Low beryllium content Zr-based bulk metallic glass composite with plasticity and work hardenable

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A modified Zr-based bulk metallic glass matrix composite Zr\textsubscript{47.67}Cu\textsubscript{40}Ti\textsubscript{3.66}Ni\textsubscript{2.66}Be\textsubscript{6} has been produced by increasing the contents of elements of Zr and Cu with higher Poisson ratio and reducing the contents of Ti, Ni, and Be elements with lower Poisson ratio based on famous metallic glass former Vitreloy 1. A compressive yielding strength of 1804 MPa, fracture strength of 1938 MPa and 3.5% plastic strain was obtained for obtained metallic glass composite. Also, work-hardening behavior was observed during compressive experiment which was ascribed to the interaction of the \textit{in situ} precipitated CuZr phase and shear bands. \copyright 2014 AIP Publishing LLC.

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I. INTRODUCTION

Bulk metallic glasses (BMGs) are being studied extensively and considered as potential structural materials because of their unique combination of high strength and elastic limit compared to their crystalline counterparts.\textsuperscript{1–4} However, because of their highly localized deformation mechanism, BMGs are typically considered to be brittle materials and are not suitable for structural applications. In 1993, Vitreloy 1, a famous Zr-based metallic glass with nominal composition of Zr\textsubscript{41.25}Ti\textsubscript{13.75}Cu\textsubscript{12.5}Ni\textsubscript{10}Be\textsubscript{22.5} (in atomic percent) was discovered by Johnson’s Group at Caltech.\textsuperscript{5} It is well known that Vitreloy 1 has a higher glass forming ability (GFA) of 25 mm, but there is still no apparent micro plastic deformation even under compressive condition. In order to improve the ductility of Zr-based BMGs, many methods have been tried, such as \textit{ex-situ} and \textit{in-situ} soft crystalline inclusions as second phase to BMGs\textsuperscript{5–8} in order to form metallic glass composites. For example, Johnson and his coworkers\textsuperscript{7,8} developed an \textit{in situ} fine dendrite-reinforced BMG matrix composite which exhibits about 7% compression plasticity.

Unfortunately, most of these BMG composites exhibit work softening behavior under compressive and/or tensile testing. For work-softening materials, the peak of stress-strain curve or the maximum stress is usually defined as failure. To solve this problem, it is necessary to fabricate metallic glass composites which have work-hardening properties to impede the propagation of shear bands of monolithic metallic glasses. For crystal materials such as steel, transformation induces plasticity (TRIP) is commonly applied when the retained austenite transforms to martensite during plastic deformation.\textsuperscript{9} In the light of TRIP idea, stress-induced martensitic transformations in CuZrAl-Ta/Co bulk metallic glass forming alloys and/or \textit{in-situ} martensite CuZr Phase reinforced metallic glass matrix composites have been discovered.\textsuperscript{10–14} These composites show distinct work-hardening behavior and large ductility even under tensile condition. Recently, significant plastic deformability and pronounced work hardening have been obtained under both compressive and tensile testing for CuZr-based BMG composites due to the presence of B2 CuZr in the amorphous matrix.\textsuperscript{13,15,16}

Another issue concerned to Zr-based BMG composites is their higher beryllium contents. It is well known that beryllium is not an environment-friendly element, especially for the higher content of 22.5 at. % in Vitreloy 1. Therefore, it is desirable that Beryllium content is close to or lower than that in commonly used commercial beryllium bronze, which will be better for the health of researchers and our cherished earth environment. In this paper, we obtained an Zr-based BMG composite with lower Beryllium content of 6 at. % and large plasticity by proper alloy designing as well as \textit{in-situ} precipitating CuZr phase in Zr-based BMG matrix.

