

Influence of laser irradiation on change properties of bulk amorphous Zr-Pd metallic alloys

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Abstract. We study the morphological features of laser irradiation zones formed on the surface of the bulk metallic glasses. We use the nanoindentation method for estimation alloys properties caused by impulse heating during irradiation.

1. Introduction

There are many investigations [1-6] of new class of amorphous materials so-called bulk amorphous metal alloys (AMS) or metallic glasses (MS) during last decade. Alloys based on ZrC are especially interesting among bulk MS [7, 8] because they have very wide supercooled liquid region which exceeds 100K for a number of alloys. These alloys are of interest in connection with the possibility to obtain nanocrystalline structure [9] by heating. Palladium-based alloys are highly resistant to damages. They combine hardness inherent in glasses with typical metal resistant for cracking. The high cost of palladium [10] is the root cause of narrow usage such glasses in technique.

A comprehensive study of the evolution structure regularities and mechanical properties of the heating bulk MS is an actual area of applied and fundamental research. MS evaluation of mechanical properties in the areas of local action, in particular, pulses of coherent radiation is practically significant challenge due to the fact that the laser radiation is one of ways to heating treatment. Objective: To establish the mechanical properties of bulk MS based on Pd and Zr, and a study of morphological features of regions formed as a result of action of laser radiation.

2. Materials and methods

We investigate bulk MSs based on zirconium and palladium. We use in experiments samples with dimensions 2x5x4 mm for both systems: Zr - Ti - Cu - Ni - Al (52,5% Zr) and Pd - Cu - Ni - P (40% Pd). We use as a laser light source "LTA-4-1" with the active element based on yttrium aluminum garnet doped with neodymium (Nd: YAG), with a wavelength $\lambda = 1064$ nm, which allows to obtain different forms of impulses and energies. We use device IEM-4-1 for the energy and influence time of the laser impulse measuring. The pulse duration $\sim 2-4$ ms. We use pulses with an energy of 0.6 J / mm². We affect on surfaces of amorphous alloys by laser radiation in a mixture of argon and air. We prepare working surfaces as a metallographic grinding. We measure material properties changing after laser radiation by the method of nanohardness measuring by Nano Indenter G200 with diamond Berkovich indenter with a radius of blunting on the top $R = 20$ nm and the loading mode with constant relative deformation rate of 0.1 s⁻¹. Amplitude (2 nm) and frequency (45 Hz) of harmonic component of the load keep constant. We use for investigation of morphological features and elemental surfaces composition by scanning ion-electron microscope Quanta 200 3D.



The focused pulsed laser radiation forms local areas of irradiated material on bulk MS surfaces (Fig. 1). Each area has its own morphological features.

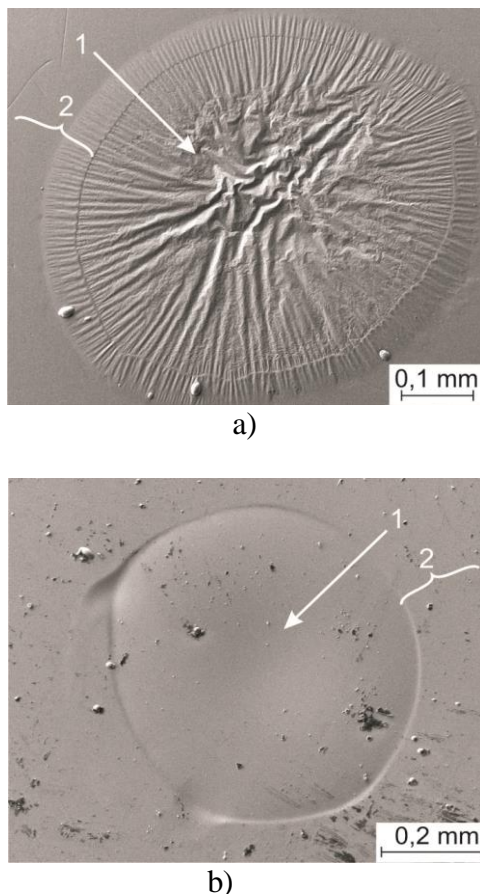


Figure 1. The morphology of the laser irradiation areas: a) Zr -based alloy MS; b) Pd -based alloy MS. 1– region of the melting, 2– heat-affected area.

Affected areas in bulk AMS have a “rosette”-appearance consists of radially growing crystals formed in the central region of the melting. The affected areas dimensions are vary depending upon the impulse energy and it ranges from 0.4 mm to 0.6 mm. There are two areas: melting area and heat-affected area. We see crystallization out of melting area, which is not related to material melting. The surface temperature at the center of the radiation-affected area is not lower than the melting temperature (~ 18550 C). The temperature of melted abroad area is not less than crystallization temperature (450^0 C by DSC researches).

