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# Free volume measurement of severely deformed $\text{Zr}_{62}\text{Cu}_{22}\text{Al}_{10}\text{Fe}_5\text{Dy}_1$ bulk metallic glass

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**Abstract.** The  $\text{Zr}_{62}\text{Cu}_{22}\text{Al}_{10}\text{Fe}_5\text{Dy}_1$  bulk metallic glass (BMG) was subjected to high pressure torsion (HPT) at room temperature and at 150 °C. XRD shows a shift of first amorphous halo towards a low angles, which corresponds to an increase in the first coordination sphere radius and an increase in free volume content approximately by 0.44 % and 0.74 % after HPT processing at temperatures of 20 and 150 °C, respectively. Direct density measurements revealed that HPT at 20 °C and 150 °C leads to a decrease in the density values by 2.1% and 1 %, respectively, in comparison with the initial state. Value of density decrease for state HPT 150 °C estimated by direct density measurements is close to value of free volume increase estimated by shift of first amorphous halo.

## 1. Introduction

Bulk metallic glasses (BMGs), have been attracting great interest due to their interesting properties [1-3]. They demonstrate high strength and a low elastic modulus, large elastic elongation, which may be interesting for certain applications [2,3]. However, deformation of amorphous alloys at room temperature occurs through the formation of highly-localized shear bands (SBs) takes place [2,3], along which the material undergoes brittle fracture during tension. In this regard, many studies are conducted with the aim to improve ductility of amorphous materials through the structural transformations by various schemes [3,4]. It has been previously demonstrated that preliminary plastic deformation (compression, cold rolling etc.) can lead to an increased ductility of BMGs by nucleation and branching of multiple shear bands, which contribute to the overall plasticity [3,4]. High pressure torsion (HPT) deformation is of interest for the structural transformations of various materials including amorphous alloys [5,6]. High imposed pressure during HPT prevent the fracture of processed samples, which is especially important for brittle and hard-to-deform amorphous alloys. In



amorphous alloys HPT modifies local atomic structure and generates the formation of a high density of localized shear bands [7-11]. It has been demonstrated in that HPT processing leads to nanocrystallization in amorphous phase in some amorphous alloy [7,12]. In melt-spun (MS) Ti-Ni-Cu amorphous alloys, partial nanocrystallization under HPT processing takes place simultaneously with the formation of a cluster-type amorphous structure [9,10]. Properties of amorphous alloys undergo considerable changes [8,13] due to structural transformations under HPT processing, including appearance of tensile ductility [14]. However, the regularities of the transformation of the structure and properties of amorphous alloys during HPT processing have not been studied enough.

An important feature of amorphous materials free volume [1,2]. XRD is one of the possible methods for the evaluation of free volume in amorphous materials including those subjected plastic deformation [15-18]. XRD studies enable determination the value of the first coordination sphere radius ( $R$ ) of the amorphous phase and the changes in free volume resulting from various structural transformations [15]. Previous studies have shown that the severe plastic deformation leads to an increase in the value of the first coordination sphere radius ( $R_f$ ), and correspondingly, an increase in free volume [15]. However, it can be assumed that the estimate of the free volume variation in HPT-processed amorphous alloys from the change of the first coordination sphere radius according to the XRD data may have a significant error. The samples of HPT-processed amorphous alloys contain many shear bands [8,10,13]. On the one hand, it is known that the atomic structure of shear bands and the areas closest to them differs from the other amorphous matrix, also in terms of density [2]. Therefore, the structure of an amorphous alloy subjected to deformation can be presented as a two-phase: amorphous structure in shear bands and amorphous structure in initial amorphous matrix. On the other hand, under large strains the free volume of a material may also change. It is interesting to use direct density measurement to estimate changes in free volume and to compare these values with the values obtained by XRD. The most widely used method for the density measurements of BMGs (that reflects free volume) is the method of hydrostatic weighing [19]. However, using hydrostatic weighing for the density measurement of HPT-processed samples is extremely complicated due to the small sizes and complex shape (a thin disc) of the HPT-processed samples. The possibility of density measurement of HPT-processed samples with small sizes and a complex shape emerged when a new unique method was developed [20]. In this paper, XRD and new method for density measurement of small samples [20] were used in order to estimate changes in free volume of amorphous alloys under HPT processing, using the  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG as an example.

