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Fabrication of ZrAlNiCu bulk metallic glass composites containing pure copper particles by high-pressure torsion

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ABSTRACT

Several pairs of $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass (BMG) plates and pure copper plates with volume ratio of 1:1 were put together and subjected to high-pressure torsion process with 10, 20 and 50 rotations separately to prepare BMG/Cu composites. For the samples processed with 10 and 20 rotations, the microstructures were not very homogeneous and some metallic glass blocks can still be observed near the center of the samples. While after 50 rotations, the microstructure becomes rather homogenous throughout the samples. Both glass phase and copper phase were transformed into small pieces and mixed uniformly with each other. No intermetallic compounds either from chemical reaction or crystallization from the glass phase could be detected for all the samples regardless of the rotation numbers. This study indicates that high-pressure torsion technique can be used as a new approach to fabricate bulk metallic glass matrix composites.

1. Introduction

With the development of bulk metallic glasses (BMGs) in many alloy families, such as Pd-, Zr-, Fe-, La-, Mg-, Ni- and Cu-based systems, BMGs acting as matrix materials for composites have attracted tremendous attention because of their relatively low melting points and high resistance to heterogeneous nucleation of crystals [1–5]. Nowadays, the fabrication of BMG matrix composites has already been regarded as a useful way to improve the plasticity of the monolithic BMG and therefore expand its potential application as engineering materials. Up to now, BMG composites with various kinds of reinforcement have been successfully obtained, including precipitated ductile dendrites, nanocrystals, or refractory metals, ceramics, carbon fiber and carbon nanotubes [6–9]. Some of these BMG composites were reported to exhibit significantly improved plasticity. However, these BMG composites usually are prepared through solidification methods and the selections of the reinforcements are rather limited. In addition, the reaction between the *ex situ* additions and the glass matrix is difficult to be avoided. For the composites containing *in situ* precipitate, the narrow composition range and the casting parameters are strict and difficult to control. In this paper, high-pressure torsion (HPT) was used to prepare Zr-based BMG composites containing pure Cu particles, which is impossible to be obtained by solidification method due to the easy melting of Cu into the alloys. HPT is a kind of severe plastic deformation (SPD) technique, which is developed with its initial purpose to produce ultrafine-grained metallic materials [10–12]. Since very high pressure is required for the generation of large equivalent strain, atomic bonding is possible even between dissimilar materials. Thus, mechanical alloying can take place to fabricate non-equilibrium alloys or even amorphous alloys. For example, CuZr, CuZrAl can be solid-state amorphized from its constitutive pure metals by means of HPT technique, under the condition that the rotation number is high enough, like 20 rotations [13,14]. Recently, HPT technique has been used to fabricate Al-based composite containing carbon nanotubes without the formation of Al_4C_3, which is harmful to Al matrix and is certainly formed in other fabrication processes like hot extrusion, hot press, and plasma spray process [15]. However, the fabrication of BMG based composite by HPT technique has never been tried so far.

In this paper, the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMGs plate, which has a high glass forming ability, and pure copper plate were put together and subjected to HPT process with 10, 20 and 50 rotations, separately. The microstructure and Vickers hardness were characterized to evaluate the feasibility of this new method to prepare BMG/Cu composites.

