Influence of high-pressure torsion on the deformation nature of Vit105 metallic glasses during microhardness tests

Vasily Astanin¹*, Ruzalina Gabbyasova¹ and Vladimir Astanin¹

¹ Ufa State Aviation Technical University, K. Marx str. 12, Ufa, 450008, Russia

*Corresponding author e-mail: v.astanin@gmail.com

Abstract. Severe plastic deformation by torsion leads to a decrease in the microhardness of Zr-based BMG, while relaxing annealing, on the contrary, increases it. It was found that the microhardness and the nature of deformation near the indentation depend on the applied load. At low loads, the formation of shear bands is observed. With increasing load, the tendency towards homogeneous deformation increases.

1. Introduction

Bulk metallic glasses (BMG) are an object of increased scientific interest due to their unique mechanical and magnetic properties, increased biocompatibility, and high corrosion resistance. However, the widespread use of amorphous alloys is significantly limited by their fragility. It is generally accepted that the mechanism of deformation of amorphous alloys at room temperature is the formation and propagation of shear bands [1,2]. However, on thin amorphous films, homogeneous deformation is possible, at which shear bands either do not appear or are indistinguishable [3,4].

It is assumed that the carriers of deformation are some mobile formations – shear transformation zones (STZ) – containing excess free volume [1,5], which is an important parameter characterizing the structure of amorphous materials. Its existence has been proven by various methods, for this, X-ray diffraction (XRD), differential scanning calorimetry (DSC), weighing method and others were used [6,7]. It is assumed that excess free volume affects the properties of amorphous materials, including microhardness. In this case, not only the value of the microhardness is important, but also the profile of the piles near the indentations, which makes it possible to evaluate the nature of plastic deformation when the diamond indenter is pressed in [8].

Severe plastic deformation (SPD) can be one of the ways to influence BMG structure and change their properties. SPD, and, in particular, high-pressure torsion (HPT), is an effective way to transform the structure of metals and alloys [9,10].

The microhardness of amorphous alloys after HPT can both decrease, which is shown, for example, for Zr₄₄Ti₁₁Cu₁₀Ni₁₀Be₂₅ [11] and Zr₅₀Cu₄₀Al₁₀ [12], and increase – as shown on the alloy Zr₅₀Cu₂₈Ni₉Al₁₂.₃ [13]. In [14–16] a significant increase in the plasticity of amorphous alloys after HPT was found. At the same time, the increase in the plasticity of BMG after HPT remains controversial and insufficiently confirmed. We tried to evaluate the effect of indentation load on microhardness in this article, and the nature of deformation around indentations, as well as the effect of HPT on these characteristics.
2. Materials and methods

Plates of bulk metallic glass alloy Zr$_{52.8}$Cu$_{17.8}$Al$_{15}$Ni$_{14.4}$Ti$_{5}$ (at.%), also known as Vit105, manufactured by Liquidmetal (USA), were used as an initial material.

To carry out deformation by high pressure torsion, disks with a diameter of 10 mm and a thickness of up to 1 mm were cut from the initial material. Then the samples were subjected to HPT at room temperature and a pressure of 6 GPa, for 2 and 5 turns.

In order to determine the effect of structure relaxation and to minimize the free volume of the material, one sample was subjected to relaxing annealing at a temperature 420 °C, above the glass transition temperature, but below the crystallization temperature. Glass transition and crystallization temperatures were preliminarily determined by DSC [17].

An automatic microhardness tester EMCO-TEST Durascan 50, with load 50, 100 and 200 grams was used to determine the microhardness. At each load, the hardness was measured in series of 15 points located in 100 μm one from another. Standard deviation (SD) when measuring microhardness on the MMTV-MET standard sample was 10 units.

The relief near the indents was investigated by two methods: the presence or absence of steps was assessed using optical microscopy, and the microrelief near the indent was examined using atomic force microscopy (AFM) in contact mode on an Integra Prima scanning probe microscope, while the topography of the sample and its relief in lateral forces were recorded.

