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Manifestations of point and extensive defects of bulk-metallic glasses

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ABSTRACT

In spite of the fact that the one-parameter free-volume model is inadequate to provide a reasonable description of structural defects of bulk-metallic glasses (BMGs), this model is still in use due to its simplicity and conformity with naive ideas on the BMG structure. Meanwhile, the polycluster model of the metallic-glass structure takes into account the occurrence of locally preferred short-range and medium-range ordering, stable point defects (vacancies, interstitials, semi-vacancies, semi-interstitials, and impurities), and extensive defects (dislocations, cluster boundaries, and triple joints). Some of the defects, such as cluster boundaries and triple joints, are accessible for the direct observation by means of the field-emission microscopy (FEM). Others manifest themselves in macroscopic kinetic and mechanical phenomena. In this report, we briefly describe the point and extensive defects of metallic polyclusters and present some results of direct and indirect observations of their manifestations. The cluster boundaries, triple joints, and sub-clusters are identified by means of FEM. Vacancies and short-range ordering are revealed through the recovery annealing kinetics of BMGs irradiated with 2.5 MeV electrons. Since the vacancy production by irradiation is accompanied by the generation of interstitials (due to the Frenkel-pair formation), one can consider these results as an evidence of the interstitial formation in BMGs. However, the stability of interstitials in metallic glasses remains to be investigated. A pronounced manifestation of dislocations (first of all, cluster-boundary dislocations) is the Kaiser effect observed in a set of BMGs. A discussion of the observed phenomena is given.

1. Introduction

To justify the structure-model applicability for amorphous solids needs thorough investigations of microscopic, mesoscopic, and macroscopic structure features of representatives of the solids. Especially the point and extended defects have to be thoroughly identified. Recently, we have given a brief overview of the results of direct and indirect investigations of the bulk-metallic glasses (BMGs) structure and structure defects [1]. In this communication after the brief information concerning the direct observation of the polycluster structure of the ZrTiCuNiBe BMG and evidence of the existence of the stable point defects in ZrTiCuNiBe and ZrTiCuNiAl BMGs, we report the presence of the Kaiser effect in ZrTiCuNiBe, ZrTiCuNiAl, and ZrCuAlEr BMGs. Since the Kaiser effect is attributed to the motion and pinning of dislocations, we conclude that dislocations exist and play an important role in the mechanical processes of metallic glasses.

2. Experimental

The field-emission-microscopy technique [2,3], the electron irradiation, accumulation and the recovery kinetics measurements [4] as well as the acoustic-emission (AE) study have been used for the experimental investigation of the BMG structures and defects. The AE experiments were performed using $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$, in atomic percent (at.%), bulk-glass samples with diameter, $d_0 = 3$ mm, and height, $h_0 = 4$ mm, and $Zr_{46.25}Cu_{45.25}Al_{7.5}Er_1$, at.%, samples with a square cross-section lateral length of $a = 2.6$ mm and height $h_0 = 5$ mm. The samples were cut from rods by the electric-spark method. The acoustic-emission study and facility were described in details in Refs. [5,6].

3. Results and discussion

3.1. Observation of polycluster amorphous structures and intercluster boundaries

The structure consisting of the set of conjoining locally regular clusters (LRCs) is named as the polycluster structure [7,8]. There are the intercluster and inner boundaries – finite two-dimensional layers with a broken local atomic order. The polycluster structure is a result of the continuous phase transformation with which the solid-like LRCs grow in the liquid (see Refs. [9–11]). The

