High-pressure torsion of Zr-based bulk metallic glasses and amorphous melt-spun ribbons

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Abstract. High-pressure torsion allows one to achieve high strains of bulk metal glasses without their destruction. The article presents the results of studies on the effect of high-pressure torsion on the amorphous alloys of the same composition but obtained in different ways: in a form of a bulk plate and a melt-spun ribbon. It is shown that the degree of nonequilibrium after high-pressure torsion, determined by the diffraction and calorimetry methods, increases for bulk metallic glass, approaching the values characteristic for melt-spun alloy.

1. Introduction

Amorphous metals and alloys are usually produced by melt spinning (MS) at high cooling rates ($10^6$ K/s) in the form of thin ribbons and at a cooling rate of about $10^2$ K/s in the form of bulk metallic glasses (BMGs) [1,2]. As produced at different melt cooling rates, these materials differ in the level of nonequilibrium (excess energy) and properties [3].

The deformation of amorphous alloys at room temperature occurs through the formation of shear bands. A transformation of the amorphous structure takes place in shear bands and surrounding regions [4]. In many cases deformation leads to the formation of an excess volume in the amorphous phase (softening of materials) [5,6]. High-pressure torsion (HPT) processing enables achieving high strains in brittle amorphous alloys, and consolidating amorphous ribbons [7,8]. HPT processing of amorphous alloys produces a high density of shear bands [9] and changes their structure and properties [10]. Partial nanocrystallization may take place in some alloys during the HPT processing [11,12]. Structural transformations as a result of HPT depend on the initial internal energy of the amorphous alloy. As a consequence, of great interest are the studies of the effect of HPT on the amorphous alloy with the same composition, but produced at different melt cooling rates and with different degrees of disequilibrium.
2. Material and methods

In this study, plates of the Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ at. % BMG (BMG Zr62) with sizes 60×10×2 mm$^3$ produced by casting at a cooling rate of $10^3$ K/s and melt-spun Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ at. % (MS Zr62) ribbons with the thickness of 0.04 mm and a width of about 2 mm produced by melt-spinning at a cooling rate of $10^6$ K/s were used.

The HPT was carried out on anvils with a diameter of 10 mm and groove depth of 0.3 mm under the pressure of 6 GPa at a rotation speed of 1 rpm at room temperature (RT). The structure was investigated by X-ray diffraction under Cu radiation on a Rigaku Ultima IV diffractometer. The parameters of broad diffraction peaks (amorphous halos) were evaluated by a PHILIPS ProFit software. The DSC tests were performed on a Netzsch DSC 204 F1 Phoenix calorimeter; the heating temperature was 520 °C (higher than the crystallization temperature in this BMG, MS) and the typical heating rate was 20 °C/min.

![Figure 1. X-ray diffraction patterns of a) BMG Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ in the initial state and after HPT n=10; b) MS Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ alloy in the initial state and after HPT n=10.](image-url)

3. Results and discussion

According to XRD results, initial BMG, MS, and the same materials after HPT processing are mostly amorphous (figure 1). The radius of the first coordination sphere, $R_1$, was determined based on the angular position of the amorphous halo maximum. $R_1$ of BMG increase as a result of HPT (table 1).

The relative change in free volume ($\Delta V$) can be calculated based on the change of $R_1$ [13,14]. According to the calculations, HPT n=10 of BMG leads to a 2% increase in $\Delta V$. HPT also leads to an increase in the values of full width at half maximum (FWHM) of BMG, that also attributed to an increase in the disequilibrium of the amorphous alloy [13].

| Table 1. XRD and DSC data for the BMG and MS Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ alloy in the initial state, and subjected to HPT n=10. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| State           | $R_1$, nm       | FWHM, deg       | $\Delta V$, %   | $\Delta$FWHM, % |
| BMG, initial    | 2.996           | 5.34            |                 | -               |
| BMG, HPT n=10   | 3.017           | 5.70            | 2.1             | 6.8             |
| MS alloy, initial | 3.022         | 5.64            |                 | -               |
| MS alloy, HPT n=10 | 3.015         | 5.76            | -0.7            | 2.1             |

HPT n=10 also lead to increase in the values of FWHM of the MS alloy (table 1). However, the relative increment in the FWHM of the MS alloy resulting from HPT is noticeably smaller than increment in the FWHM for the BMG. The $\Delta V$ values of the MS alloy, calculated on the basis of the $R_1$ change, even slightly decrease as a result of the HPT. This may be due to a large error in the determining $R_1$ by XRD. On the whole, the FWHM parameters of the MS alloy and BMG become closer due to HPT processing.
Based on the DSC data, the $H_{\text{relax}}$ of the initial MS Zr62 is higher than $H_{\text{relax}}$ of the Zr62 BMG. This is attributed to the more disequilibrium of the MS alloy in comparison with the BMG. The HPT of the BMG leads to a notable increase in $H_{\text{relax}}$ (from $\approx 9$ to $\approx 18$ J/g), which is the result of growth of the energy of amorphous alloy and $\Delta V$ [1].

The relative increase of $H_{\text{relax}}$ in the MS resulting from the HPT, is not as large as that in the BMG resulting from the HPT. The gain is close to the measurement error of $H_{\text{relax}}$ based on DSC. Thus, the following tendency can be observed: in the Zr62 BMG, as a result of HPT processing, the structure becomes more non-equilibrium, while in the MS Zr62 alloy, as a result of HPT processing, the state does not change that much, and on the whole, the characteristics ($H_{\text{relax}}, \text{FWHM}$) of the Zr62 BMG and MS Zr62 alloy become closer as a result of HPT processing. This is explained by the competition between the processes of deformation and relaxation during the HPT of amorphous alloys, and the intensification of relaxation with an increase in the disequilibrium of the amorphous alloy.

Figure 2. DSC of: a) BMG Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ in the initial state, subjected to HPT n=10, b) MS Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ alloy in the initial state and subjected to HPT n=1; c) relaxation of the BMG Zr62; d) relaxation of the MS Zr62.

4. Conclusions
As HPT of BMG Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ at. % results in a noticeable increase in the energy state, whereas in MS Zr$_{62}$Cu$_{22}$Al$_{10}$Fe$_5$Dy$_1$ at. % a change in the disequilibrium is not so manifested and, in the whole, the characteristics ($H_{\text{relax}}, \text{FWHM}$) of BMG and MS converge as a result of the HPT. This may be explained by the competition between the processes of deformation and relaxation during the HPT of amorphous alloys, and the intensification of relaxation with an increase in the disequilibrium of the amorphous alloy.
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