

BEHAVIOR OF AMORPHOUS METALLIC ALLOYS UNDER THE ACTION OF DESTABILIZING INFLUENCES

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Abstract. The paper describes the investigations on the change of metallic glass (MG) plasticity for two techniques of annealing: on a ceramic substrate and in stable plates at different temperatures. The change of metallic glass mechanical characteristics under action of laser irradiation and the behavior of annealed metallic glass under the uniaxial tension are studied.

1. INTRODUCTION

Metallic glasses (MG) play an important role as promising materials of new generation. The attention to MG grows because of unique combination of high parameters of magnetic characteristics, durability, hardness, resistance to attrition, specific electric resistance, stability to radiation and corrosion; in this connection they in many respects surpass traditional crystal metals. Now amorphous alloys are known for many metallic systems [1]. During practical use of MG, questions about their thermal stability arise. Under the influence of different destabilizing factors (irradiation, mechanical and/or thermal influences, chemical processing), there exist transition to new, more stable state. The transition is accompanied by the change of the set of properties for MG; in particular, the essential decrease in macroscopical plasticity [2]. Because of this, the problem of thermal stability for MG and the control over change of physicommechanical characteristics of MG is one of the biggest problems in physics of disordered environments. Thus, the problem of MG thermal sta-

bility, arising normally during annealing, is an important part of physics of disordered systems [3].

The research described in the paper is devoted to the following questions:

- change of MG plasticity for two techniques for annealing: on a ceramic substrate and in stabilizing plates at different temperatures;
- change of MG mechanical characteristics due to the action of laser irradiation;
- behavior of annealed MG under the uniaxial tension.

2. EXPERIMENT METHODOLOGY AND MATERIALS

The experiment was conducted on the Co-based metallic glass that was received by fast hardening from melt (melt-spun). The tapes thickness was 20 microns. The samples of the size 3.5×15 mm, 3.5×20 mm, and 3.5×90 mm were used for investigating plasticity, microhardness and durability, respectively.

Before the test, the samples were subjected to the isochronal annealing in a furnace at the given

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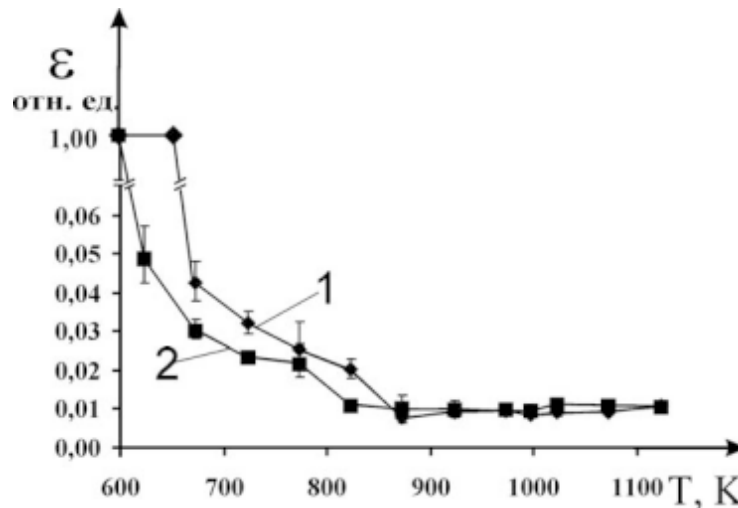


Fig. 1. Dependence of plasticity on annealing temperature: 1 – on ceramic substrate; 2 – in stabilizing plates.

temperatures for 10 min. The time was recorded from the moment of placement of the samples either on a ceramic substrate or in the region between plates. Furnace annealing on a ceramic substrate is accompanied by the temperature drops due to loading and unloading samples. Because of this, for the MG ribbon samples, the annealing technique for stabilizing plates with the big thermal capacity was offered. The given temperature between plates remains practically constant during sample loading, leading to the annealing mode optimization [4]. The output time for an annealing mode in stabilizing plates is much less than on a ceramic substrate which mostly correspond to the annealing time at the given temperature.

The bend method [5,6] was used to investigate the character of change of MG plasticity depending on annealing temperature. The plasticity measure was estimated from expression [5]:

$$\varepsilon = h / (D - h),$$

where h is the ribbon thickness, D is the distance between the parallel plates at which the arched sample collapsed.