3. Results and discussion

An identical dependence of the microhardness on the indentation load is observed on the samples in all states. At low loads (50 g), the microhardness turned out to be ~40 units lower than at 100 and 200 g. This fact is interesting in itself, since it contradicts the usual laws for crystalline materials [18].

In the initial material, the microhardness is characterized by a small scatter of values, less than the instrumental error determined by the standard, which indicates a high homogeneity of the material (Table 1). At a load of 50 g, all indents have visible steps from the shear bands in the pile area. With an increase in the load, the determined value of hardness increases by ~40 units, and the proportion of indents with visible shear bands decreases to 15-20%.

Table 1. Average value and standard deviation (SD) of microhardness of Vit105 alloy in different states. The fraction of indents with visible shear bands near them is given.

| Condition                  | Indentation load |
|----------------------------|------------------|
|                            | 50 g             | 100 g            | 200 g           |
|                            | HV0,05 SD fraction | HV0,1 SD fraction | HV0,2 SD fraction |
| initial                    | 479 8 100%       | 520 9 20%        | 514 7 13%       |
| HPT n=2                    | 465 17 27%       | 499 11 13%       | 501 15 20%      |
| HPT n=5                    | 471 16 67%       | 511 17 20%       | 501 13 0        |
| relaxing annealing         | 494 10 87%       | 532 13 73%       | 521 9 27%       |

In the material subjected to HPT, there is a slight decrease in microhardness in comparison with the initial state, by 15-20 units, but its values have a rather wide scatter, which can be seen from an increase in the standard deviation to 11-17 units, which is higher than the instrumental error. Also in the piles around the indents, steps from the shear bands are observed, near most of the indents at low load (50 g), and near only a few at 100 and 200 g.

Relaxing annealing leads to an increase in microhardness by 10-15 units, while the scatter of microhardness over the sample is small, within 10-13 units. Figure 1 shows images of indents after indentation with a load of 50 g, 100 g, and 200 g.

The volume of material displaced during indentation should be located above the original plane and distort it in one way or another. The nature of this distortion is determined by the ability of the material to plastic deformation. It is known that the lower the plasticity of the material, the sharper the pile near the indentation site, and the less area of the material will be affected. This elevation will have the form...
of a wave [19], the height of which and the position of the crest are determined by the relative value of the plastically deformed volume. If the plastic deformation is determined by a relatively small volume, then the height of the wave will be large, and it will be in the immediate vicinity of the edges of the indent.

Figure 1. Indents of microhardness on the HPT \( n = 2 \) sample: a) indents with visible steps, load 50, 100 and 200 g; b) indents without visible steps, load 50, 100 and 200 g.

As shown by optical and AFM microscopy, piles near many indents are formed not only with the formation of shear bands, but, near many indents, without visible traces of shear bands. Direct comparison of the heights of the piles does not allow to estimate the change in plasticity. In [8] it was proposed to introduce a parameter of plasticity, that is, to correct the height of the heap by the value of the microhardness of the indent. Figure 3 shows the plasticity parameter for samples at 50, 100, and 200 g. With this method of correction, the volume displaced during indentation can be considered constant.

Figure 2. Relief near microindentation indents, in areas with steps (a, b), and in areas with homogeneous deformation (d, e), wave profile in areas with steps (c) and in areas without steps (f). Atomic force microscopy, topography (a), images in lateral forces (b, d, e).

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The authors of [8] believe that an increase in the height of the elevation testifies in favor of larger plasticity, which, however, contradicts the principles expressed in [19], according to which larger plasticity should manifest itself in the expansion of the deformation zone, rather than an increase in the height of the elevation. At the same time, the plasticity parameter, depending on the load, changes in
different directions with the accumulation of deformation. At a load of 50 g, it decreases, and at a higher load, 100 and 200 g, the plasticity parameter first increases for a low number of revolutions n, and then also decreases. Relaxation annealing leads to a decrease in the plasticity parameter at all indentation loads.