The relief formed on the surface relates with volume effect during crystallization. Dilatometric researches confirm it. Our dilatometric researches demonstrate that the crystallization of the sample based on alloy Zr occurs in two stages. Volume effect corresponding to the second conversion step is more than volume effect in the first stage. Full volume effect of crystallization is about 2%, which is a typical value for the crystallization of metallic glasses [11].

We see the presence of the crystallization in the laser affected area [12] (Fig. 2). Radiographic researches confirm this.

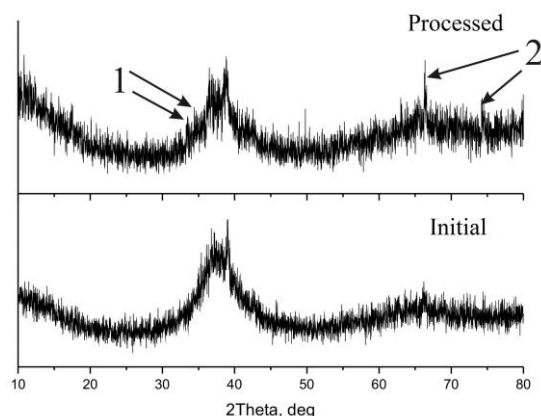


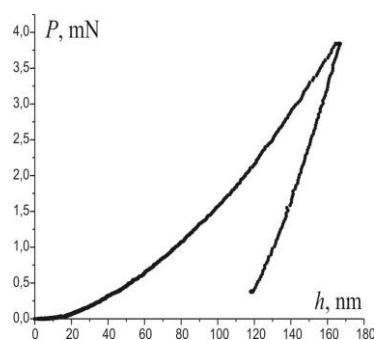
Figure 2. The diffractograms of Zr-based alloy surface: in laser irradiation area and fresh surface. Arrow 1 shows the peaks linked with crystallization, 2 - peaks linked with the oxides of zirconium formation.

We do not observe any structural changes in the center of the affected by radiation zone in Pd-based alloy (Fig. 2b). The impact zone has appearance of a "moon crater". Metallographic method cannot detect affected by heating zone. Crystals are growing after the rising of impulse quantity in Zr-based alloys. Changes in affected area in Pd-based alloys are not significant.

We determine element compound in different points of affected areas. It presents that oxygen contents in the middle of affected areas in Zr-based alloys is growing more than 4 times in accordance with fresh material. There are not any same changes in Pd-based alloys.

We use the nanoindentation-method for researching of mechanical properties in laser affected areas which are formed on bulk MS surfaces in comparison with fresh condition.

Figure 3 shows P-H diagram for Zr-based alloy before irradiation. We can select several typical sections on this diagram: monotonic increase h during increase of load and creep. Diagram P-h for fresh material has differences from diagram inside irradiation zones for both values – P and h . In addition, P-h diagrams occur into irradiation zones and are followed by irregular deformation during indenter indentation (fig.3b). Values of P and h are close to values of P-h of fresh material.



a)

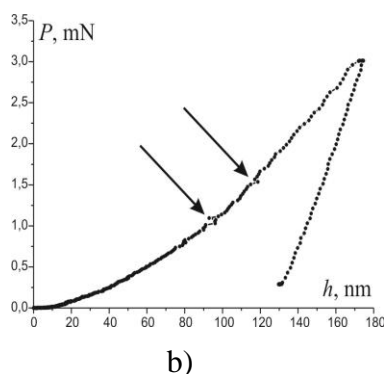


Figure 3. $P - h$ diagram for Zr-based alloy a) fresh condition б) in affected area; P – load, h – the indentation depth, arrows mark the plot of changing deformation.

We can see $P-h$ diagrams on fig.4 for Pd-based alloy inside and outside of affected area. They are similar. We can separate typical sections: monotonic increase h during increase of load and irregular increment of h .

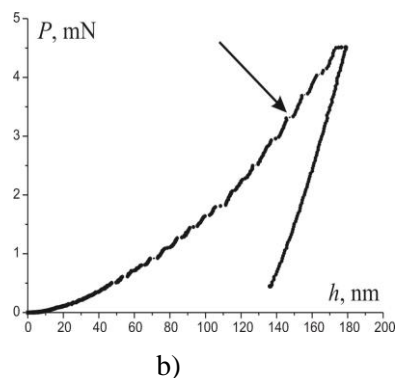
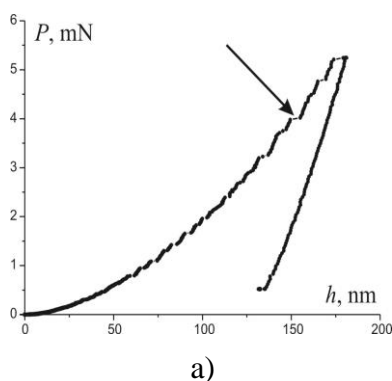


Figure 4. $P - h$ diagram for Pd-based alloy: a) fresh condition, б) in affected area arrows mark the plot of changing increment h .

