MILLISECOND LASER PROCESSING OF Cu-Zr-Ag-Al BULK METALLIC GLASS WITH SINGLE PULSES

V.A. Fedorov[1)], A.A. Shlykova[2)], M.F. Gasanov[3)]
[1-3)]*Tambov State University n.a. G.R. Derzhavin, 392000 Tambov, Russia,*
[1)]*feodorov@tsu.tmb.ru,* [2)]*alexandra.shlykova@list.ru,* [3)]*gasanovmf@yandex.ru*

Influence of laser emission on a $Zr_{46}(Cu_{4/5}Ag_{1/5})_{46}Al_8$ amorphous alloy was analyzed in the paper. A sample was exposed to single laser pulse impact of millisecond duration (3 ms) with 3 J energy. Subsequent research was performed with methods of autoelectronic emission scanning electronic microscopy and X-ray diffraction (XRD). In a COMSOL Multiphysics 5.2 package computer modeling of temperature fields generated by laser emission was performed. Crater topological singularities resulting from laser impact were explained in the paper. A specific role of atomic oxygen at nanocrystals forming was determined. Among other things it was demonstrated that manipulation with external factors such as presence of surface active agents (for example, oxygen) and cooling rate control can be used for production of amorphous composites with a preprogrammed structure.

Introduction

Bulk metal glasses (BMG) is a relatively new class of materials produced with quenching from a liquid phase at sufficiently low cooling rates. Amorphous alloys have a variety of advantages due to ordered internal structure absence, such as high strength, plasticity, low elasticity modulus [1] and superior corrosive resistance [2]; owing to that BMG can be used as constructional materials [3] and materials for bioimplants production [4, 5]. However, their industrial application becomes complicated due to unpredictable amorphous structure properties change when affected by various processing factors that can lead to crystallization [6, 7], structure relaxation [8] and phases separation. Understanding these processes and reducing their subsequent negative effect when obtaining new class of materials is the goal of this paper.

The paper is dedicated to the research of structural condition in an infrared band (λ=1064 nm) laser emission-affected area (i.e. a crater) of millisecond duration in a $Zr_{46}(Cu_{4/5}Ag_{1/5})_{46}Al_8$ bulk glassy alloy.

Experimental procedures

The used samples dimensions were 6×5×3 mm. Sample's surface was prepared as a metallographic specimen. The structure of the as-cast samples was examined by XRD and differential scanning calorimetry (DSC) at a heating rate of 20 K/min. For alloy irradiation solid-state laser single shots (Nd:YAG) were used with 1064 nm wavelength, 3 ms pulse length and 3 J maximal energy.

Micrographs of surface, elements distribution on the surface and sample's phases identification in laser emission-affected area were obtained using an autoelectronic emission scanning electronic ultrahigh resolution Zeiss Ultra plus microscope based on an Ultra 55 one.

Alloy surface X-ray diffraction patterns were obtained using a Rigaku UltimaIV X-ray powder diffractometer (CuKα, Kβ filter – Ni). X-ray diffraction patterns in a laser emission-affected area were obtained with a Diffray 401 X-ray diffractometer.

Temperature fields distribution computer modeling was performed in the COMSOL Multiphysics 5.2 package. A heat conduction equation complemented with the equations considering phase transition (a solid body-liquid) was used for modeling.

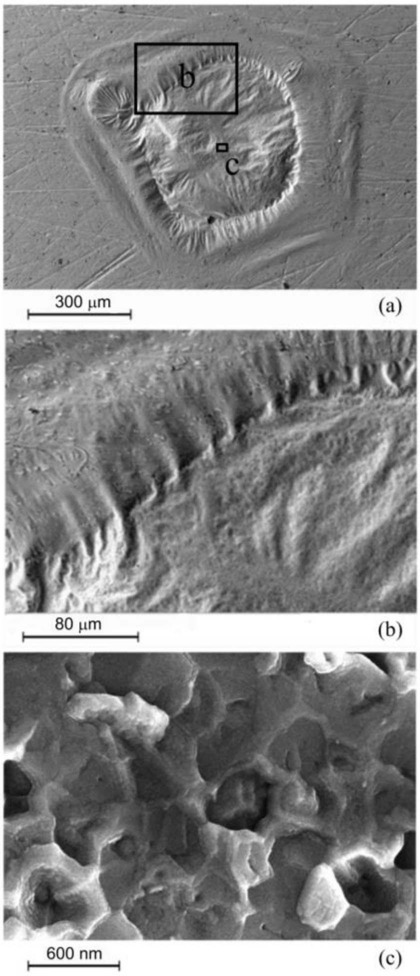

Fig. 1. A SEM micrograph of a sample surface in a laser emission-affected area of: (a) a crater, (b) a shear zone, (c) nanocrystals

The Bouguer-Lambert-Beer law was used for description of a heat source generated by laser heating. As a condition on sample's surface adiabatic boundary conditions were selected (i.e. thermal insulation); this is due to a short-time thermal effect as compared with thermal diffusion duration and ratio of laser heating zone and sample dimensions.

