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# High Specific Strength and Improved Ductility of Bulk $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$ Metallic Glass Composites

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The monolithic  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  bulk metallic glass always shows brittle fracture with a plastic strain of near zero even under a compressive load. Improved ductility and enhanced compressive strength were simultaneously achieved at room temperature in  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 0, 2.5, 5$  and  $7.5$  at%) metallic glass composites. The compressive strength ( $\sigma_f$ ) reached 940 MPa, and a plastic strain ( $\varepsilon_p$ ) of about 0.8% was undergone for the bulk metallic glass composite at  $x = 5$ . The glass composites were formed by doping  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  bulk metallic glass with adequate lightweight titanium with a density near that of  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  bulk metallic glass. The composite sustains the features of lightweight and very high specific strength which are the same as those of the Mg-based bulk metallic glass. Thus, the addition of Ti does not cause distinctly harmful influence on the glass-formation ability of the matrix glass. [doi:10.2320/matertrans.MRP2007181]

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## 1. Introduction

In the last decade, great efforts have been devoted to exploring and synthesizing bulk metallic glass (BMG) due to their potential applications and scientific significance. As a result, a large number of multicomponent BMGs have been developed. Among them, Mg-based BMGs have attracted more researching interests due to their high (specific) strength and low cost as nature candidates for new structural materials ever since the first synthesis of a Mg-based BMG in the ternary Mg-Cu-Y system.<sup>1)</sup>

However, Mg-based BMGs show to appear brittle fracture without appreciable plasticity. Lack of plasticity makes them susceptible to catastrophic failure and restricts their widespread application therefore, which is a remaining challenge. The poor ductility of BMGs seems to result from the formation of highly localized shear bands in load-bearing conditions.<sup>2)</sup> Methods focused around solving this problem have been attempted and significant advances have been made. Introducing ductile crystalline phases into the glassy matrix has been considered to be the dominant and effective approach to toughening of brittle BMGs. In this aspect, Zr-based BMGs were investigated at the most while the other BMGs were also less studied. For example, BMG matrix composites have been synthesized in Zr-Ti-Cu-Ni-Be,<sup>3)</sup> Zr-Cu-Ni-Al,<sup>4-6)</sup> Zr-Cu-Pd-Al,<sup>7)</sup> Zr-Ti-Al-Cu-Ni,<sup>8)</sup> Zr-Nb-Al-Cu-Ni,<sup>8-11)</sup> Cu-Ti-Zr-Ni,<sup>8)</sup> Cu-Zr-Ti-Ta,<sup>12)</sup> Cu-Hf-Ti-Ta,<sup>13)</sup> Cu-Zr-Ti-ZrC,<sup>14)</sup> Ti-Cu-Ni-Sn-(Ta, Nb)<sup>15)</sup> and Fe-Co-B-Si-Nb-Cu<sup>16)</sup> systems. The plastic strains of the mentioned BMGs were increased from less than 2% to 5%, 2% to over 34%, 2% to over 14% and 0% to near 1% for Zr-based,<sup>5)</sup> Cu-based,<sup>13)</sup> Ti-based<sup>15)</sup> and Fe-based<sup>16)</sup> BMGs, respectively, by introducing second crystalline phases including ductile metal or refractory ceramic particles into the glassy matrices. The principle of strengthening/ductilizing effects utilizing this method is to introduce stress disturbance near the second phase surrounded by the glassy matrix during the process of loading, which is attributed to the large elastic mismatch between the second phase and glassy matrix. The disturbed

stress field near the second phase can serve as an effective barrier to the direct propagation of the shear bands, which conducts the formation of multiple shear bands.<sup>5-16)</sup> Very recently, super plasticity with a true strain of more than 1.6 was found in Zr-Cu-Ni-Al BMGs, indicating that the plastic BMGs are composed of hard regions surrounded by soft regions.<sup>17)</sup> Following the same way, limited work for reinforcing the Mg-based BMGs has been carried out. The BMG matrix composites have been prepared in Mg-Cu-Ni-Zn-Ag-Y system doped with Fe or TiB<sub>2</sub>,<sup>18,19)</sup> Mg-Cu-Gd system doped with Fe,<sup>20)</sup> and Mg-Cu-Y-Zn system.<sup>21)</sup> The similar of strengthening/ductilizing effects have been reported. However, there exist some limitations in the present method for Mg-based BMGs. The later transition metals have much higher densities (for example, 7.86 and 7.14 g/cm<sup>3</sup> for Fe and Zn, respectively) as compared to the Mg-based BMGs (for example, 3.69 g/cm<sup>3</sup> for  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  BMG). Such a large discrepancy in the densities of constituent phases increases the holistic densities of alloys, which weakens the characteristics of lightweight of the Mg-based BMGs, and usually causes a gravitational segregation of the heavier refractory metal (or the lighter ceramic phase) and BMG elements, resulting in inhomogeneous alloying. Furthermore, the wettability along the interface between refractory ceramic particles and matrix alloy is usually not ideal.