II. EXPERIMENTAL PROCEDURES

Ingots of nominal composition (at. %) Zr\textsubscript{41.25}Ti\textsubscript{13.75}Cu\textsubscript{12.5}Ni\textsubscript{10}Be\textsubscript{22.5} (Vitreloy 1) and Zr\textsubscript{47.67}Ti\textsubscript{3.66}Cu\textsubscript{40}Ni\textsubscript{2.66}Be\textsubscript{6} (ZQ1) were prepared by arc melting a mixture of Zr, Cu, Ti, Ni, and Be with purities better than 99.9% (wt. %) under a Ti-gettered argon atmosphere. Alloy ingots were melted several times to ensure compositional homogeneity. After melting, the liquid alloy was sucked into a cylindrical copper mold with a diameter of 6 mm or 2 mm and a length of about 70 mm. The microstructures of the as-cast samples and fracture surfaces of the samples were investigated in a FEI Quanta 250 FEG scanning electron microscope (SEM). The cross-sectional surface of the as-cast rods were analyzed using x-ray diffraction (XRD) in a Rigaku D/max 2400 diffractometer with monochromated Cu Ka radiation. Thermal behavior was examined by differential scanning calorimetry (DSC).
calorimetry (DSC) (Netzsch 404C, Germany, and alumina crucible, with a constant heating rate of 20 K/min). The compressive sample was 2 mm in diameter (as-cast), and the height is about 4 mm. Mechanical properties were measured on material testing system (Instron 5582, USA) at a constant strain rate of $\frac{1}{10^5}$ s$^{-1}$.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns taken from the cross-sectional surface of as-cast rods with 6-mm diameters for Vitreloy 1 and with 6-mm and 2-mm diameters for the ZQ1 alloy. It is seen that the rod with a diameter of 6 mm for Vitreloy 1 exhibits a fully amorphous feature. And no other phases are detected within the sensitivity limits of x-ray diffraction. While for the 6-mm diameter rod of ZQ1, a glassy matrix coexists with several crystalline intermetallic phases, including B2 CuZr and B19' CuZr. For the 2-mm diameter of ZQ1 composite, there is only B2 CuZr peaks imposed on a broad amorphous diffraction peaks.

Figure 2 shows the DSC scans of 6 mm for Vitreloy 1 fully glassy rod and of 2 mm rod for ZQ1 BMG composite, with a heating rate of 20 K/min. In all cases, a sharp exothermic peak caused by crystallization is observed, with a clear endothermic event associated with the glass transition. The onset temperature of glass transition $T_g$, onset temperature of the first crystallization event $T_{x1}$, the supercooled liquid region $\Delta T_x$, defined as $T_{x1}-T_g$, and heat of crystallization $\Delta H_x$ for these two alloys are determined, as listed in Table I. It was noticed that Vitreloy 1 has a higher $T_{rg}$ value than that of ZQ1 which shows a better glass forming ability. However, ZQ1 has a higher onset crystallization temperature $T_x$ and glass transition temperature $T_g$ which indicates a higher resistance to crystallization and higher thermal stability.

The SEM image of a polished cross section of the as-cast composite of ZQ1 with a diameter of 2 mm is shown in Fig. 3. It can be seen that the precipitated phase with an average size of about 0.5 μm are dispersed throughout in the glassy matrix. The precipitated phase has a spherical shape and does not seem to possess a dendrite structure. The average chemical composition of precipitated phase was measured using EDX (Energy-dispersive X-ray spectroscopy) analysis (not shown here) and was reduced to be Cu$_{50}$Zr$_{50}$.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$T_g$ (K)</th>
<th>$T_{x1}$ (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>$T_{rg}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitreloy 1</td>
<td>616</td>
<td>688</td>
<td>72</td>
<td>5.05</td>
<td>924</td>
<td>1003</td>
<td>0.614</td>
</tr>
<tr>
<td>ZQ1</td>
<td>657</td>
<td>717</td>
<td>60</td>
<td>5.53</td>
<td>995</td>
<td>1166</td>
<td>0.563</td>
</tr>
</tbody>
</table>

FIG. 1. XRD patterns taken from the cross-sectional surface of as-cast rods with 6-mm diameters for Vitreloy 1 and with 6-mm and 2-mm diameters for the ZQ1 alloy.