The high resolution and spatial nature of the data obtained using AFM makes it possible to study in detail the nature of plastic deformation near the indentations (Figure 2). Microhardness indents on all BMG samples have the correct shape, do not have a pronounced concavity of the sides. Some indents show slight edge convexity. The wave crest of the plastically deformed material is located close to the indentation. On the free surface of the samples, a micrelief is observed, which is probably associated with the polishing of the sample, the height of the elements of which is about 12 nm, the width of the micrelief elements is 0.25 μm.

It is generally accepted that at low temperatures, i.e. at room temperature, metallic glasses are deformed only with the formation of shear bands. However, as shown by optical microscopy, piles near many of the indents are not formed by visible bands, but rather represent a uniform elevation above the sample surface. While the formation and movement of shear bands is well described in the literature, the nature of such a uniform or quasi-uniform deformation is not entirely clear. At room temperature, diffusion processes, which strongly depend on temperature, are unlikely to happen. More probable is the assumption that this deformation is also carried out due to the formation of shear bands, but not expressed in the form of steps on the surface associated with the passage of the main bands, but microscopic bands evenly distributed over the volume of the material.

**Figure 3.** Plasticity parameter for initial, HPT n=2, HPT n=5 and subjected to relaxation annealing samples.

There is a tendency to the formation of shear bands at low loads, and at the same time - to their disappearance at high loads. Such features of the behavior of the material under various loads may be explained as follows. The microindentation cycle consists of the following sections - application of a load, holding under a load, unloading, and loading. In this case, at different applied loads, in fact, different strain rates are realized in the material. At the same time, it is known that the strain rate sensitivity parameter for bulk metal glasses can range from negative values, i.e. m = -0.0026 [20] to small positive, i.e. 0.036 [21]. Strain rate \( \dot{\varepsilon} \) is related to the flow stresses by the relation, where \( \dot{\varepsilon} \sim \sigma^n \), and n is the exponent of stress, equal to \( n=1/m \) [22]. Thus, metal glasses exhibit a high sensitivity of the strain rate to flow stresses. The deformation pattern at different speeds is as follows. Shear transformation zones (STZ) have some mobility in the material, and this mobility is very limited. If deformation occurs at a low rate, then STZs are able to unite, forming an intense shear band, which comes out to the surface in the form of a clearly visible step. The accelerated formation of shear transformation zones can be promoted by an increase in temperature near the region of the shear band [23]. If the deformation is carried out at high rates, an intense shear band is not formed, and the deformation looks more uniform.

Severe plastic deformation increases the nonequilibrium of the structure, imparting an additional free volume to it, presumably due to an increase in the number of elementary carriers of deformation - shear
transformation zones, which can stimulate deformation. This is supported by a decrease in the microhardness of samples subjected to HPT (Table 1). An increase in the STZ number provides many points of band nucleation and leads to an increase in the number of bands with a simultaneous decrease in their scale to the nanometer level and, as a consequence, to a more uniform deformation, including at low loads and deformation rates. The development of coarse bands increases the likelihood of cracking, while uniform deformation can increase ductility.

4. Conclusions
Plastic deformation of bulk metal glasses has a complicated, complex nature. Apparently, there are two ways of deformation – in the form of shear bands generation and propagation, as well as a homogeneous flow of the material, the carriers of which can be fine elements of the internal structure, such as nanobands, which do not appear in the form of steps. HPT leads to a decrease in microhardness, which indicates an increasing free volume of the material. In this case, HPT also leads to an increase in the inhomogeneity of the microhardness values. In turn, the excess free volume facilitates the formation and movement of a large number of microbands, which is expressed in the form of quasi-uniform deformation near microhardness indents. HPT is able to increase the plasticity of the material.

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