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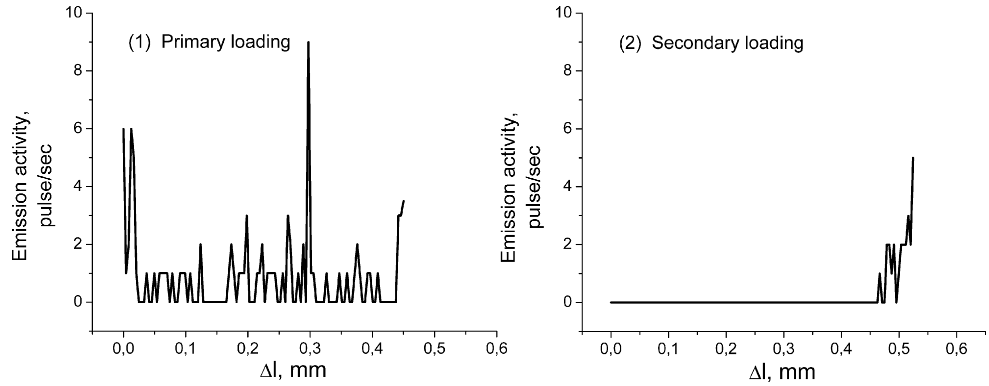

Fig. 1. (1) AE activity vs. deformation, Δl, during the primary uniaxial loading of $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ BMG sample; (2) AE activity vs. Δl of unloading during the secondary loading after primary loading of $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ BMG sample. Compressive stress maximum during the secondary loading was 190 kg/mm^2 [6].

polycluster structure and intercluster boundaries were observed by means of the field-emission microscopy. The intercluster boundaries are clearly seen in the obtained images of the BMG, $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ in atomic percent (at.%) [1,2,5,12,13].

The cluster sizes of Zr-based BMGs are varying from 5 to 15 nm. The same cluster sizes are observed in thin metallic glassy ribbons obtained at large cooling rates [8]. A weak dependence of the mean LRC size on the melt cooling rate shows that the density of the cluster growth centers is large (as it has to be in the heterophase liquid state [9–11]), and the cluster structure relaxation time is large compared to the melt cooling time for both BMGs and thin ribbons. Thus, the density of boundaries in metallic glasses is $\sim 10^8\ m^{-1}$. This fact is important for understanding the radiation resistance and peculiarities of the mechanical properties of the metallic glasses [1,3,7,8].

3.2. *Point defects of BMGs*

To generate the point defects in BMGs, the electron irradiation was used. The kinetics of accumulation and relaxation of radiation defects in BMGs of two compositions, $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ in at.%, was studied [4,14,15]. The specimens were exposed to 2.5 MeV electrons at ~80 K. The technique of the low-temperature electron irradiation of the specimens with their subsequent isochronal annealing at temperatures between 85 and 300 K was used.

The recovery curve and its derivative (spectrum) at the isochronous annealing of the irradiated samples were obtained. Two annealing stages are revealed at $T \sim 130$–150 K and $T \sim 225$ K with estimated effective migration energies of $E_{150\,K} = 0.46$ eV and $E_{225\,K} = 0.69$ eV for these glasses.

The observed annealing stages are attributed to the vacancy kinetics. They suggest that the vacancies are stable in metallic glasses, and their mobility is a thermally activated process. The activation energy of the vacancy migration in the glass is lower than that in crystals. Since the vacancy production by irradiation is accompanied by the generation of interstitials (due to the Frenkel-pair formation), one can consider these results as an evidence of the interstitial formation in BMGs. However, the stability of interstitials in metallic glasses remains to be investigated in details.

3.3. *Manifestations of the boundaries and dislocations of BMGs during mechanical processes*

Although a direct observation of dislocations in BMGs is a difficult problem due to the lack of the structure translational invariance, there are typical processes and effects in solids, which are controlled by the dislocation motion. Thus, the dislocation motion in BMGs can be detected by the observation of these effects.

Evidently, the energy of the boundary-dislocation formation is considerably lower than the energy formation of a dislocation in the cluster body. For this reason, dislocations within the cluster boundary layers are forming and climbing at a much lower shear stress than in the cluster body.

