Mg-based bulk metallic glass composites with plasticity and high strength

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Composite alloys of \( \text{Mg}_{x} \text{Cu}_{y} \text{Ni}_{z} \text{Zn}_{t} \text{Ag}_{u} \text{Y}_{v} \text{Fe}_{w} \) have been produced through copper mold casting, based on a good bulk metallic glass former. Upon cooling the melt, an \( \alpha \)-Fe solid solution precipitates uniformly with sizes in the 1–10 \( \mu \text{m} \) range while the remaining melt undergoes a glass transition. The \textit{in situ} composite has a compressive strength as high as \( \sim 1 \text{ GPa} \), a factor of 1.6 higher than the single-phase metallic glass. In contrast to all the previous Mg-based monolithic glasses that always fail in the elastic regime, a plastic strain to failure of the order of 1% was obtained for the Fe-toughened composite. © 2003 American Institute of Physics. [DOI: 10.1063/1.1616192]

The extensive research worldwide on bulk metallic glasses (BMG) is motivated by their potential applications as new high-strength structural materials. However, all BMGs face a challenging problem which they fail by the formation of highly localized shear bands, which lead to catastrophic failure without much macroscopic plasticity. To solve this problem, BMG matrix composites with ductile metal or refractory ceramic particles as reinforcements were developed to hinder the propagation of runaway shear bands and encourage the formation of multiple shear bands. Recently, a more convenient route has been established that forms the composites \textit{in situ} during processing. Such composites exhibit enhanced compressive strains and occasionally even tensile strains to failure and a significantly improved impact toughness compared with monolithic BMGs. However, such composites are achieved mostly in the Zr-based BMGs. To our knowledge, \textit{in situ} composites containing ductile phase have never been prepared in any Mg-based BMG-forming alloy. Mg-based BMGs have never been prepared in any Mg-based BMG-forming alloy. Mg-based BMGs have never been prepared in any Mg-based BMG-forming alloy.

The choice of Fe as the ductile reinforcement agent is based on the following design strategy. Fe has a positive heat of mixing with the majority element, Mg, as well as with several other alloying elements present (Ag, Cu, Zn). Consequently, while Fe can be dissolved in the high-temperature liquid, it would segregate together upon cooling, and subsequently solidify in the form of dendrites or particles, in a uniform fashion. This leaves behind a melt with a composition essentially identical to the original Mg-based BMG former. As such, Fe 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 good glass forming ability. The uniform distribution of ductile Fe is expected to improve the plasticity and toughness of the alloy.

Elemental pieces (>99.9% purity) were used as starting materials. Cu–Ni–Ag–Y or Cu–Ni–Ag–Y–Fe ingots as an intermediate alloy were prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper crucible. This alloy was then melted together with Mg and Zn pieces by induction melting under inert atmosphere to obtain master alloys with the desired compositions. The compositions are designed based on a good BMG former, Mg–Cu–Ni–Zn–Ag–Y, with the addition of Fe limited to 13% to preserve the low density of the alloy, i.e., \( \text{Mg}_{x} \text{Cu}_{y} \text{Ni}_{z} \text{Zn}_{t} \text{Ag}_{u} \text{Y}_{v} \text{Fe}_{w} \) (\( x = 9 \) and 13, in atomic percentage). The alloy was then remelted in a quartz tube using induction melting and injected in a purified inert atmosphere into the copper mold to obtain the rod samples 4 mm in diameter and 50 mm in length.

The cross-sectional surfaces of the as-cast rods were analyzed using x-ray diffraction (XRD) in a Rigaku D/max 2400 diffractometer with monochromated Cu \( K\alpha \) radiation. The thermal stability of the monolithic glass and Fe-containing composites were investigated using a Perkin-Elmer differential scanning calorimeter (DSC-7) under flowing purified argon. A heating rate of 20 K/min was employed. The as-cast rods were also examined in a Cambridge S360 scanning electron microscope (SEM) with energy dispersive x-ray (EDX) analysis. The compression test samples were 8 mm in height and 4 mm in diameter and the loading surfaces were polished to be parallel to an accuracy of less than 10 \( \mu \text{m} \). Room-temperature compression tests for four or five

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samples of each alloy were carried out using a strain rate of \(1 \times 10^{-4} \text{ s}^{-1}\). The strain was determined from the platen displacement after correction for the machine compliance.

Figure 1 shows XRD patterns taken from the cross-sectional surface of the as-cast \((\text{Mg}_{0.65} \text{Cu}_{0.075} \text{Ni}_{0.075} \text{Zn}_{0.05} \text{Ag}_{0.05} \text{Y}_{0.1})_{100-x} \text{Fe}_x(x=0, 9, \text{and} 13)\) rods with a 4 mm diameter.