The objective of the present work is to synthesize Mg-based BMG composites with improved ductility and enhanced compressive strength. Specifically, the preparation of the composites was carried out based on a BMG former  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  BMG matrix with the addition of Ti acting as ductile phase. The choice of Ti as the ductile reinforcement agent originates from the following design strategy. The early transition metal Ti holds the density near that of the BMG alloy, which would avoid an increase in the holistic densities of alloys and a gravitational segregation of the heavier refractory metal in melting process. Furthermore, Ti has a positive heat of mixing with the majority element Mg and with rare earth element Gd. Consequently, Ti can be dissolved in the high-temperature liquid by melting Mg and

Cu-Ti (or Cu-Ti-Gd) pre-alloys. Upon cooling it would tend to uniformly segregate together, leaving behind a melt with a composition essentially identical to the original Mg-based BMG former. Thereby, Ti has little chance of reacting with the other elements to form brittle intermetallics, or of changing the composition of the base Mg alloy to interfere with its high glass-formation ability (GFA). According to any reports up to date, Ti has not been used as reinforcement agent for Mg-based BMG. Herein, the uniform distribution of ductile Ti is expected to improve the plasticity and ductility of the alloy. In the paper, the GFA, phase structure and mechanical properties of the bulk metallic glass composites were investigated.

## 2. Experimental Procedure

Elements with purity higher than 99.9% were used as starting materials. Cu-Gd and Cu-Gd-Ti ingots as an intermediate alloy were first prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The end master alloys with desired composition were then obtained by induction melting the intermediate alloy with Mg under an inert atmosphere. The nominal compositions are  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 0, 2.5, 5$  and  $7.5$  at%). The rod samples with diameters of 1–4 mm were fabricated by induction remelting the master alloy in a quartz tube and injecting it into the copper mold in a purified inert gas atmosphere. The casting temperature is controlled in the vicinity of 200 K above melting point of the alloys.

The cross-sectional surfaces of the as-cast rods were examined by X-ray diffraction (XRD) in a diffractometer (Rigaku RAD-8) with Cu  $K\alpha$  radiation. The thermal stability of the monolithic glass and Ti-containing composites was investigated using a differential scanning calorimeter (DSC) (Seiko SII DSC6300) under flowing a purified argon gas atmosphere employing a heating rate of 0.67 K/s. The as-cast rods were also examined in a scanning electron microscope (SEM) (Hitachi S-4800) with energy dispersive x-ray spectroscopy (EDXS) analysis. Compression tests for four or five samples of each alloy were conducted with an Instron testing machine using a strain rate of  $6 \times 10^{-4} \text{ s}^{-1}$  at room-temperature. The strain was determined from the platen displacement after correction for the machine compliance.

## 3. Results and Discussion

Figure 1 shows XRD patterns taken from the cross-sectional surface of the as-cast rods with the composition of  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 0, 2.5, 5$  and  $7.5$  at%). For the Ti-free alloy as shown in Fig. 1(a), only a broad peak in the vicinity of  $2\theta = 35^\circ$  is observed, indicating the formation of a single-phase BMG. For the Ti-containing alloys as shown in Fig. 1(b), crystalline peaks appear on the broad glassy peak and become sharper with an increase of Ti content, of which the location is in agreement with that of crystalline Ti phase, implying that a glassy phase matrix coexists with a Ti crystalline phase, *i.e.*, the formation of metallic glass composites.

The SEM micrograph of a polished cross section of the as-cast composite at  $x = 5$  is shown in Fig. 2 as a typical

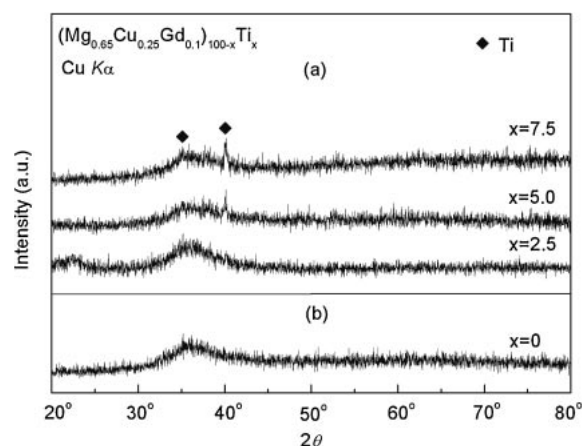


Fig. 1 XRD patterns taken from the cross-sectional surface of the as-cast  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 0, 2.5, 5$  and  $7.5$  at%) rod samples with a 4 mm diameter.