Based on our experiments results we calculate nanohardness (H) and Young's modulus (E) inside irradiation zone and in fresh condition for researched alloys (see table).

Table 1. The mechanical characteristics of alloys in irradiation area and in fresh condition.

	Alloy	H (GPa)	E (GPa)	H_{out}/H_{in}	E_{out}/E_{in}
Zr-based alloy	in irradiation area	$4,3 \pm 0,5$	$90,2 \pm 5$	1,8	1,08
MS	fresh material	$7,8 \pm 0,5$	98 ± 5		
Pd-based alloy	in irradiation area	6	96,5	1,1	1,05
MS	fresh material	6,7	101		

3. Discussion of results

We interpretive this results next ways. Structure changed bulk glass→GPU crystal is the root cause of nanohardness (H) and Young's modulus (E) variation in Zr-based alloys. GPU- crystals growth is parallel to observe plane along the main c-axes. In connection with this the basal plane (0001) – easy glide plane – becomes the area of crystals deformation. We connect this reason with lower values of nanohardness and Young's modulus. Based on chemical composition of Zr-based alloys we can make a conclusion that oxygen, which is rising into irradiation zone, react with Zr. This reaction produces poorly soluble oxides which become central points of crystallization. Also such oxides are the root cause of crystals rising into the heat affected area. We research laser affected zones by a probe microscope. We can determine linear crystallization central points along the border of melting. Values are in the range from 900 to 2100 cm^{-1} (Fig.5).

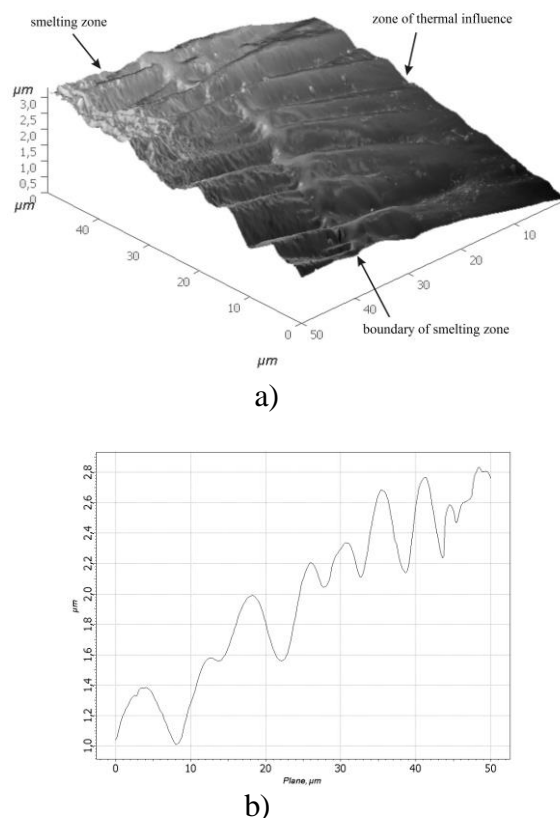


Figure 5. The crystallization on the surface of the heat affected area (a) and its profilogram in the direction of transverse to the crystal growth direction (b).

We can confirm of ZrO₂ inclusion inside the irradiation affected area by $P - h$ diagram (Fig. 3b). Deformation jumps onto diagram (Fig. 3b) are connected with the formation of microcracks. The values of the Young's modulus and nanohardness, which we calculate for this chart, are close to the corresponding values of zirconium ceramics [13]. We can see processes of the secondary vitrification in irradiation affected areas of Pd-based alloy. This is due to high values of viscosity coefficient of Pd-based alloy and thermal conductivity [14]. First complicates crystal growth the second - ensures rapid dissipation of thermal energy in the sample. Derating E and H for 5% and 10%, respectively, may be associated with a decrease of initial hardening stresses inside irradiation affected zones. Thus we make a conclusion that laser pulse changes mechanical properties of researched material by the result of material local heating in affected area. Kind of irradiation affected zones in these cases is different, due to differences in thermal properties of materials. The directional solidification is coming in the center of the affected zone of Zr-based alloy. Crystals grow from the center to the periphery. The affected area on Pd-based alloy surface looks like "moon crater" without any heat affected area due to the high viscosity of the alloy, which prevents processes crystallization. The morphology of the affected zone on the surface of a Zr-based alloy depends on the shape and the number of impulses of the irradiation by laser. The laser irradiation forms on the Pd-based surface relief which form does not depend from shape and quantity of laser impulses. Nanoindentation method shows that affected zones values of nanohardness and elasticity module for volume Zr,Pd-based MSs are changed in comparing with the original material in the area of laser irradiation. In the Zr -based alloy the reduction of nanohardness and Young's modulus are related to the structural transformation of metallic glass=>GPU chip. In Pd-based alloy such reduction processes associated with secondary vitrification, which is going on the surface.

Acknowledgments

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