of Mg–Cu–Y–Ag BMGs with 5% and 7% Ag is that the vein and river patterns are much finer for the BMG with higher Ag. This kind of fracture morphology indicates that the addition of Ag makes the Mg-based metallic glass tougher, and the deformation in Mg-based bulk metallic glass proceeds through the local strain softening.

As shown in previously sections, the addition of Ag into Mg-based BMGs indeed results in the improvement in fracture strength and plasticity. Although there are many ways to account for the reason for this phenomenon, one of the most possible mechanism is that the high elastic moduli and high Poisson's ratio of the components are beneficial to the strengthening and toughening of BMG

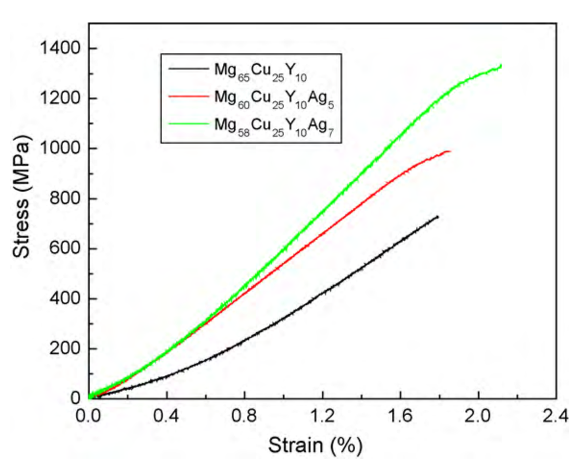


**Fig. 4.** Compressive stress-strain curves of as-cast $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) BMG alloys.

**Table 1**
Compressive properties of Mg-based BMGs including data from the literature ($D_f$ is the size of sample).

| Alloys | $\sigma_f$ (MPa) | $\varepsilon_p$ (%) | $D_f$ (mm) | Reference |
|---|---|---|---|---|
| $Mg_{65}Cu_{25}Y_{10}$ | 729 | 0 | 3 | This work |
| $Mg_{60}Cu_{25}Y_{10}Ag_5$ | 990 | 0.11 | 2 | This work |
| $Mg_{58}Cu_{25}Y_{10}Ag_7$ | 1330 | 0.18 | 2 | This work |
| $Mg_{65}Cu_{20}Ag_5Gd_{10}$ | 909 | 0.5 | 1 | [2] |
| $Mg_{65}Cu_{25}Gd_3Y_7$ | 973 | 0.35 | 1 | [5] |
| $Mg_{65}Cu_{7.5}Ni_{7.5}Ag_5Zn_5Gd_5Y_5$ | 928 | 0.57 | 1 | [5] |
| $Mg_{58.5}Cu_{30.5}Y_{11}$ | 1022 | 0.35 | 1 | [20] |
| $Mg_{57}Cu_{31}Y_{6.6}Nd_{5.4}$ | 1188 | 1.2 | 1 | [20] |
| $Mg_{65}Cu_{20}Ni_5Gd_{10}$ | 904 | 0.15 | 2 | [21] |
| $Mg_{70}Cu_{15}Ni_5Gd_{10}$ | 854 | 0.1 | 2 | [21] |
| $Mg_{65}Cu_{15}Ag_5Pd_5Y_{10}$ | 770 | 0 | 5 | [22] |
| $Mg_{75}Cu_{15}Gd_{10}$ | 743 | 0 | 2 | [23] |
| $Mg_{65}Cu_{20}Zn_5Y_{10}$ | 760–810 | 0 | | [24] |

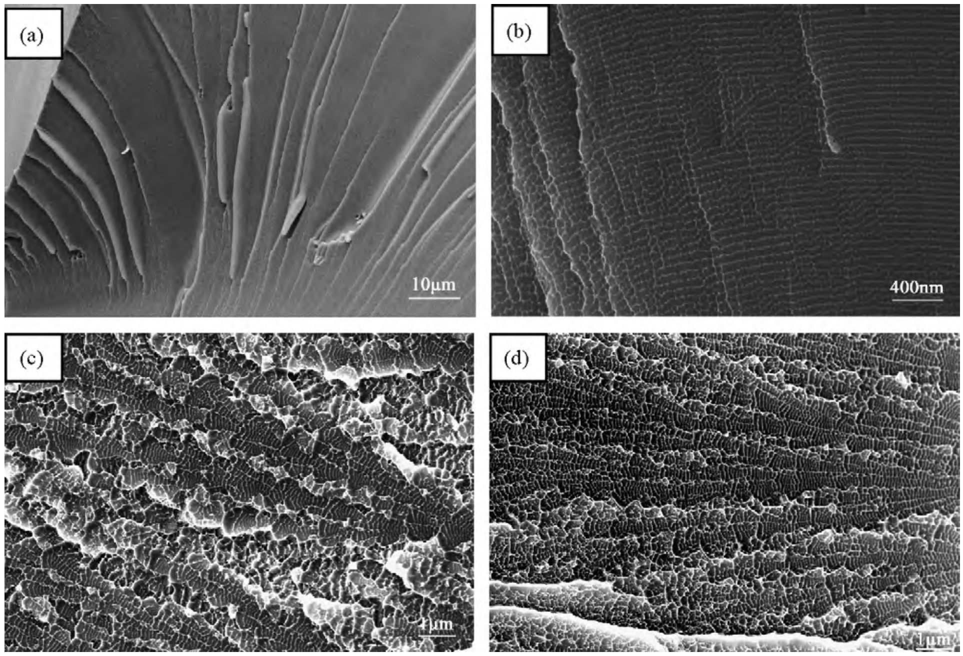


**Fig. 5.** SEM images of the fracture surfaces of (a) and (b) $Mg_{65}Cu_{25}Y_{10}$, (c) $Mg_{60}Cu_{25}Y_{10}Ag_5$ and (d) $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMG alloys.

materials. This deduction has been proved in many metallic glass systems. In this work, the enhancement in the mechanical properties of Mg base BMG alloys is attributed to the high values of Young's modulus and Poisson's ratio of Ag.

## 4. Conclusions

By partial substitution of Mg with Ag, $Mg_{65-X}Cu_{25}Y_{10}Ag_X$ ($X$ = 5, 7) BMGs have been prepared by copper mold casting. Compared with $Mg_{65}Cu_{25}Y_{10}$ ternary system, the addition of Ag makes the thermal stability of Mg–Cu–Y–Ag BMGs decreased.Significant improvement in the mechanical properties of Mg–Cu–Y–Ag BMGs has been achieved. Especially, the fracture stress of $Mg_{58}Cu_{25}Y_{10}Ag_7$ BMG alloy reaches 1330 MPa, which is the highest strength among those of Mg-based BMGs reported to date. The plastic strain of this BMG alloy is about 0.2%. Fine vein patterns and dimples are observed on the fracture surfaces of these Mg–Cu–Y–Ag BMGs.The strengthening and toughening effect of Mg–Cu–Y–Ag BMGs may be attributed to the higher elastic modulus and Poisson's ratio of Ag. This work provides a liable way to improve the mechanical properties of Mg-based BMGs by composition design.

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