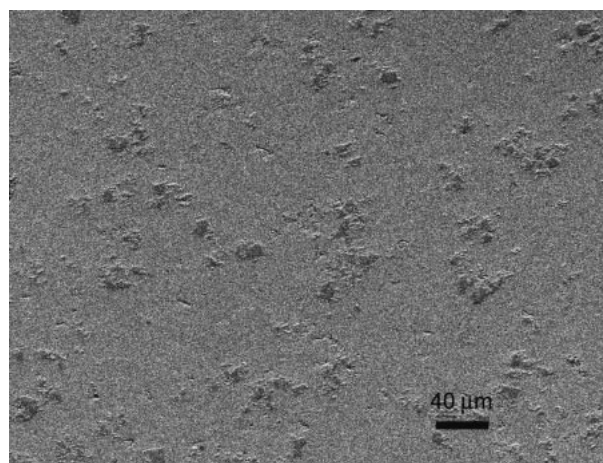


Fig. 2 SEM backscattered electron image of an  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  metallic glass composite.

example. It can be observed that particles with an averaged size of less than about  $40 \mu\text{m}$  are uniformly dispersed throughout in the glassy matrix. The average chemical composition of the crystalline particles was measured to be over 98% using EDXS analysis, supporting the XRD results of Ti crystalline phase, while the matrix is close to the nominal composition of the monolithic  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  BMG. Figure 3 is a composition mapping on the as-cast rod specimen by using EDXS attached on SEM. It is evident that the precipitated grains are a Ti crystalline phase.

The DSC traces measured at a heating rate of 0.67 K/s are shown in Fig. 4. In each of all the traces, an endothermic signal associated with glass transition and one main exothermic reaction caused by crystallization are obviously observed. From the traces, it can be noticed that the Ti-containing composites exhibit nearly the same thermal properties as those of the monolithic glass, suggesting that the matrix composition does not change with Ti addition. For the Ti-containing alloys the crystallization temperature ( $T_x$ ) slightly shift toward low temperature within 7 K, which is promoted by *in-situ* Ti particles herein as the sites of heterogeneous nucleation. The different degree of shifts in  $T_x$

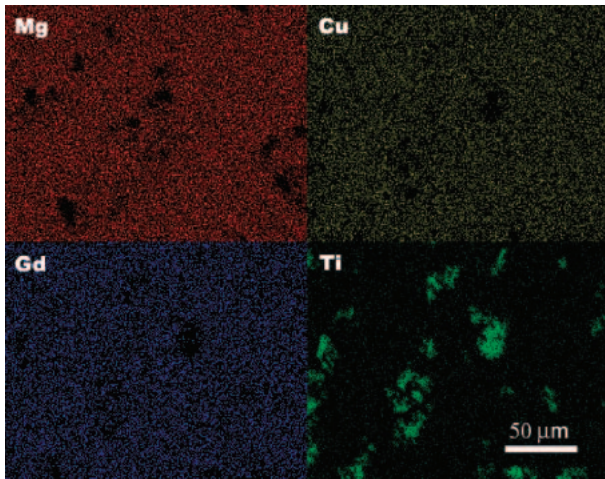


Fig. 3 Composition mapping on as-cast rod specimen by using EDXS attached on SEM for the  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  metallic glass composite.

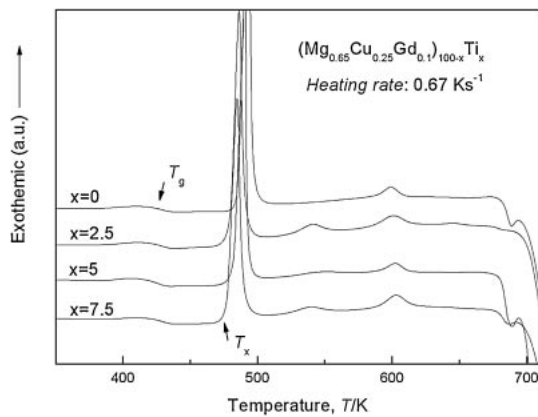


Fig. 4 DSC traces of  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 0, 2.5, 5$  and  $7.5$  at%) BMG and its composites.

is caused by the difference in the volume fractions of Ti particles. However, considering all the thermal properties of the present alloys, there is no appreciable chemical reaction between the Ti particles and the matrix glass leading to the change of the glass-forming ability of the matrix alloy. This is similar with the case of adding  $\text{TiB}_2$  into  $\text{Mg}_{65}\text{Cu}_{7.5}\text{Ni}_{7.5}\text{Zn}_5\text{Ag}_5\text{Y}_{10}$ ,<sup>19)</sup> but different from that of adding  $\text{SiC}$  into  $\text{Zr}_{57}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ <sup>10)</sup> or  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$ <sup>22)</sup> BMGs, where considerable silicon or carbon atoms were dissolved into the matrix.