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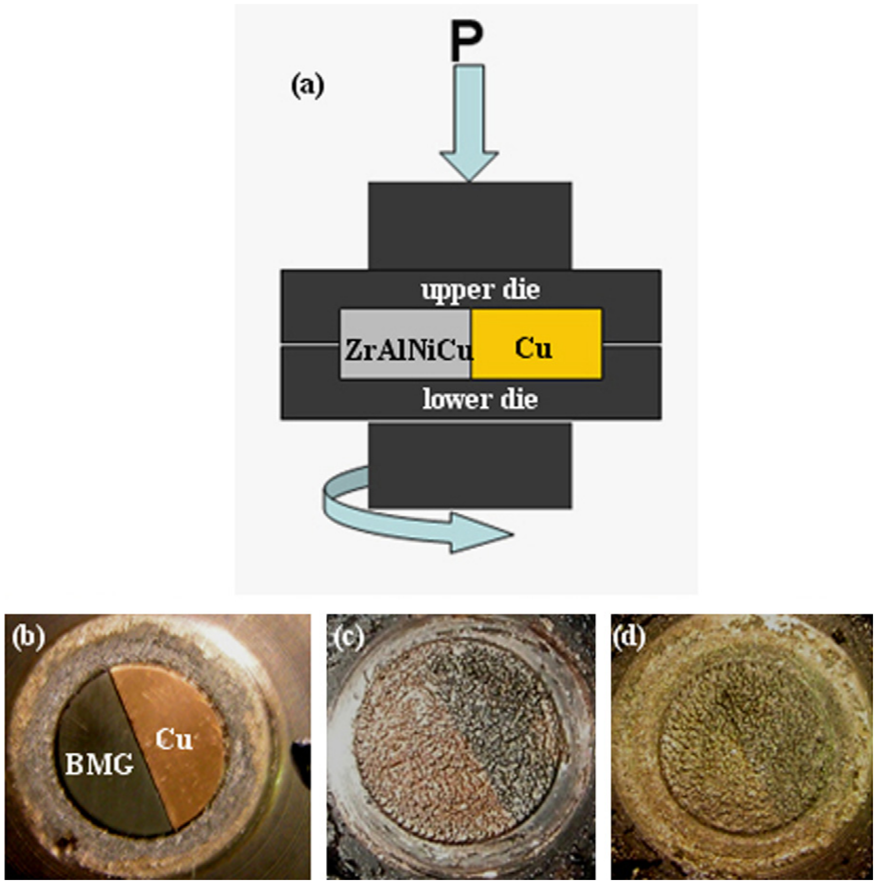

Fig. 1. (a) Schematic illustration of the HPT process and the appearance of the BMG/Cu sample (b) before and after HPT process with (c) 20 and (d) 50 rotations.

2. Experimental procedure

For the HPT experiments, several as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMGs plates and pure copper plate were electric discharge cut into semi-circular shape with diameter of 10 mm. Then the semi-circular materials were mechanically polished to 0.65 mm in thickness and were applied to HPT process. In order for the materials to be successfully atomic bonded, the surface of Zr-BMG and pure Cu were first cleaned by acetone and then slightly wire brushed. The brushed samples were put between the upper die and the lower die in the HPT machine. During the HPT process, the upper die keeps static while the lower die rotates at a rotation speed of 0.2 rpm under an applied pressure of 5 GPa. Therefore the disks were deformed gradually to achieve a very high equivalent strain with the increase of the HPT rotations. Various numbers of rotations, namely 10, 20, and 50 were completed separately. After the HPT process, pancake-like sample with diameter of 10 mm and thickness of 0.3 mm were obtained. The schematic illustration of the HPT process and the appearance of the sample before and after HPT process can be understood from Fig. 1. The appearance color of the sample becomes homogeneous after HPT process and no macro crack or fracture can be observed. The temperature rises induced by plastic deformation were also measured by inserting thermal couples near the sample surface. During the entire HPT process, the maximum temperature rise was less than 10 K due to the low rotation speed. Therefore, the thermal effect on the HPT processed sample can be neglected.

Following HPT process, the phase constitution of the obtained samples were analyzed by X-ray diffraction (XRD) with Co target and the microstructural observation from the sample surface was conducted with field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The specimens for TEM observations were cut from the HPT processed sample about 4 mm away from the geometry center and mechanically polished to about 100 μm in thickness. Then the polished sample was thinned to form an electron transparent thin film by an ion slicer instrument (JEOL EM09100IS).

3. Experimental results

Fig. 2 shows the XRD patterns of the HPT processed samples with various rotations, together with that of the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG plate. The as-cast BMG only shows a broad halo peak on the XRD curve, which is the typical characterization of amorphous phase. While the XRD curves of the HPT processed samples all exhibit a superimposition of broad halo peak from the amorphous phase and several sharp peaks characteristic for crystalline phase, indicating the existence of a mixture of the amorphous and crystalline phases. After indexing, the position and the intensity of the sharp crystalline peaks match exactly with that of pure copper. No other phases can be detected within the sensitivity limit of XRD, which indicates that neither chemical reaction between the two