The influence of laser irradiation on the MG surface was carried through the optical quantum generator "KWANT-15" with radiation wavelength = 1064 nanometers. The impulse energy was varied within the limits of $E = 4-6$ Dzj/cm². The impulse duration was made 4 ms.

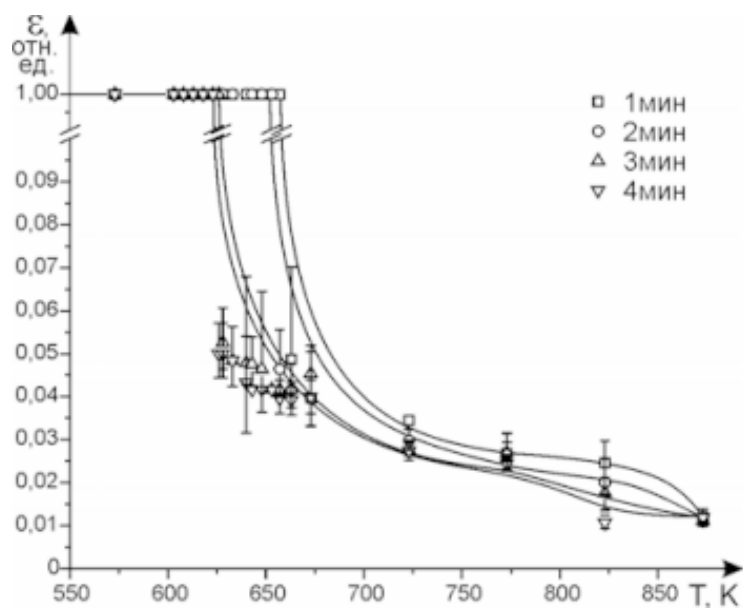
Indentation of irradiated ÌG, as well as research on the type of deformation and destruction, was

conducted with the help of PMT-3 microhardness gauge. Microhardness size was measured during indentation from the smooth surface of the ribbon (adjoining at reception to a hardening drum) as well as its face surface. Initial MG samples were put on a substrate for which there was used a polyester composite. The substrates with thickness ≈ 1 mm were preliminary put on a metal plate [7]. Specifics of preparation of samples for last technique consists of manufacturing compounds from epoxy resin with premise in it of ÌG and their subsequent mechanical polishing and polishing before indentation [8].

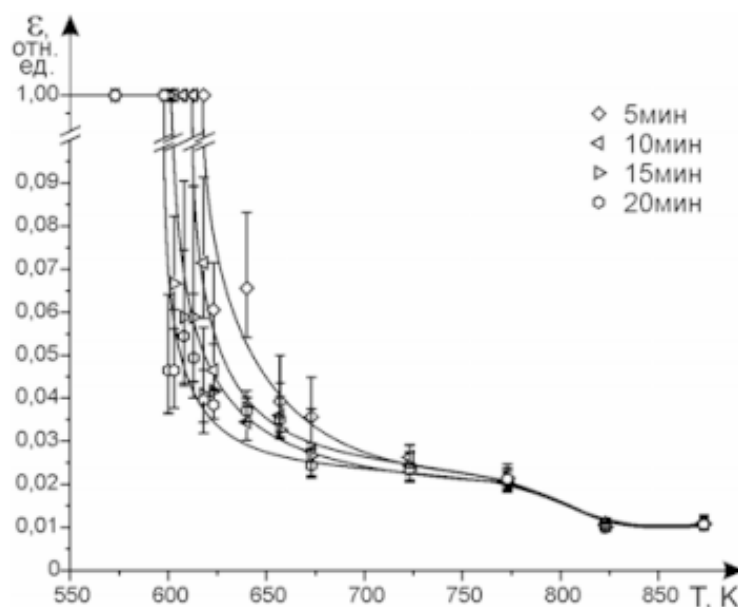
Experiments on uniaxial tension were conducted with the high rigidity machine Instron 5565. With this purpose, special captures have been made.

