High pressure torsion of Cu-based metallic glasses

S Hóbor¹, Zs. Kovács¹ A. P. Zhilyaev², L. K. Varga³, P. J. Szabó⁴ and Á. Révész¹

¹ Department of Materials Physics, Eötvös University, Budapest, H-1518, P.O.B. 32, Budapest, Hungary
² Centro Nacional de Investigaciones Metalúrgicas, 28040 Madrid, Spain and Institute for Metals Superplasticity Problems, RAS, 450001 Ufa, Russia
³ Research Institute for Solid state Physics and Optics, Hungarian Academy of Sciences. H-1525 Budapest, P.O.B. 49, Hungary
⁴ Department of Materials Science and Engineering, University of Technology and Economy, Budapest, H-1111 Hungary

hobors@metal.elte.hu

Abstract. Cu-Zr-Ti metallic glass was subjected to high pressure torsion applying different revolution times (180s, 120s, 60s). Both deformation and deformation rate dependent microstructural and thermal properties were characterized by scanning electron microscopy, X-ray diffraction and calorimetry, respectively. In order to estimate the temperature rise in the metallic glass during high pressure torsion, quasi three-dimensional heat conduction equation with a source term was considered. Solutions indicate that the saturation temperature strongly depends on the revolution time, i.e. on the deformation rate.

1. Introduction
Recently high pressure torsion (HPT) based on severe plastic deformation [1] was successfully applied to induce nanocrystals in amorphous alloys [2-4]. As known, shear deformation in metallic glasses is localized in very thin shear bands (~10 nm) below the glass transition temperature (Tg), characterized by enhanced atomic mobility and local temperature rise [5-7]. Approaching Tg, the plastic deformation shows a transition from localized to homogenous viscous flow [8].

In a recent study, the observed morphological and microstructural features introduced by HPT of an amorphous Cu₆₀Zr₃₀Ti₁₀ alloy was interpreted by temperature profiles obtained from a simple model based on one-dimensional heat-conduction [9]. Later a quasi three-dimensional model was developed and the effect of the instrumental parameters on the temperature rise in the disk-shaped samples was investigated in detail [10]. In this paper the role of the most important parameter, i.e. the revolution time on the microstructure and thermal stability of amorphous Cu₆₀Zr₃₀Ti₁₀ alloys is presented.

2. Experimental
An ingot of nominal composition of Cu₆₀Zr₃₀Ti₁₀ was prepared by induction melting of high purity (99.9 %) Cu, Zr and Ti metals. Ribbon was obtained by using single roller melt spinning technique in inert atmosphere with a rotating Cu-wheel. Pieces of the ribbon were placed between HPT-anvils and...
compressed into several porosity free, round shaped disks with an average diameter of 8 mm and an average thickness of about 150-250 µm under an applied pressure of 6 GPa, with 5 whole turns and three different revolution times (t_{rev} = 180 s, 120 s and 60 s). Hereafter the corresponding samples are denoted as #180, #120 and #60, respectively. The accumulated shear strain for HPT deformation at a radius r can be represented by $\varepsilon(r, t) = 2\pi \cdot r / L \cdot t_{rev}$, where L and t are the thickness of the disk and the time, respectively. Microstructure was examined by a special high resolution double crystal diffractometer with negligible instrumental broadening equipped with a fine focus rotating copper anode (Nonius, FR 591). The cross-section of the beam impinging the specimen was 0.1x2 mm². Diffraction patterns were registered by FUJI Imaging Plate (BAS MS2025). Morphology studies were performed on a Philips XL 30 scanning electron microscopy (SEM) in backscattered electron (BSE) mode on the mechanically polished cross-section of the disks, while the compositional changes were quantitatively determined by energy dispersive X-ray (EDX) analysis with a relative accuracy of 3 %. A Perkin Elmer power compensated differential scanning calorimeter (DSC) was applied to investigate the thermal behavior and crystallization applying continuous heating experiments performed at scan rate of 40 K/min. Transformation enthalpies were obtained as the area of the exothermic peaks.

