

The effect of cryogenic treatment on the microstructure and mechanical properties of $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ bulk metallic glass matrix composites

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The influence of cryogenic treatment (CT) on the microstructure and mechanical properties of $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ glassy matrix composite fabricated by the process copper of mould suction casting. The distribution and morphology of test samples of CuZr phase changed under CT. After CT, the second phase is distributed more homogenously, and the morphology was transformed from dendrites to plates. This change in the microstructure improved the mechanical properties of the composite. Although compression fracture was still the brittle mode, the compression fracture strength was improved greatly after CT. Due to the morphological changes, the microhardness was increased about 18.55% when the treatment time was 72 h.

Keywords: $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ glassy matrix composite; cryogenic treatment (CT); microstructure evolution; mechanical properties

1. Introduction

Bulk metallic glasses (BMGs) represent an exciting class of materials with a wide range of potential applications [1]. Recently, a series of Cu–Zr and Cu–Zr–Al based BMGs or BMG composites have been found to exhibit extraordinarily high strength and good compressive ductility [2–5]. Although the localized shear transformation is still the predominant deformation mechanism, some CuZr intermetallic compounds with martensite structure or austenite-like structure formed in these materials and are believed to play an important role in improving mechanical properties [6]. The CuZr phase, as the second phase in the matrix, could affect the shear band, which is relevant for the deformation of the composite [1]. Frick et al. discovered that stress forces could induce a martensite phase transformation in nano-scaled NiTi shape memory alloys by means of nanoindentation [7]. Interestingly, the CuZr intermetallic phase shows a deformation-induced phase transformation from austenite to martensite bits

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shape memory behaviour just like NiTi [8]. Similarly, the martensitic transformation and shape memory behaviour of the intermetallic CuZr phase have also been previously reported [9].

Traditionally, CT is widely used in the manufacture of high precision parts, and has been shown to significantly improve mechanical properties of steels such as D-2 and M-2 which was predicted due to the reduction in the amount of retained austenite structure and changed to martensite structure induced by the internal stress of CT[10]. If internal stresses caused by CT could induce martensite phase transformations in Cu–Zr and Cu–Zr–Al-based BMG and BMG composites, the mechanical property of the composite would also be improved, and the range of application would be broadened.

Cu₄₆Zr₄₆Al₈ was selected for this study, as among the alloys of (Cu₅₀Zr₅₀)_{100-x}Al_x it has the best glass-forming ability (GFA) [11, 12]. This paper aims to explore and discuss how CT changes the microstructure, and the other properties, of Cu based bulk glass composites.

2. Experimental

The Cu₄₆Zr₄₆Al₈ alloy was prepared by arc melting under an argon atmosphere, and then it was suction cast into a copper mould to form cylindrical rods of 4 mm in diameter. Then the samples were immersed into liquid N₂: specifically, the samples were subjected to cryogenic treatment (CT) for 2, 4, 8, 12, 24, 48, 60 and 72 h. The effects of the CT on the microstructure of Cu₄₆Zr₄₆Al₈ composite were investigated by X-ray diffraction (XRD) with CuK_α radiation and scanning electron microscopy (SEM, JSM-6700F). The density measurement was based on the Archimedes Principle. In order to examine the influence of the duration of the cryogenic treatment on the mechanical behaviour of the glassy matrix composite, the Vickers microhardness test and uniaxial compression test were conducted. A HBRVU-187.5 hardness tester was employed to measure the Vickers hardness of these alloys subjected to the load of 200 g for 15 s. The compressive tests were conducted under quasi-static loading at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at room temperature, and the fracture surfaces were examined by SEM. The dynamics of the cryogenic process on the Cu-based composite were discussed. The bars of the fluctuation of experimental error of the ultimate compression fracture strength and the Vickers hardness were not beyond 15 and 10, respectively.

3. Results and discussion

Figure 1 shows the dependence of mechanical properties of the composite on the CT duration. The compression fracture strength of all CT samples increased compared with the as-cast specimens with no CT, as shown in Fig. 1a. The compression fracture strength of the untreated sample was measured five times and the average value was 1342 MPa. However, for the CT samples, the lowest compressive strength was

1540 MPa and the highest value was 1750 MPa. It is worth noting that the fracture strength of all the samples after CT was higher than the as-cast samples.