3. EXPERIMENT RESULTS AND THEIR DISCUSSION

At certain temperatures of preliminary annealing within the limits of the amorphous condition stability, noncrystal alloys become partially or fully fragile at room temperature. The phenomenon of amorphous alloys plasticity loss has not only purely scientific but also big practical interest. This phenomenon somewhat bounds the temperature interval for thermal processing of industrial alloys. It is known that the plasticity decrease occurs in two stages: first, at a low temperature; second, at a higher temperature. At the low-temperature stage



(a)



(b)

Fig. 2. Dependence of plasticity on an annealing temperature: a) 1 – with endurance of 1 min.; 2 – 2 min.; 3 – 3 min.; 4 – 4 min.; b) 1 – with endurance of 5 min.; 2 – 10 min.; 3 – 15 min.; 4 – 20 min.

of embrittlement, plasticity decreases from 1.0 to 0.1. At the second high-temperature stage plasticity changes within the limits of several hundredth decimal units. Besides it should be remembered that change in the interval by ± 0.1 lays within the bounds of the confidence interval for bend plasticity measuring. Thus, during the experiments, the second stage of embrittlement can be ignored. The

phenomenon of plasticity loss is well described in literature on annealing in vacuum [5]. Fig. 1 demonstrates the derived dependencies of plasticity on annealing temperature. Each point in the graph is found by averaging 10 measurements.

From the figure, it is seen that for the two techniques of annealing, the type of dependence of plasticity on temperature differs noticeably for tem-

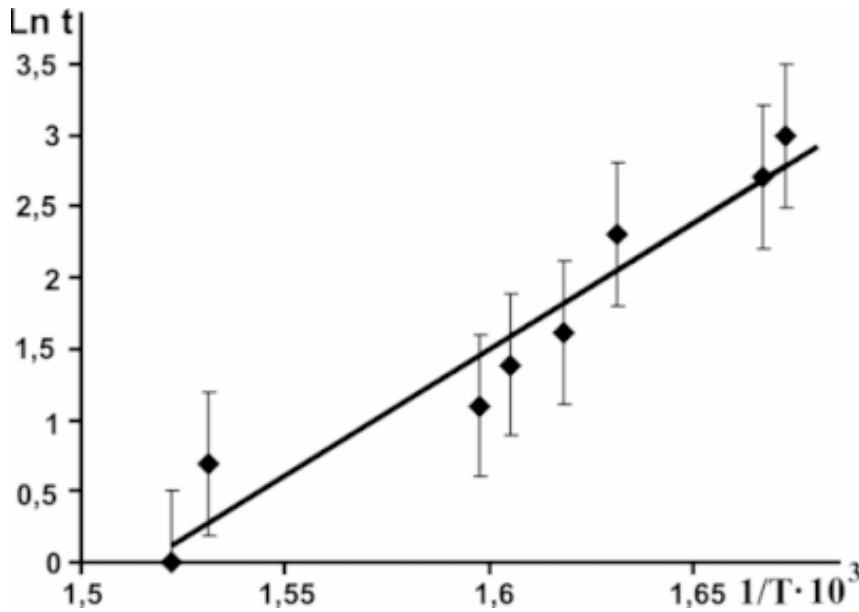


Fig. 3. Dependence of time on an annealing temperature.

temperatures up to $\sim 850\text{K}$, whereas for high temperatures the type of dependence is within the limits of measurement errors. The decrease in plasticity during annealing in stabilizing plates begins at the temperature smaller by 50K , than during annealing on a ceramic substrate. Two-level character of plasticity decrease is more noticeable during annealing in stabilizing plates. The annealing temperature that corresponds to the maximal embrittlement (minimal plasticity) was below by 50K compared with the annealing on a ceramic substrate. Moreover, the range of plasticity values at each temperature of annealing in stabilizing plates is significantly narrower. The experiments show that annealing in stabilizing plates allows sustain the given (pre-assigned) annealing mode more precisely, both with regard to temperature and to time, and as a consequence, allows estimate better the thermal stability of an alloy.