## 2. Experimental procedures

Cylindrical rods of 5 mm in diameter and 50 mm in length from the  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG were fabricated by copper mold casting [19]. Rods with a thickness of 2 mm were placed between anvils with a diameter of 10 mm. HPT processing was carried out under applied pressure of 6 GPa for 5 full revolutions with a rotation speed of 1 rpm at temperature of 20 and 150 °C. As a result, samples with a thickness of 0.2-0.3 mm and a diameter of 10 mm were produced.

An amorphous structure was investigated by X-ray diffraction under Cu radiation employing a Rigaku Ultima IV using flat graphite monochromator. The diffraction patterns were collected with a step size of 0.05 degree and 10-second exposure per point. Parameters of amorphous halos were evaluated by PHILIPS ProFit software. Direct density measurements were made according to the procedure precise technique «bulk density measurements of small solid objects using laser confocal microscopy» described in Ref. [20] with an accuracy  $\leq 0.5\%$ .

## 3. Results and discussion

According to XRD, the structure of the as-cast  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG and states after HPT processing is amorphous (Fig. 1). Angular position of first amorphous halo shift towards the lowest angles after HPT processing (Table 1). Values of shortest interatomic spacings (radius of first coordination sphere,  $R_f$ ) could be estimated using following Ehrenfest equation [17,18]:

$$2R_1 \sin\theta = 1.23\lambda \quad (1)$$

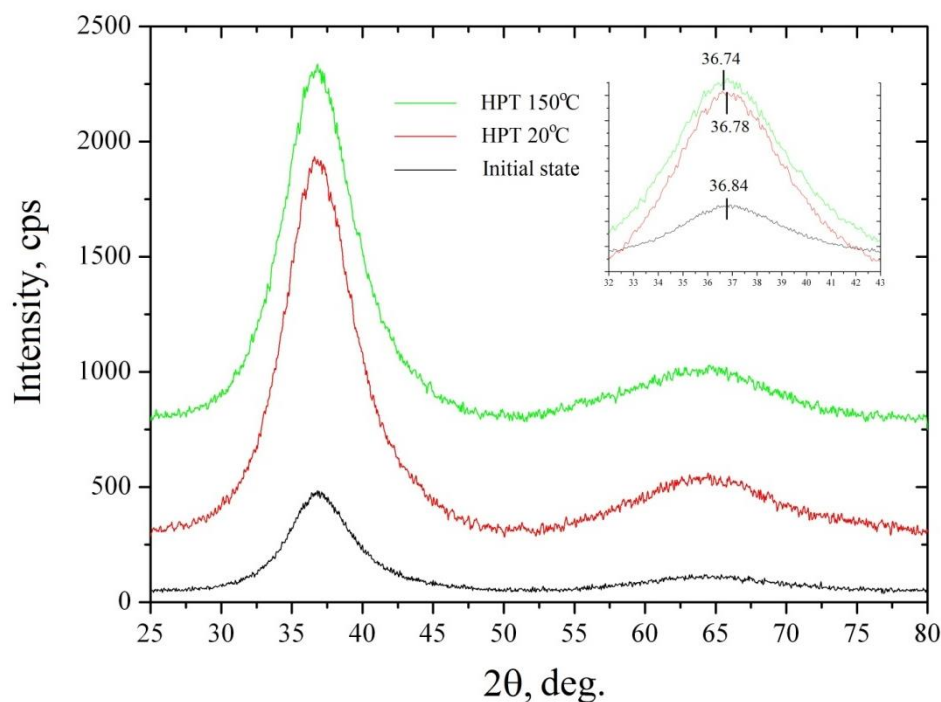
where  $\theta$  is the scattering angle,  $\lambda$  is the radiation wavelength. Decrease in value of angular position of first amorphous halo after HPT processing means increase values of  $R_1$ , i.e. average interatomic distances. As-cast BMG and states after HPT processing at temperatures of 20 and 150 °C have the following values of  $R_1$ : 2.999, 3.003 and 3.006 Å, respectively (Table 1). The third power of  $R_1$  is correlated with the mean atomic volume by equation [21]:

$$\frac{R_0^3}{R_{HPT}^3} = \frac{V_{HPT}}{V_0} \quad (2)$$

where  $R_0$  and  $R_{HPT}$  is the radius of first coordination sphere of as-cast and HPT-processed BMG, respectively;  $V_0$  and  $V_{HPT}$  is the mean atomic volume of as-cast and HPT-processed BMG, respectively. Relative changes in free volume could be estimated according to:

$$\Delta V = \frac{R_{HPT}^3 - R_0^3}{R_0^3} * 100\% \quad (3)$$

Thus, HPT at temperatures of 20 and 150 °C lead to increase in free volume content by 0.44 and 0.74 %, respectively. HPT processing leads to increase in values of FWHM along with values of  $R_1$ . The increase in FWHM was also explained by the increase in the free volume content [16].