3. Results
As seen, the XRD patterns taken on both the centre and perimeter of the #180 sample are dominated by a broad, featureless amorphous halo at around 40.5 deg, however, severe deformation induce a couple of faint Bragg-peak for the perimeter of #120 disk (see Fig. 1). The largest shear rate (sample #60) results in the formation of intense peaks corresponding to hcp Cu_{51}Zr_{14} (p6/m a = 1.13 nm and c = 0.82 nm) and to hcp Cu_{2}ZrTi (p6_{3}mmc, a = 0.505 nm, c = 0.82 nm) phases even for the centre, while the amorphous halo becomes almost negligible for the perimeter of the disks.

![Figure 1. X-ray diffractograms taken at the centre and perimeter of the HPT-disks.](image1)

![Figure 2. (a) DSC curves of the fully amorphous alloy and the centre and perimeter of the disks. (b) Total crystallization enthalpies obtained from the DSC curves.](image2)

The DSC thermograms of the #180 and #120 samples exhibit similar features as of the as-quenched ribbon, i.e. T_g is followed by two exothermic peaks (Fig 2a). For each disk the glass transition become less pronounced with increasing deformation, furthermore it totally disappears for the largest deformation rate (#60). At the same time the exothermic peak shift to lower temperatures.
and considerably broaden. The variation of the amorphous content with different shear rates can be characterized by the total enthalpy release ($\Delta H_{TOT} = \Delta H_1 + \Delta H_2$). For the slowest $t_{rev} (=180$ s) a $23\%$ drop in $\Delta H_{TOT}$ is observed both for the centre and perimeter, independently from the magnitude of deformation, in line with the XRD data (see Fig 2b). In the case of samples #120 and #60 the decrease in $\Delta H_{TOT}$ for the centre is $19\%$ and $35\%$, respectively, nevertheless a remarkable increase occurs for the perimeter.

The microstructural differences associated with various shear rates are visualized in the SEM BSE images (Fig. 3a-c). As seen in Fig. 3a, the entire sample #180 is characterized by several bunches of elongated dark grey bands of 20-40 µm slightly enriched in Ti (Cu$_{59}$Zr$_{27}$Ti$_{14}$) dispersed in the amorphous matrix (Cu$_{61}$Zr$_{29}$Ti$_{10}$). On contrary, the morphology of sample #120 (Fig. 3b) obeys a stronger deformation dependence, dominated by elongated particles of about 10-30 µm in the centre and much smaller ones (~5 µm) at the perimeter. Furthermore the central region of sample #60 contains several robust, dark grey blocks of 15-25 µm, homogeneously dispersed in the matrix (Fig 3c). However, the BSE image of the perimeter exhibits only contrastless homogenous microstructure without any detectable crystalline blocks.

4. Discussion

The contrast between the microstructure and thermal behaviour of the HPT-disks processed by different deformation rates can be explained in terms of a three-dimensional thermoplastic model based on heat conduction [10]. In brief, the temperature evolution in the disk can be derived from the heat conduction equation

$$c(r) \cdot \rho(r) \cdot \frac{\partial T(r,t)}{\partial t} - \Delta(k(r) \cdot T(r,t)) = S(r,t),$$

where $c(r)$, $\rho(r)$ and $k(r)$ are the heat capacity, the density and the heat conductivity, respectively. $S(r,t)$, the plastic deformation induced heat release, can be calculated as

$$\beta \cdot \sigma \cdot \varepsilon \cdot \frac{d \varepsilon}{dt}, \quad \text{if } T<T_g$$

$$\beta \cdot \eta \cdot (\varepsilon \cdot \frac{d \varepsilon}{dt})^2, \quad \text{if } T>T_g,$$

where $\beta$, $\varepsilon$ and $\eta$ are the fraction of plastic work converted to thermoplastic heating, the shear strain and the viscosity that can be obtained from the Vogel-Fulcher equation [11].