Further, the samples were subjected to isochronal annealing in the furnace with different time durances, ranging from 1 to 20 minutes in stabilizing plates. Fig. 2 shows the temperature dependence of plasticity for different annealing times. The first graph is for annealing on the ceramic substrate. The second graph is for annealing in stabilizing plates. It is possible to locate the temperature $T = 780\text{K}$ as the beginning of the second stage of decrease in plasticity. In Fig. 2a, up to this temperature the change of plasticity practically does not

depend on annealing time, taking into consideration the allowed errors. With increase in temperature, the curves differ and the type of dependency changes. The dependencies received characterize dynamics of plasticity decrease at the second stage. It is seen that for small annealing times (1-2 minutes.) some increase in temperature occurs, prior to the beginning of the second stage. The increase can possibly be caused by relaxation of hardening pressure, instead of transformations. The dependence in Fig. 2a at $t = 4$ minutes practically coincides with dependence in Fig. 2b for 5 minutes at $T > 780\text{K}$. In Fig. 2b, up to the temperature $T = 780\text{K}$ the dependencies characterize dynamics of the processes responsible for the plasticity decrease at the first stage. From literature, it is known that the main role in plasticity decrease plays excessive free volume and the character of its evolution under thermal influences on amorphous structure; and that this phenomenon has a relaxation nature. In Fig. 2a, the kinetics of evolutionary processes for small annealing times (1-4 minutes) can be observed. In Fig. 2b, at the first stage there is a free volume evolution that causes the plasticity decrease. At the second stage, at times 5-20 min., the evolutionary processes end and the plasticity-decrease dependencies merge into one curve.

From the figure, it is clear that with the increase in the annealing time the plasticity decrease be-

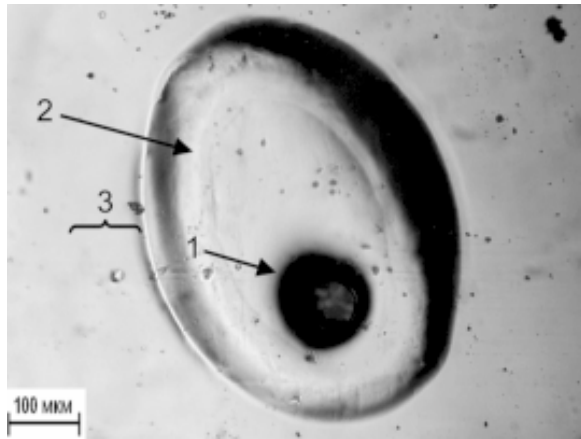


Fig. 4. MG surface area influenced by laser impulse: a 1-zone of annealing, a 2-zone of melting, a 3-zone of thermal influence.

gins at even smaller temperatures. The difference in dependencies is clearly noticeable at small temperatures. With increase in temperature and endurance time, the dependencies practically coincide within the limits of errors.

The critical temperature of embrittled annealing (the first stage of plasticity decrease) which value corresponds to decrease in value e of plasticity twice, with increase in time of endurance decreases (Fig. 2b). So for example, at endurance in 5 minutes, the plasticity decrease begins at temperature 623K, in 20 minutes – at temperature 603K, and at endurance in 60 minutes at temperature 593K. This testifies, certainly, that the embrittlement is inspired by thermal activation.

The experiments show that with small endurance times the first stage of plasticity decrease does not change. The second stage of plasticity decrease remains constant for larger annealing times.

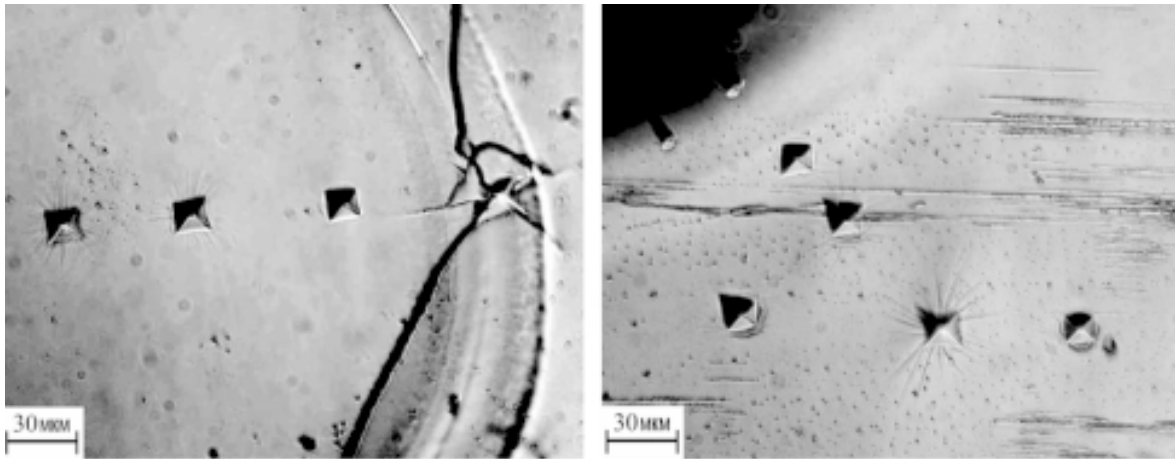
The results obtained are in agreement with data for plasticity change for annealing in vacuum, known from literature. The results allow define the temperature interval for thermal processing of industrial alloys, as well as to conclude that character of plasticity change has two-level one for all temperature-time annealing modes.