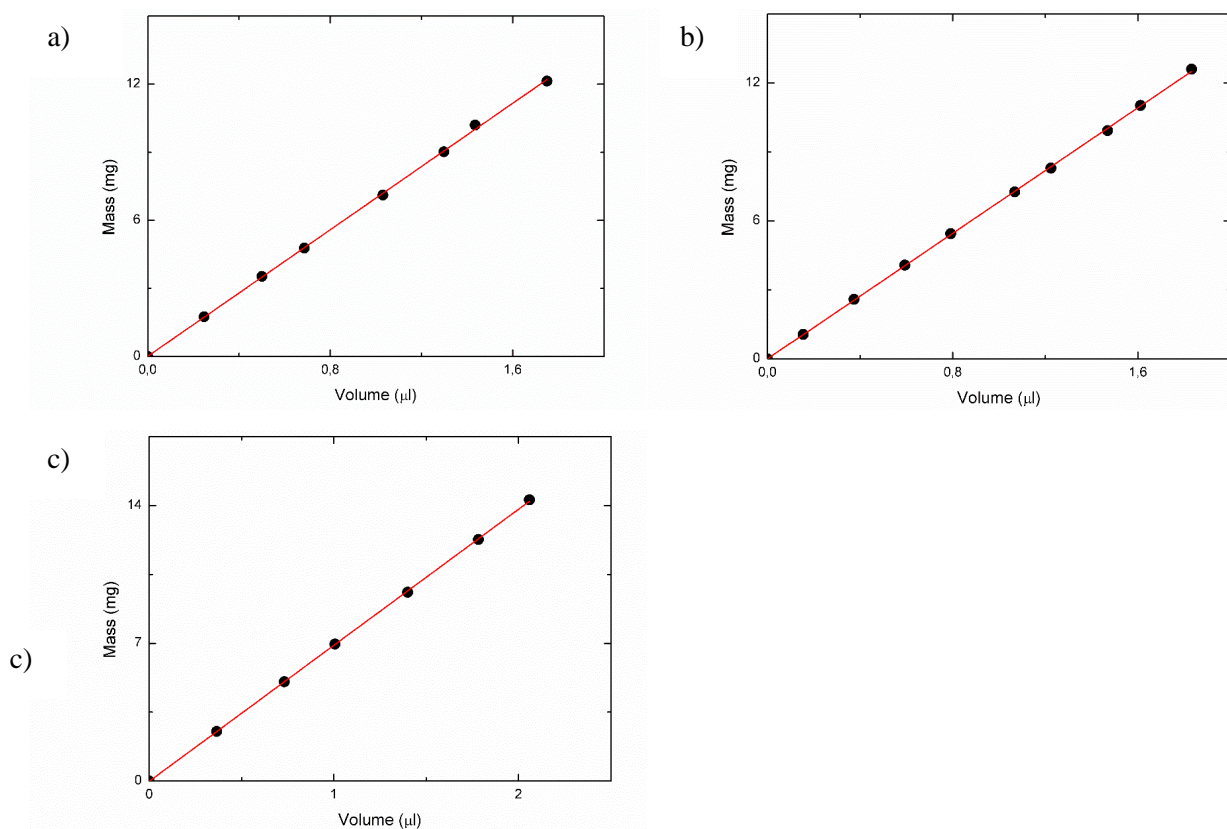
**Figure 1.** X-ray diffraction patterns of as-cast  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG and states subjected to HPT at temperatures of 20 and 150 °C.

It is known that the formation of an asymmetrical halo reflects the separation of the amorphous phase into phases with different chemical composition [17]. Previously, the effects of separation of the amorphous phase under HPT in Nd-Fe-B and Al-Ni-RE amorphous alloys were observed [7,18].

Amorphous halo of as-cast  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG retains its symmetrical shape after HPT processing. On the one hand, this observation means the absence of HPT-driven chemical separation

in  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG. On the other hand, XRD does not show that in the process of HPT processing of BMG lead to formation of two-phase amorphous structure «high density of shear bands and initial amorphous matrix».