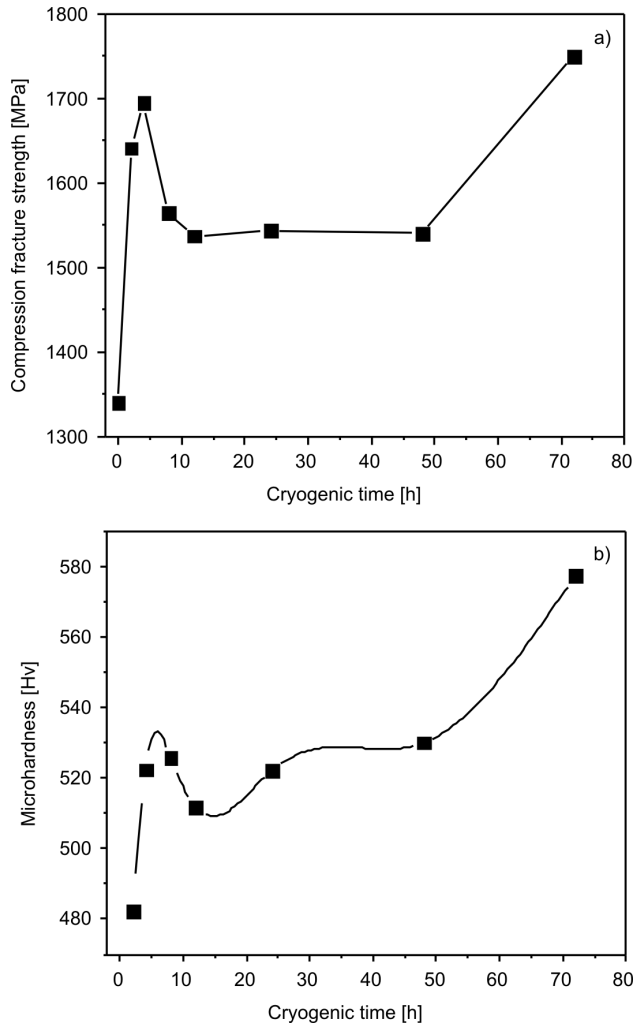


Fig. 1. Dependences of mechanical properties on the cryogenic time: a) fracture strength, b) microhardness

In order to evaluate the efficiency of atomic packing, the densities of samples before and after CT were measured. Table 1 lists the densities and microhardness of samples before and after CT. The density of all the samples increased after CT. The increase in the density indicated that the free volume was reduced, in addition to the change in the structure. The morphologies of the fracture surfaces were examined carefully. Representative SEM images were primarily observed for the samples before and after CT treatment for 72 h.

Table 1. The density and hardness before and after CT^a

T [h]	Density [g/cm ³]	Increase of density [%]	Hardness {Hv}	Increase of hardness [%]
2	7.0923/7.0780	0.2	482.07/473.64	1.78
4	7.1090/7.0702	0.55	522.37/484.76	7.76
8	7.0991/7.0492	0.71	525.67/508.86	3.33
12	7.1114/7.0408	1.0	511.84/497.6	2.86
24	7.1320/7.0659	0.94	522.19/493.69	5.77
48	7.1167/7.1075	0.13	530.01/502.99	5.37
60	7.1888/7.1075	1.14	505.24/461.16	9.34
72	7.1470/7.1376	0.13	577.57/487.2	18.55
84	7.1439/7.1103	0.47	492.49/480.69	2.45
108	7.1765/7.1372	0.55	510.14/481.74	5.90
132	7.1888/7.1642	0.34	511.74/479.26	6.78

^aThe density and hardness represent the value after CT/before CT, increase of density and increase of hardness represent the ration of difference of density (or hardness) to the original density (or hardness), respectively.