Figure 3. SEM BSE images of the cross-section of HPT-disks with different revolution time (a) with $t_{rev}=180$ s where the inset is the enlargement of an elongated block, (b) with $t_{rev}=120$ s (c) with $t_{rev}=60$ s
The calculated temperature curves clearly show that the rate of the temperature rise as well as the saturation temperature drastically depends on the $t_{rev}$ (Fig. 4). According to the model the temperature increases by $\sim 180K$ for both samples #180 and #120, during the entire process of five whole revolutions, indicating that it remains below $T_g$, corresponding to extreme deformation in the narrow shear bands [7]. As a consequence plenty of nanocrystalline nuclei can form in the amorphous matrix near these locally heated deformation zones [9], that partly coalesce in the plane of shear deformation, forming bunches of elongated crystalline bands, as seen in Fig. 3a-b. For sample #180 the shear rate is the lowest, explaining the lack of deformation dependent microstructure confirmed by XRD and SEM. However, higher shear rate for sample #120 moderately limits the coalescence of the nuclei in the outer regions of the disk (Fig. 3b), in line with the observed slight increase in $\Delta H_{TOT}$ (Fig. 2b) corresponding to the excess grain boundary enthalpy of these nanocrystals. As seen in Fig. 4, for the sample deformed by the highest shear rate (#60) the temperature reaches $T_g$ in a relatively short time (~55s), thereafter the rate of the temperature rise decreases abruptly, yielding a temperature saturation at around 715 K. Accordingly the HPT-process may be divided into two distinct stages according to the deformation mode. During the first stage of deformation plenty of nuclei form in the in the entire sample similarly to samples #180 and #120. However, after the temperature exceeds $T_g$ the growth and coalescence of these nanocrystals is strongly limited by the persistent shear in the perimeter of the disk. Nevertheless this effect is less pronounced in the centre, moreover the devitrification is enhanced by the high temperature, yielding the formation of robust crystalline blocks seen in Fig. 3c, and the reasonable drop in $\Delta H_{TOT}$ in Fig. 2b.

5. Conclusions
Numerical calculations based on quasi three-dimensional heat conduction equation have satisfactorily described the microstructural features and thermal behaviour of amorphous Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy processed by HPT with different shear rate.

Acknowledgement
We appreciate the support of the Hungarian Scientific Research Fund (OTKA) under grant No. 67893. Á. R. is indebted for the Bolyai Scholarship of the Hungarian Academy of Sciences.

References
[1] Valiev R Z, Islamgaliev R K and Alexandrov I V, 2000 Prog. Mater. Sci. 45, 103.
[2] Boucharat N, Rösner H and Wilde G, 2007 J. Non-Cryst. Solids 354, 592.
[3] Kovács Zs, Henits P, Zhilyaev A P and Révész Á, 2006 Scripta Mater. 54, 1733
[4] Révész Á, Hóbor S, Szabó P J, Zhilyaev A P, Kovács Zs, 2007 Mater. Sci. Eng. A 460-461, 459.
[5] Chen H, He Y, Shiflet G J and Poon S J, 1994 Nature 367, 541.
[6] Zhang Y and Greer A L, 2006 Appl. Phys. Lett. 89, 071907.1
[7] Lewandowski J J Greer A L, 2006 Nature Mater. 5 15.
[8] Schuh C A, Hufnagel T C, and Ramamurty U, 2007 Acta Mater. 55, 4067.
[9] Hóbor S, Révész Á, Szabó P J, Zhilyaev A P, Kovács Kis V, Lábár J L and Kovács Zs, 2008 J. Appl. Phys. 104 033525
[10] Hóbor S, Kovács Zs and Révész Á, 2009 J. Appl. Phys. 106, 023531
[11] Fulcher G S, 1925 J. Am. Ceram. Soc. 8, 339.