Density of as-cast  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG and states processed by HPT at temperature of 20 and 150 °C was measured using technique described in Ref. [20]. From 6 to 9 fragments of samples were used to determine the density of each condition. Figure 2 shows the relationship between the mass of sample pieces and their volume, from which the density values were determined. Density was determined as the tangent of angle of the approximating straight line. The density measurements demonstrate that the initial  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG has a density  $\rho$  equal to  $6.98 \text{ kg/m}^3$  (Table 1), which correlates with a rather good accuracy with the data for bulk samples of this BMG obtained by hydrostatic weighing [19]. HPT at temperatures of 20 °C and 150 °C leads to decrease in the density values ( $\Delta\rho$ ) by 2.1 and 1 %, respectively in comparison with the initial state (Table 1).



**Figure 2.** Relationship between the mass (mg) of sample pieces and their volume ( $\mu\text{l}$ ): a) as-cast  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG; b) BMG after HPT at temperature of 20 °C; c) BMG after HPT at temperature of 150 °C.

The decrease in the density values  $\Delta\rho$  for the sample after HPT processing can be associated with an increase in free volume. The value of  $\Delta\rho$  (from direct density measurements) is close to the value of  $\Delta V$  (from XRD) for  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG processed by HPT at temperature of 150 °C. The corresponding value of  $\Delta\rho = 2.1 \%$  for the state processed by HPT at temperatures of 20 °C is much larger than value of  $\Delta V = 0.44 \%$ . Probably, this is related to the fact that HPT at 20 °C (at a lower temperature) can more easily facilitate the formation of pores or cracks in the HPT-processed sample, although the studies by SEM did not reveal the presence of cracks in the sample. However, this may be related to the nano-sizes of the pores. This feature introduces an additional error in the values of  $\Delta V$

determined by the direct method. Previously the nano-sized pores and nano-voids in the SPD-processed alloy were discovered in Ref. [22]. We should note that the increase in values of  $\Delta V$  by 0.44 and 0.74 %, obtained in this work, is close to values of  $\Delta V$  (up to 1%) observed in other works on the HPT processing of BMGs [15,23].

**Table 1.** Parameters of amorphous structure of  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG in initial state and after HPT processing at temperatures of 20 and 150 °C from the XRD and direct density measurements.

State	$2\theta$ , deg.	$R_1$ , Å	FWHM, deg	$\Delta V_{XRD}$ , %	$\rho$ , g/cm <sup>3</sup>	$\Delta\rho$ , %
Initial BMG	36.84(3)	2.999	5.50	-	6.98	-
HPT at 20 °C	36.780(16)	3.003	6.106	0.44	6.83	2.14
HPT at 150 °C	36.743(15)	3.006	6.309	0.74	6.90	1.07

Value of  $\Delta V = 0.44$  % resaved from XRD for BMG processed by HPT at temperature of 20 °C is smaller than value  $\Delta V = 0.74$  % for state processed by HPT at temperature of 150 °C, i.e. processing at a higher temperature leads to a more pronounced formation of free volume. This can be explained by the following. The increase in the HPT processing temperature to 150 °C, on the one hand, should accelerate the annihilation of free volume (which is observed during the heating of amorphous alloys up to the relaxation temperatures [2]), and on the other hand, it should facilitate the deformation of the sample and the generation of shear bands in the sample. From the obtained data it can be assumed that the latter process prevails, which leads to a larger increment in free volume content for HPT processing at temperature of 150 °C.

#### 4. Conclusions

XRD shows that the HPT processing of the  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG induces a shift of first amorphous halo towards a low angle, which corresponds to an increase in the first coordination sphere radius  $R_1$  and an increase in free volume. HPT processing at temperatures of 20 and 150 °C leads to increase in free volume by 0.44 and 0.74 %, respectively.

Direct density measurements made according to the procedure described in Ref. [20] revealed HPT processing at temperatures of 20 and 150 °C leads to a decrease in the density values by 2.1 % and 1 %, respectively, as compared to the initial state. The value of  $\Delta\rho = 1$  % (from direct density measurements) is close to the value of  $\Delta V = 0.74$  (from XRD) for  $Zr_{62}Cu_{22}Al_{10}Fe_5Dy_1$  BMG processed by HPT at temperature of 150 °C. The corresponding value of  $\Delta\rho = 2.1$  % for the state processed by HPT at temperatures of 20 °C is much larger than value of  $\Delta V = 0.44$  %. Probably, HPT at temperature of 20 °C leads to the formation of nano-sized pores and nano-voids in processed sample.

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