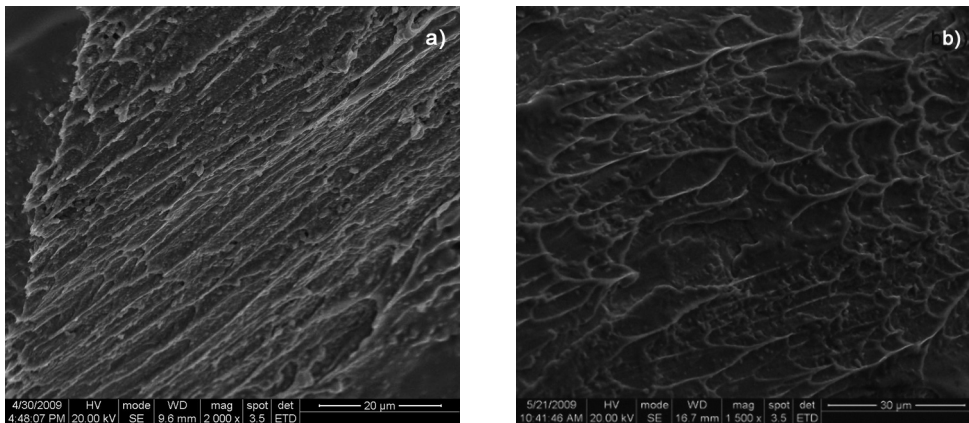


Fig. 2. SEM micrographs of fracture surfaces of: a) as-cast, b) treated for 72 h

In Figure 2, the SEM micrographs of fracture surfaces of as cast and CT samples are shown. After 72h of CT, the fracture feature consists mostly of well developed striated vein patterns, which were fine and homogeneous. Yet, in contradiction to the smooth fracture surface of Fig. 2b, the dominating features of as-cast sample are rugged planes and an elongated vein pattern with melt zone. As is well known, the fracture of the samples causes an adiabatic heating of the fracture surface [13, 14] which significantly decreases the viscosity of the samples and leads to the formation of vein patterns along the fracture planes. The well developed vein pattern of the sample subjected to 72 h CT may somewhat decrease the degree of the softening at the initial

stage of crack propagation and may contribute to the higher compressive strengths of the CT samples than the as-cast samples.

In order to understand the unique mechanical properties, the dynamics of microstructural changes was investigated. The dynamics of phase morphology induced by CT may be responsible for the enhancement of the mechanical properties. A similar phenomenon was found for AZ91 magnesium alloy [10]. In the research, CT changed the distribution and the morphology of the second phase, which resulted in a significant improvement of the mechanical properties of the alloy.