From the conducted research, the dependence allowing predict the annealing temperature and time, when the embrittlement has not started yet, was discovered (Fig. 3).

It was established that, because of the influence of focused impulse laser radiation on the areas of MG with diameter $d = 50-500$ microns, the local zones of irradiated material are formed. If the area of the irradiated surface is small and the radiation energy is sufficient, the melting is formed, approximately in the zone center. The zone dimensions for melting and annealing depend on the impulse energy and on the area of the irradiated surface (Fig. 4). The boundary of the melting looks like a “crown” consisting of stratifications melted off from the center of the material zone.

Microindentation of the zone of the laser-impulse-thermal influence leads to appearance of typical pictures of destruction. By analyzing these pictures, it is possible to locate zones that correspond to different physical transformations, occurring because of irradiation. Under irradiation with small energies, i.e. irradiation without full melting of a material in the center of irradiated area, there is sufficient plasticity; the imprint from an indenter is surrounded by multiple deformation strips oriented radially from the indenter’s border. With approaching the boundary of melting, similar imprints are not observed. In some cases, the indentation leads to alloy cracking along the boundary of the melting (Fig. 5a). Comparing morphology of the deformation zones in the laser radiation influence areas with morphology of the deformation zones of the furnace annealed samples, it is possible to draw conclusions about real temperatures for MG heating by laser radiation impulse. Then, removed by ~ 200 microns from the boundary of the melting, there exists another plasticity zone as well as characteristic imprints surrounded by radial deformation strips (Fig. 5b).

By investigating the MG microhardness after the influence of laser radiation on smooth and face surfaces, parameters and properties of zones of melting and of thermal influence were established. Microhardness (H_v) is maximal near to boundary of the melted area. It gradually decreases with moving away from the boundary, and at some distance, it takes on the value typical for non-irradiated alloy. After the influence of laser irradiation in amorphous matrix, crystal phase areas arise. With crystallization of amorphous substance, during occurrence and “optimum” distribution of the small disperse crystal particles, along the volume of the MG amorphous matrix, hardness grows. Cooperative processes of the beginning of the long-range order establishment, in turn, contribute to pore curing and excessive free volume diminishing [9]. It is believed that crystallization inside of the melted area



a)

b)

Fig. 5. Characteristic imprints from an indenter in a Co-based alloy: a) in the center of irradiated area without annealing; b) in process of removal from a boundary of melting.