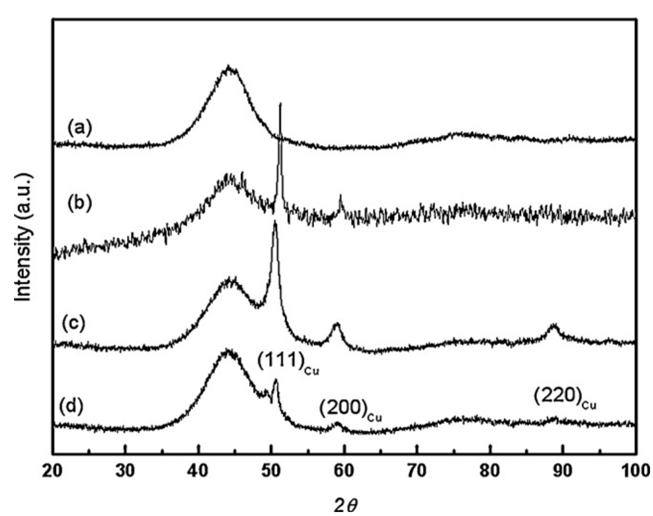

Fig. 2. XRD curves of the HPT processed sample and the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG. (a) As-cast BMG, (b) 10, (c) 20 and (d) 50 HPT rotations.

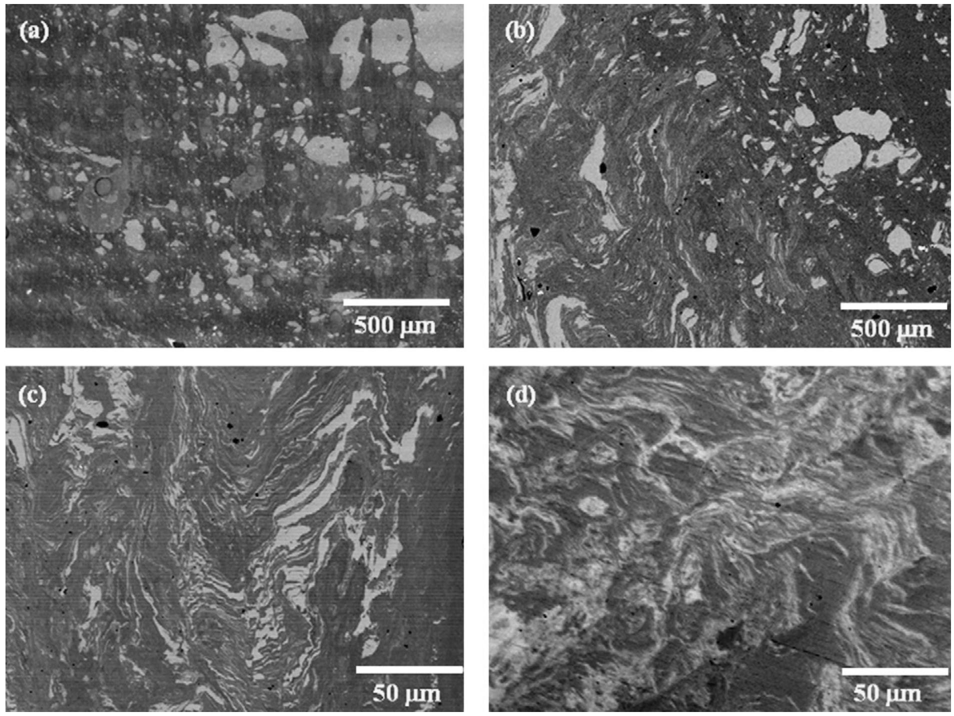

Fig. 3. SEM-BSE images showing the microstructure of HPT processed samples with (a) 10, (b, c) 20 and (d) 50 rotations.

phases nor crystallization from the amorphous phase took place during the entire HPT process.