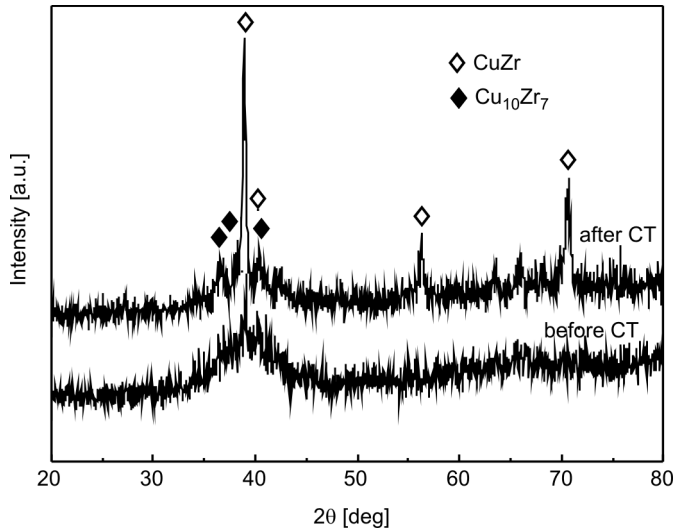


Fig. 3. XRD pattern of $Cu_{46}Zr_{46}Al_8$ BMG composites before and after CT

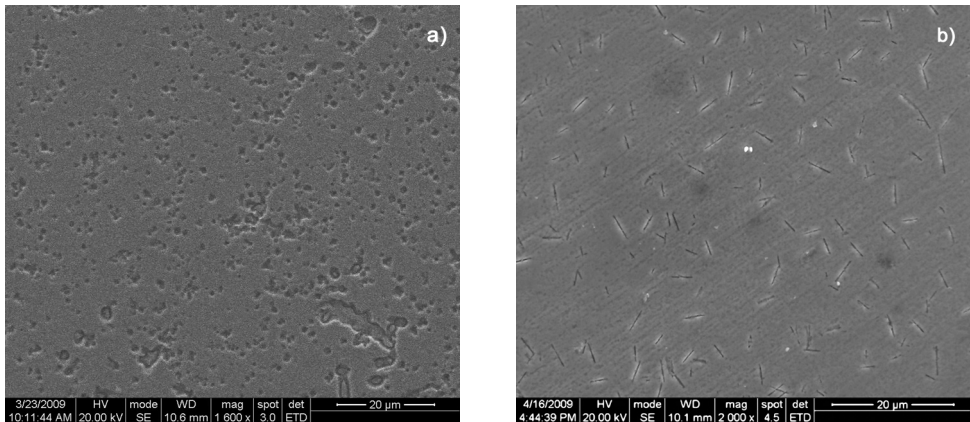


Fig. 4. SEM image of the cast glassy alloy rods $Cu_{46}Zr_{46}Al_8$ before and after CT

Figures 3 and 4 show the XRD patterns of the composite and SEM images of the sample before and after CT. In Figure 3, more crystalline peaks, which may corre-

spond to the appearance of $\text{Cu}_{10}\text{Zr}_7$ phase or monoclinic CuZr phase, were observed after CT, while only CuZr phase was seen before CT. After CT, the change of morphology was observed, as seen in Fig. 4b. There are flakes dispersed in the matrix, while only dendrite phase or rotundity grain is observed before CT, as can be seen in Fig. 4a. Furthermore, after CT, the precipitates became finer and the distribution of the second phase was more homogeneous. An important point worth noting here is that the crystalline CuZr phases exhibit quite different microstructure. The morphologies of this CuZr intermetallic compound (either $B2$ parent phase or monoclinic martensite phase) can be rather diverse, depending on the different alloy systems or on the different cooling rates, although the alloy composition might be similar. Particle sizes range from micrometer sized dendrites in a slowly solidified alloy to nanometer sized particles formed under a high cooling rate [1].

According to the binary alloy phase diagram [15] and previous investigations, $\text{Zr}_{50}\text{Cu}_{50}$ could solidify due to non-equilibrium solidification into intermetallic CuZr ($B2$) phase at 1208 K, with the decrease in temperature, and undergo eutectoid decomposition into $\text{Cu}_{10}\text{Zr}_7$ and Zr_2Cu below 988 K. But due to the sluggish diffusion kinetics of the eutectoid reaction, the CuZr ($B2$) phase transforms to a monoclinic martensitic phase, which is conducive to the improvement of mechanical properties [16, 17]. Although the CuZr phase is principally responsible for the strengthening effect on the BMG, its instability is the main reason for poor mechanical properties of these alloys. So, in order to obtain good mechanical properties, the Cu-based BMG composites should possess a stable phase microstructure. Sun [1] reported that stress forces could induce martensitic transformations in Cu–Zr–Al bulk metallic glass forming alloys and result in outstanding mechanical properties. The deformation induced martensitic transformation is believed to cause the hardening and to contribute to the high compressive deformability in Cu–Zr–(Al,Ti) [18]. The homogenization and stabilization of the internal microstructure caused by CT is the most probable reason for this observable phenomenon. In fact, CT could lead to structural change as well as to phase transformation by internal stresses and can improve the mechanical properties [19]. Some authors report that structural relaxation may be one of the microscopic mechanisms responsible for a change in the macroscopic properties and the structure of samples after CT [18]. However, at low temperatures the influence of structural relaxation is negligible [21] because its intensity I is determined by the expression

$$I \sim \exp\left(-\frac{U_i}{kT}\right) \quad (1)$$

where U_i is the mean value of the energy barrier, k is the Boltzmann constant and T is the temperature.

Therefore, the internal stress of CT changed the structure and thus leads to the improvement in the mechanical properties. These findings show $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ glassy matrix composite may offer unique possibilities for improving the mechanical properties of BMG composites.

4. Conclusions

In summary, CT can successfully improve the compression fracture strength, microhardness as well as the density of the Cu₄₆Zr₄₆Al₈ composites. The best improvements to the fracture strength and the microhardness were increases of about 30% and 18.55%, respectively: these improvements associated with microstructural changes induced by CT. After CT, the distribution and the morphology of CuZr precipitates were changed. The second phase was homogeneously distributed and the morphology was transformed from dendrite to plate forms. This microstructural modification resulted in a significant improvement of mechanical properties. This cryogenic process may provide a way of improving the properties of BMG and its composites. It may also broaden the range of potential industrial applications of BMGs in the future.

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