FIG. 2. DSC scans of the Vitreloy 1 glassy rod with the 6-mm diameters and ZQ1 composite with the 2-mm diameter (heating rate of 20 K/min).

FIG. 3. SEM image of a polished cross-sectional surface of the as-cast composite of ZQ1 alloy with a diameter of 2 mm.
Figure 4(a) shows the engineering compressive stress-strain curves for Vitreloy 1 and ZQ1 alloys with a diameter of 2 mm rods loaded to failure. The curves are shifted relative to each other for clarity.

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The monolithic glass of Vitreloy 1 exhibits linear elastic behavior and about 0.5% plastic strain before fracture and ultimate strength is about 2010 MPa. In contrast, apparent yielding and plastic deformation were observed in the CuZr-containing composites. For ZQ1, the ultimate fracture strength is 1938 MPa and plastic strain is about 3.5%. It is worth noting that CuZr-containing composites have work-hardening behavior after yielding, as the true stress-strain curve shown in Fig. 4(b). Compared to the monolithic glass, the compressive strength of ZQ1 composite does not lose much strength. Moreover, the plastic strain increased by up to a factor of 7. Also, from the linear region (elastic region) of both alloys, the Young’s modulus values can be obtained, which are 100 GPa and 88.5 GPa for Vitreloy 1 and ZQ1, respectively.

Additionally, Fig. 5(a) shows the side surface of Vitreloy 1. For the fractured sample, the angle between the fracture surface (shear plane) and the compressive loading axis was about 41°. And only a few primary shear bands were formed, as shown in Fig. 5(b). For ZQ1 composite, on its side surfaces, it can be seen that there are multiple shear bands formed during deformation, as shown in Fig. 5(c). Especially, due to the intersection of primary and secondary shear bands, much more shear bands are formed (see white circle in Fig. 5(d)). Other reasons for the improved plastic strain possibly is ascribed to the interaction between the in situ precipitated CuZr phase and shear bands, and the blocking the propagation and facilitating the formation of the multiple shear bands. This has been certified in the early stage of fabricating of in situ bulk metallic glass composites.17 Another contribution of plastic strain may come from the deformation induced martensite transformation of B2 CuZr into B19' CuZr, which has been proved in Refs. 12 and 13.

Currently, it is not clear about the intrinsic factors that affect the macro-plasticity of monolithic BMG. Some research results indicate that there is a certain correlation between Poisson ratio \( \nu \) and plasticity of BMG. \(^18\) BMGs with higher Poisson ratio may have larger plasticity. \(^19\) Based on the idea of higher Poisson’s ratio, higher plastic strain, the contents of elements such as, Cu and Zr, with higher Poisson’s ratio in Vit 1 (Zr\(_{41.25}\)Ti\(_{13.75}\)Cu\(_{12.5}\)Ni\(_{10}\)Be\(_{22.5}\) were increased, while the contents of elements with lower ones, for example, Ti, Ni, and Be were decreased.

Generally, for an alloy, its elastic constants may agree well with the calculated value expressed by the relation\(^21\)

\[
M^{-1} = \sum f_i M_i^{-1},
\]  

where \( M \) denotes any elastic constants and \( f_i \) is the atomic percentage of the constituent element. According to Eq. (1), the calculated Poisson’s ratio of Vit 1 and ZQ1 is 0.265 and 0.320, respectively, when Poisson’s ratio values are directly input. But, this is not consistent with the experimental values. The reason comes from the very small Poisson’s ratio of
0.032 for Be element and this will give much higher error. Also, according to Wang’s calculation results, there is also a larger deviation between the calculated value and experimental one for shear modulus. But, for Young’s modulus \( E \) and bulk modulus \( B \), both calculated and experimental values match very well. Therefore, the Young’s modulus and bulk modulus can be first obtained using Eq. (1). Then, Poisson’s ratio value was obtained from the following equation:

\[
v = \frac{3B - E}{6B}. \tag{2}
\]

In this way, the calculated Poisson’s ratio of Vit 1 and ZQ1 are 0.347 and 0.365, respectively. This shows that the increasing of elements with higher Poisson’s ratio, while decreasing the elements with lower Poisson’s ratio can artificially tune the final alloy’s Poisson’s ratio.