The acoustic-emission study is a known method of the identification of the microscopic and mesoscopic inelastic structure

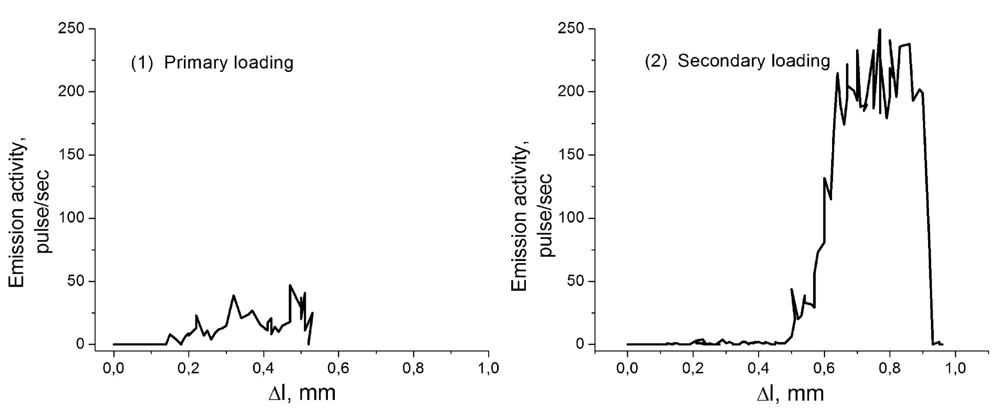

Fig. 2. (1) AE activity vs. deformation, Δl, during the primary uniaxial loading of the $Zr_{46.25}Cu_{45.25}Al_{7.5}Er_1$ BMG sample; (2) AE activity vs. Δl of unloading during the secondary loading after primary loading the $Zr_{46.25}Cu_{45.25}Al_{7.5}Er_1$ BMG sample (sample was brought to destruction). Ultimate compressive strength during the secondary loading was 182 kg/mm^2.

changes under an external stress [5]. The Kaiser effect appears during testing samples in the repetitive loading and unloading regimes and is found in the fact that the acoustic emission originates in each subsequent loading only when the stress exceeds its maximum value achieved in the preceding loading. It is known that the Kaiser effect in crystals is caused by the dislocation motion under the stress and consequent pinning in a non-equilibrium state when the specimen is unloaded.

A dislocation can be prepared in any continuous elastic medium by means of Volterra procedure: cut + shift + "glue". Therefore, if the Volterra dislocation is stable and if the width of the glued cut layer, d_c, and size of the dislocation core, ρ_d, are much larger than the atom diameter, a, one can accept the existence of these defects in the material. Exceptional property of the dislocations in translation invariant structures is that $d_c = 0$, if the cut is made along a proper atomic plane, and $\rho_d \sim a$. The antiphase boundaries and stacking faults, accompanying dislocations in multicomponent alloys, have non-zero widths, $\geq a$. In these materials, $d_c \sim a$. The cluster boundaries are natural cuts within polyclusters. While they are not planar in general, the boundary-dislocation loops can be formed within the boundary layer under a shear stress. These dislocations are responsible for the Kaiser effect in metallic glasses [5,6].

In Refs. [5,6,16], the Kaiser effect was observed in ZrTiCuNiBe and ZrTiCuNiAl BMGs. Recently, we have studied this effect also in the $Zr_{46.25}Cu_{45.25}Al_{7.5}Er_1$ BMG. Results of the Kaiser effect observation in the mentioned BMGs are presented in Figs. 1 and 2.

As pointed out in Refs. [5,6], the acoustic emission in BMGs under deformation is initially caused with the motion of the boundary dislocation and, then, with the penetration of dislocations in the LRCs body at triple joints. The Kaiser effect in BMGs of different compositions suggests that the carriers of the plastic deformations have the same structure in all glasses. This conclusion is supported by the data of the field-emission microscopy (Section 3.1).

The given examples show that the extensive defects are resident in metallic glasses and are manifesting in the inelastic mechanical processes.

4. Conclusion

Direct and indirect observations show that the point and extended defects, such as dislocations, and cluster boundaries – are stable in BMGs. They are manifesting in the recovery annealing kinetics of irradiated BMGs and in the Kaiser effect.

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