Results and Discussion

It was found that due to laser impact on a surface of the amorphous glass under testing a typical socket, i.e. crater is formed. According to qualitative observations of the SEM micrograph [see Fig. 1 (a)] it can be said that the volume of a new solidified melt is quite substantial. A crater surface can conventionally be divided into two areas. Zone I, in which melting occurred and Zone II, i.e. a shear zone [see Fig. 1 (b)].

Fusion zone geometrical dimensions make ≈500 μm in diameter. Computer modeling provides good correlation with the experiment. Numerical evaluation also showed that the temperature in crater's center reached 2500 K and melted surface layer depth equals to h≈60 μm.

A thermal effect zone, that is, an area where temperature was in the range from glass-transition temperature to melting one made ≈ 70 μm.

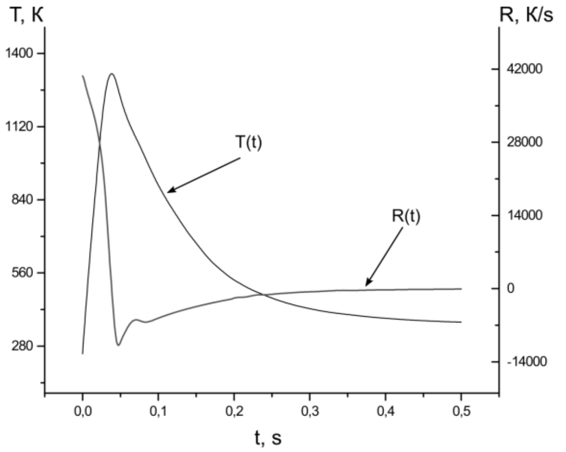

Fig. 2. Temperature in a point of a laser beam at a fusion zone edge ((h = 60 μm) from current time T(t); cooling rate R(t) at the same point

Nanocrystals formed [see Fig. 1 (c)] in an amorphous matrix were found in the first zone using scanning electronic microscopy and XRD. During the XRD, it was discovered that crystallites appeared to be crystal structures of the following composition: $Cu_{10}Zr_7$, $AgCu_4Zr$.

Modeling showed that cooling rate on sample's surface reached ~ 10^4 K/sec and drops to zero within a comparatively inconsiderable time range equal to 40 ms (see Fig. 2).

During the experiment at the observed cooling rate the growth rate is insufficient for crystals to fill crater's entire volume; and the resulting structure is a composite (an amorphous phase + nanocrystals).

Therefore, such high cooling rates should not result in crystallization and the melt after cooling should have an amorphous structure [9]. The reason for such behavior can be atomic oxygen absorbed from air due to oxidation reactions [10]. It is confirmed by crater surface elemental analysis data. Oxygen concentration in a surface layer along its radius to a fusion zone edge changes from 17 to 57 per cent (see Fig. 3). Among other things, modeling showed that dependence of crystallization rate along crater's radius fairly well correlates with oxygen distribution along the same line; that is, a slower crystallization front is able to absorb considerably more oxygen from air. It is also worth noting that difference in oxygen concentration does not essentially impact on crystallites size and form.

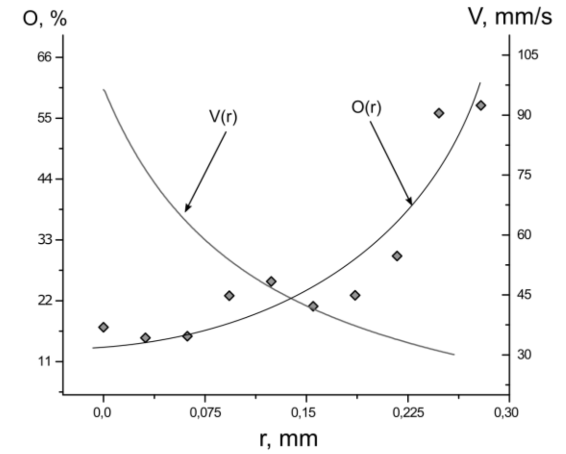

Fig. 3. Crystallization rate V(r) and oxygen concentration O(r) along crater radius

Conclusion

In conclusion, as part of this project, the influence of laser impulse on the surface of $Zr_{46}(Cu_{4/5}Ag_{1/5})_{46}Al_8$ was analyzed, computer modeling of laser heating processes was performed, and crater topology and changes due to laser impact were explained.

A specific role of atomic oxygen and melt zone cooling rate in nanocrystals formation was shown and the oxygen absorption from air, which leads to crystallization center formations, that solidify after this phase and form a composite structure were explained.

Finally, developing technologies aimed at regulation and control of sorption processes will allow for the possibility of engineering "preprogrammed" structures on the surface of BMG.

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