Except for the alloy composition design, the in-situ CuZr phase was obtained during solidification process as strengthening phase to improve the mechanical properties. The obvious result is that the obtained composite has a larger plastic strain compared to monolithic Vit 1 metallic glass. The reasons of larger plastic strain and working hardening behavior may come from six aspects: First, the precipitated CuZr phase can block the propagation of the formed shear bands during compressive process. Second, according to Pauly’s results, B2 CuZr has a Young’s modulus of 89 ± 2 GPa. And, the Young’s modulus of Vit1 is 97.2 GPa as reported in Ref. 5. Thus, there is no stress concentration between in-situ precipitated CuZr and the amorphous matrix. Each shear bands formed in the matrix can extend into CuZr phase. And, this can effectively transfer loading form amorphous matrix to CuZr phase. Third, compared to amorphous matrix, CuZr phase is a softer phase. Additionally, CuZr is in-situ formed, and has a better interface with the amorphous matrix compared to ex-situ phase strengthened metallic glass composites. So, CuZr can facilitate multiple shear bands formed at the interface, and these multiple shear bands will surround CuZr phase, and impede the extending of crack. Fourth, martensite phase transformation may happen during compressive process. Correlation work is under investigation. And this phenomenon has been approved in Refs. 10–14. Fifth, the interaction of shear bands will also contribute to the plastic strain, just as shown in white circle of Fig. 5(d). Finally, the larger plastic strain may be ascribed to the improved Poisson’s ratio of obtained BMG composite with a higher value of 0.365.

Another factor need to be considered is the size/diameter and spacing of second phase. Hoffman pointed out that the scale of diameter and spacing should be less than, but of the order of the characteristic dimension \( R_c \) of a crack tip’s “plastic zone.” In Suh’s report, the plastic zone size of Vit 1 varies from 69 to 500 \( \mu \)m. Recently, Sarac et al. systematically studied the artificially designed metallic glass heterostructures. They pointed out that there exists a maximum peak when \( d/s = 1 \) in Fig. 4(a) of Ref. 25 which gives the relationship between the ratio of diameter (d) and spacing (s) of second phase and fracture stress/fracture strain under tensile condition. In our current research, the diameter of CuZr phase is about 0.5 \( \mu \)m and the spacing is about 2.0 ~ 7.0 \( \mu \)m and d/s is 0.25 ~ 0.07 which is located in the range of d/s = 0 ~ 1 in Fig. 4(a) as shown in Ref. 25. Also, according to Fig. 4(a) in Ref. 25, therefore the fracture strength does not change much compared with monolithic glass, and there is a certain plastic strain. Also, this will give us some clues to fabricate this kind of metallic glass composite: that is to achieve a larger size of the precipitated in-situ CuZr, such as ten or tens of micrometers using semi-solid solidification method as mentioned in Ref. 5.

IV. CONCLUSIONS

In summary, CuZr-containing Zr-based BMG composites were successfully developed. The composite with uniformly distributed CuZr of 0.5 \( \mu \)m in size can be produced by copper mold casting. The reinforcement increased plastic strain by a factor of 7, but did not lower the fracture strength so much. It is believed that our current finding can be applied to other BMG systems containing Zr and Cu, in order to precipitate B2 CuZr crystalline phase. Another highlight in our finding is that in our obtained CuZr-containing Zr-based BMG composite, the Beryllium content is 6 at. %. And this value is much lower than that in Vitreloy 1. Additionally, the atomic ratio of Be and Cu in ZQ1 alloy is 3/20, which is equal to 2.08 wt. % in beryllium bronze. Thus, commercial beryllium bronze (usually beryllium content is 0.2 ~ 2.75 wt. %) can be applied, other than pure Beryllium, and this will reduce the environment pollution.

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