Fig. 3 shows the SEM backscattering electron (BSE) micrographs of the samples processed after various HPT rotations. The Cu phase and the metallic glass phase appear in different contrast under BSE mode, namely Cu in dark and the other in bright. In general, for all the HPT processed samples, both the glass phase and pure Cu were fractured into smaller parts from its original one body shape and were mechanically mixed with each other. However, for the HPT processed sample with 10 and 20 rotations as shown in Fig. 3(a) and (b), the microstructure is not homogenous due to the different extent of plastic deformation in the HPT processed samples. That is, the outer part of the samples undergoes larger plastic deformation while smaller in the center part. As a result, some glass blocks larger than 200 μm can still be found near the very center part of the sample. While in the area away from the center, much smaller metallic glass particles can be found homogeneously distributed. Fig. 3(c) shows the microstructure in the outer part of the HPT processed sample with 20 rotations at higher magnification, in which no glass blocks can be discerned any more. The white glass phase is long and bended, which also reflects the plastic flow of the materials during the HPT process. When the HPT process increases to 50 rotations, the sample reveals much homogenous microstructure as shown in Fig. 3(d). The glass phases were greatly curved, which implies the plastic but not brittle feature of BMGs under high pressure. In some very local area, very thin-layered structure of the metallic glass can be distinguished. For all the HPT processed samples, the pure Cu phase was also severely deformed. However, no separated Cu block or fragments can be found due to its much softer and ductile properties.

Fig. 4 presents the TEM images showing the typical microstructure of the HPT processed sample with 20 and 50 rotations. For both HPT processed samples, two kinds of areas with remarkably different microstructure can be easily observed. One region is distributed with dense nanoscaled particles and the other is gray and homogenous with no contrast inside. From the corresponding selected areas electron diffraction (SAED) pattern inserted in Fig. 4(a) and (b), both broad diffraction ring and some sharp narrow crystalline diffraction rings can be distinguished. It reveals that the regions without contrast inside are amorphous phase while the nanoscaled particles can be confirmed to be pure Cu according to the inserted SAED pattern. In addition, the amorphous region and

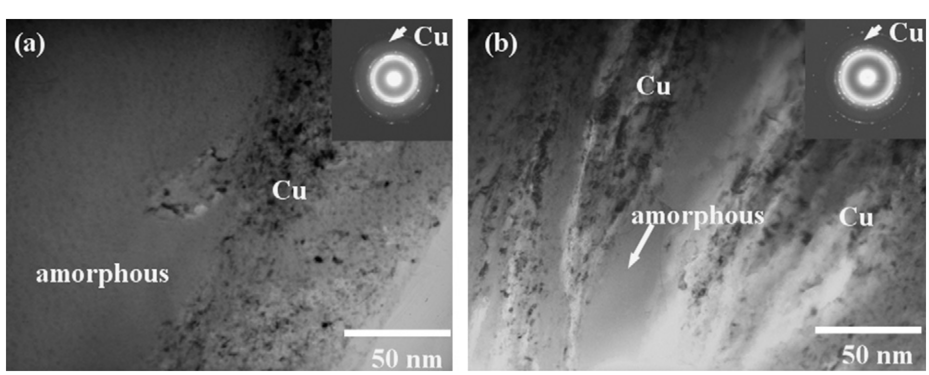

Fig. 4. TEM images showing the microstructure of the HPT processed sample with different rotations. (a) 20 rotations inserted with SAED pattern and (b) 50 rotations inserted with SAED pattern.

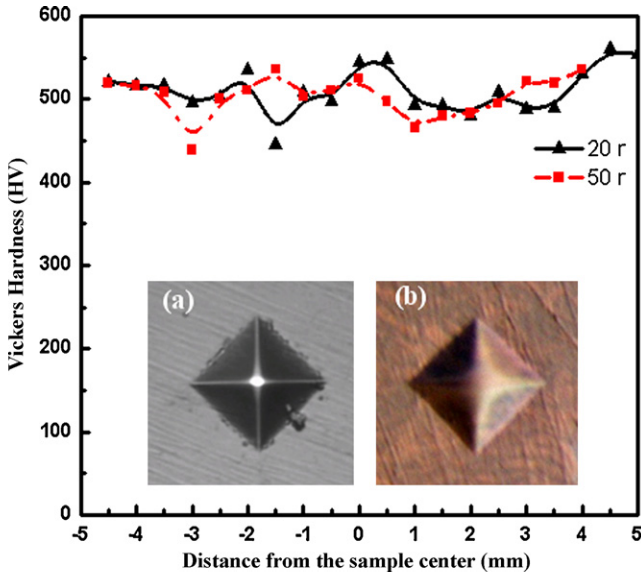

Fig. 5. Vickers hardness profile across the sample HPT processed with 20 and 50 rotations, inserted with the appearances of the indent of (a) monolithic BMG and (b) HPT processed BMG/Cu with 50 rotations.