FIG. 1. XRD patterns taken from the cross-sectional surface of the as-cast \((\text{Mg}_{0.65} \text{Cu}_{0.075} \text{Ni}_{0.075} \text{Zn}_{0.05} \text{Ag}_{0.05} \text{Y}_{0.1})_{100-x} \text{Fe}_x(x=0, 9, \text{and} 13)\) rods with a 4 mm diameter.

The SEM micrograph of a polished cross section of the as-cast composite at \(x=13\) is shown in Fig. 2 as a typical example. It can be observed that particles with an averaged size of about 5 \(\mu\text{m}\) are dispersed throughout in the glassy matrix. The particles are oblong in shape and do not appear to possess a dendritic structure. The average chemical composition of the crystalline particles was measured using EDX analysis to be Fe$_{95}$Ni$_5$, consistent with the XRD result of an Fe-based bcc solid solution, while the matrix is close to the nominal composition of the Mg$_{65}$Cu$_{7.5}$Ni$_{7.5}$Zn$_5$Ag$_5$Y$_{10}$ monolithic glass.

SEM observation and EDX analysis reveal that after melting the Cu–Ni–Ag–Fe–Y intermediate alloy together with the Mg and Zn elements, some Fe-rich \((\text{Fe}_{94}\text{Ni}_5\text{Cu}_1)\) particles \(1–10 \mu\text{m}\) in diameter, and \((\text{Fe},\text{Ni})_2\text{Y}_6\) and \(\text{Fe}_1\text{Y}_2\) particles \(15 \mu\text{m}\) in size, were present in the master alloy ingot. The particles are uniformly distributed in the ingot. During remelting this ingot for casting, the Fe particles did not melt due to their high melting temperature, but the larger particles of Fe–Y phases did dissolve in the melt. When the melt undergoes cooling in casting, additional smaller Fe particles precipitate out from the melt. The remaining liquid with a composition close to Mg$_{65}$Cu$_{7.5}$Ni$_{7.5}$Zn$_5$Ag$_5$Y$_{10}$ subsequently freezes to the glassy state. This process is quite similar to the case of the Ta particles formed in a ZrNiCuTaAl BMG.

Figure 3 shows the compressive stress–strain curves for the Mg$_{65}$Cu$_{7.5}$Ni$_{7.5}$Zn$_5$Ag$_5$Y$_{10}$ monolithic glass and the in situ composites. The monolithic glass samples exhibit linear elastic behavior with varying ultimate fracture strength \(\sigma_f\) in the range of 500–600 MPa and a corresponding elastic strain limit \(\varepsilon_y\) \(=2.6\%\). These samples failed without any macroscopic yielding and plasticity, as is well known for many amorphous alloys, and especially Mg-based BMGs that shatter into pieces easily during testing (hence little data are available so far for these BMGs). SEM micrographs of the fractured surface showed only cleavage features typical...
of brittle glasses. In contrast, apparent yielding and plastic deformation were observed in the Fe-containing composites. At $x = 9$, the ultimate fracture strength, $\sigma_f$, and plastic strain to failure, $\epsilon_p$, of the composites are $860–930$ MPa and $\sim 0.8\%$ for the samples tested. At $x = 13$, these properties are improved to $950–990$ MPa and $\sim 1.0\%$. Compared to the monolithic glass, the compressive strength increased by up to a factor of 1.6. Moreover, the fracture stress increased with increasing Fe content in the composite. These results indicate that the lower strength of the monolithic Mg-based glasses is a result of its premature failure before reaching its elastic limit, due to brittle fracture triggered by minor sample flaws. Such failure in the elastic regime is suppressed after introducing the uniformly distributed ductile Fe reinforcement, which blunts and stops small cracks and hence imparts toughness to the composite. Yielding and plasticity are then observed as a result. The increase of Fe content ($x$) allows more Fe particles to tackle failure mechanisms such as narrow shear bands and cracks, improving ductility. In addition, some increase in strength with increasing Fe content is also expected because Fe has a higher modulus than the other alloying elements. The more Fe introduced, the higher the composite modulus becomes. The yield strength of a material, in turn, usually scales with its shear modulus. Note that the yielding mechanism often onsets when a certain elastic strain is reached. The latter occurs at a higher stress level for a material with a higher modulus.

In summary, we have successfully developed Fe-containing Mg-based bulk metallic glasses. These in situ composites with uniformly distributed ductile $\alpha$-Fe phase particles of 1–10 $\mu$m in size can be produced readily using copper mold casting. The Fe added, and the composite microstructure, have no adverse effect on the glass forming ability of the matrix Mg-based alloy. The reinforcement delayed the catastrophic failure of the BMG, leading to observable yielding and a high compressive strength up to the order of 1 GPa (the highest so far for Mg-based BMGs). More importantly, the very brittle Mg-based BMGs have exhibited usable plasticity. We therefore believe that our findings have implications in the development of lightweight, high-strength BMG-based alloys for load-bearing applications. The BMG composite design scheme outlined above, which takes advantage of the immiscibility of the components, can also be applied to many other reinforcing metals in a variety of BMG systems.

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