Figure 5 shows the compressive stress-strain curves for the  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  monolithic glass and the BMG composites. The BMG sample exhibited only a linear elastic behavior with the ultimate fracture strength  $\sigma_f$  of 823 MPa. The monolithic glass failed to macroscopically yield and plastically deform subsequently, implying the typical nature of brittle glass. SEM micrographs of the fractured surface showed only a typical cleavage feature of brittle glasses. In contrast, the BMG composites appeared apparent yielding and plastic deformation. It was found that both ductility and compressive strength of the composites were enhanced. The composite at  $x = 5$  was the best for improving comprehensive mechanical properties. The ultimate fracture strength  $\sigma_f$

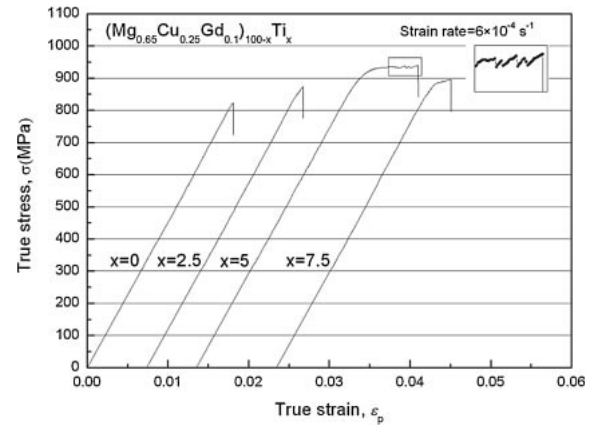


Fig. 5 Compressive stress-strain results for the  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  monolithic BMG and the  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  ( $x = 2.5, 5$  and  $7.5$  at%) BMG composites.

and plastic strain  $\varepsilon_p$  to failure of the  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  metallic glass composite reached about 940 MPa and 0.8%, respectively. The compressive strength increased by up to a factor of 1.2, compared to the monolithic glass. The stress-strain curve of the composite at  $x = 5$  exhibits a serrated characteristic as shown in its amplified section in the inset of Fig. 5, which is attributed to the formation of shear bands. The specific strength of  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  composite, defined by the ratio of fracture strength  $\sigma_f$  to density  $\rho$ , is about  $2.51 \times 10^5 \text{ N m for kg}^{-1}$  achieving an increase of 4.2 percent compared to the monolithic glass, where the values of  $\rho$  measured in this experiments are 3.69 and 3.75  $\text{g/cm}^3$ , respectively for the monolithic glass and composite. Premature failure of the monolithic Mg-based glass before reaching its elastic limit is regarded to be responsible for the lower strength.<sup>19)</sup> Unexpected premature failure usually develops from brittle fracture triggered by minor flaws preexisting in the sample. Such failure in the elastic regime can be suppressed in the case of introducing the uniformly distributed ductile Ti reinforcement, which blunts and stops small cracks and hence imparts ductility to the composite. Besides, enhancing of strength after adding Ti is also reasonably related to the large elastic mismatch between Ti phase and the BMG.<sup>18)</sup> Specifically, the elastic modulus of Ti is over two times higher than that of the Mg-based glass. The modulus of present BMG in our investigation is about 51 GPa while the composites exhibit almost the same modulus. The large elastic mismatch between the second phase and glassy matrix introduces stress disturbance near the second phase surrounded by the glassy matrix during the process of loading, serving as an effective barrier to the directive propagation of the shear bands, which also constitutes the principle of ductilizing effects using this method.

#### 4. Conclusions

In summary, we have successfully synthesized BMG composites in  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{100-x}\text{Ti}_x$  alloys. The structure effects on GFA and mechanical properties of the studied Mg-based BMG composite were investigated and the following results were obtained.

- (1) The BMG composites based on a glassy phase matrix coexisting with uniformly distributed ductile Ti phase particles with an averaged size of less than about 40  $\mu\text{m}$  can be readily produced using copper mold casting.
- (2) The glass composites with adequate lightweight Ti exhibited nearly identical thermal properties as the monolithic glass, which implies that the matrix in the composites is nearly the same as the monolithic glass and that the addition of Ti has no significantly adverse effect on the GFA of the matrix glass.
- (3) Compared to the monolithic BMG, the compressive strength  $\sigma_f$  of  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  composite increased by up to a factor of 1.2. The present composites have exhibited macroscopical yielding and apparent plasticity. Especially, the  $(\text{Mg}_{0.65}\text{Cu}_{0.25}\text{Gd}_{0.1})_{95}\text{Ti}_5$  BMG composite undergoes a plastic strain  $\varepsilon_p$  of about 0.8% before the ultimate fracture.
- (4) The design strategy is suggestive of developing many other Mg-based BMG composites with the aim of strengthening/ductilizing brittle Mg-based BMGs.

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