the region with particles have a clear boundary. The two different regions in the sample with 20 HPT rotations are much larger than those regions in the sample with 50 HPT rotations. In the HPT processed sample with 50 rotations, the two kinds of regions are layer-like with width of about 50 nm and arrayed parallel with each other, probably caused by the shear stress during the HPT process.

Fig. 5 shows the Vickers hardness distribution measured on the cross-section of the HPT processed samples with 20 and 50 rotations. Although the Vickers hardness of the starting materials of copper plates is about 90 HV, the measured hardness value for the HPT processed sample was about 520 HV and was found almost constant across the entire materials, except some fluctuations on the curves. The fluctuations might be caused by the different volume fraction ratio of the two phases in some local areas. Compared with the hardness of 560 HV for the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG, the BMG composites can keep the excellent mechanical properties of the monolithic BMG. The images of the typical surface deformation features of the as-cast monolithic BMG and the HPT processed composites were inserted into the hardness profiles as shown in Fig. 5(a) and (b), respectively. The as-cast BMG was featured by some debris around the indent. The debris was the fragments generated at the brim of the indenter due to the brittle fracture of the BMG and was extruded to the surface during the indentation. In contrast, relatively smooth and clear indent can be observed for the HPT processed BMG/Cu composite, indicating a ductile feature of the materials.

4. Discussion

As a kind of SPD technique, very high equivalent strain can be easily obtained in the HPT process and it is usually used to produce ultrafine grained metallic materials. In this paper, pure copper is refined into nanostructured particles with average diameter of less than 100 nm, which is much smaller than the grain size of ECAP and HPT processed pure Cu with same purity [16]. It is probably caused by the existence of glass phase, which might affect the deformation behavior of Cu and the grain boundary structures during the HPT process. Simultaneously, the $Zr_{55}Cu_{30}Ni_5Al_{10}$ glass phase was also fractured into small pieces from its original one body alloy. The mixing of pure copper particles will inevitably influence the mechanical properties of the monolithic BMG counterpart. The deformation behavior changes from brittle fracture of the as-cast BMG to the continuous stress flow of the BMG/Cu composites. The effects of the second phase like particles, dendrite, etc, on the plastic deformation of BMGs have been studied widely. However, in the present study, the improved ductility of the BMG/Cu composites might be related with two aspects. First, the BMG plate itself also was severely deformed after the HPT process. As a result, a great quantity of free volume could be certainly introduced into the deformed alloys. The increase of free volume has been found in the cold-rolled BMGs and can help improve the plasticity of the as-cast counterpart [17–19]. Recently, the change of free volume was also studied in the HPT processed Zr-based BMGs [20,21]. It can be assured that the increase of the free volume will exert the same effect on the mechanical properties of the BMG/Cu composites in this study. On the other hand, the small copper particles can also interfere with the propagation of shear bands under indentation. The interaction between the particles and shear bands has been studied rather deeply and it is believed that the resultant multiple shear bands generation can therefore accommodate more plastic strain, however, under the condition that the particles size is larger than the thickness of the shear bands [22,23].

In addition, compared with the solidification method, HPT technique can produce BMG composite containing metallic materials with much wider options and much wider composition range. It is believed that other materials like pure metals, ceramics or even polymers can also be used as reinforcement to prepare BMG composites by HPT technique. And the content of the reinforcement can be selected in a wide range and can be easily controlled.

5. Conclusions

In summary, HPT technique can be used to fabricate BMG/Cu composites from their bulk BMG plate and pure copper plates. The dimension of the copper phase and the $Zr_{55}Cu_{30}Ni_5Al_{10}$ metallic glass phase decrease greatly with the increasing of HPT rotation numbers. No intermetallic compounds caused by either chemical reactions or crystallization from the glass phase can be detected in the composites and the composites can obtain improved mechanical properties.

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