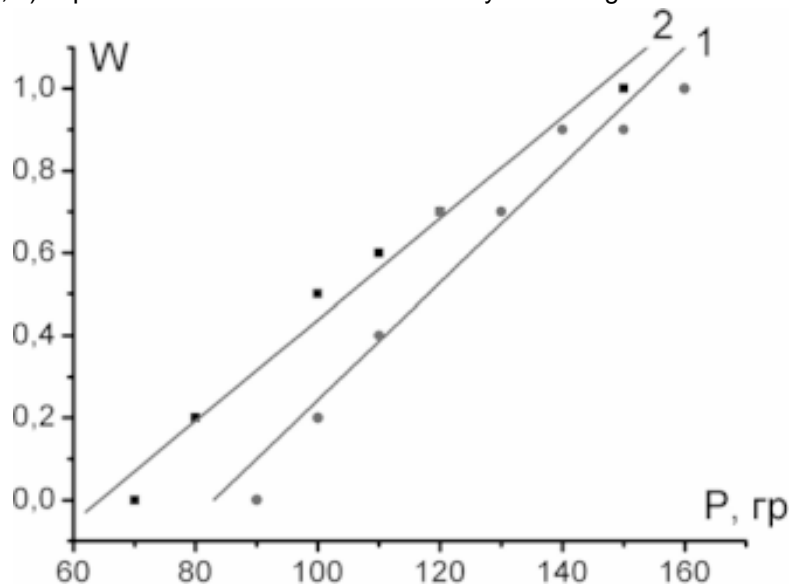


Fig. 6. Probability of crack formation (W) from loading (P) on indenter for MG sample, subjected to pulse laser irradiation – 2 and thermal processing at temperature $T_{an}=773K$ – 1.

leads to formation of large grains, possible change of a chemical compound because of evaporation of some components of an alloy. Change of microhardness in this zone has a monotonous character. The greatest growth of microhardness is observed near the boundary of the melting and is connected mostly with pressure appearing because of the formation of a transition zone from amorphous matrix with small disperse inclusions to areas with crystal phase. Due to the action of rather powerful and short laser impulse leading to local heating of a material, change of mechanical characteristics on the thermal influence zone boundary

is observed [10]. Cracks arise at indentation only in the zone of thermal influence or on the zone's boundary. Outside of thermally processed zone, viscous-brittle transition was not observed.

Each sample was repeatedly loaded by different loadings, starting from $P=40$ g when cracks are not formed, and gradually increasing with step 5–10 g until occurrence of cracks at each indentation. If there were cracks because of indentation, the probability of their formation (W) was considered to be equal to one. If cracks were absent, that probability was considered zero. From statistical analysis of the experimental data received for MG

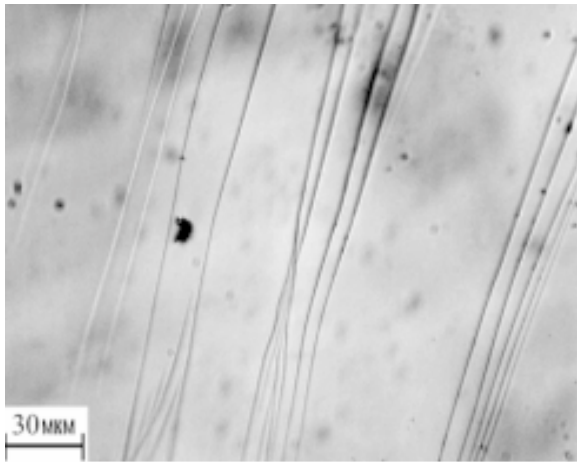


Fig. 7. Deformation strips received due to MG stretching: $T_{an}=473K$.

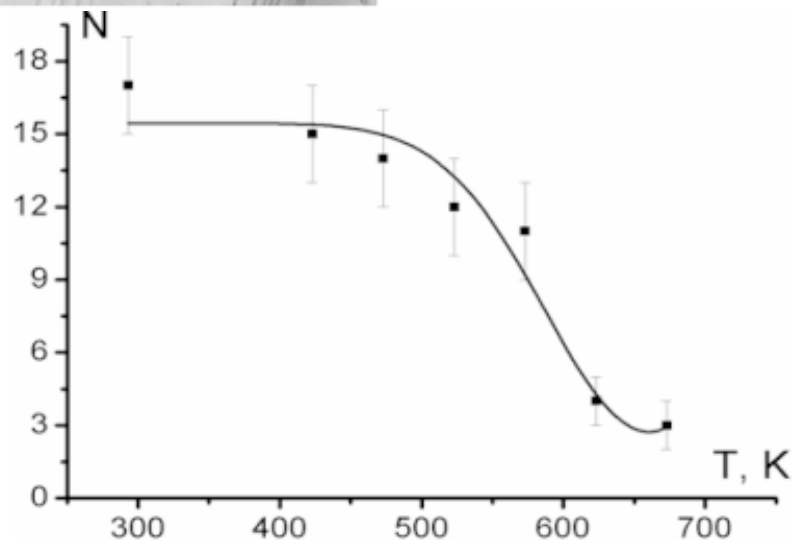


Fig. 8. Dependence of number of deformation strips on preliminary annealing temperature of MG.

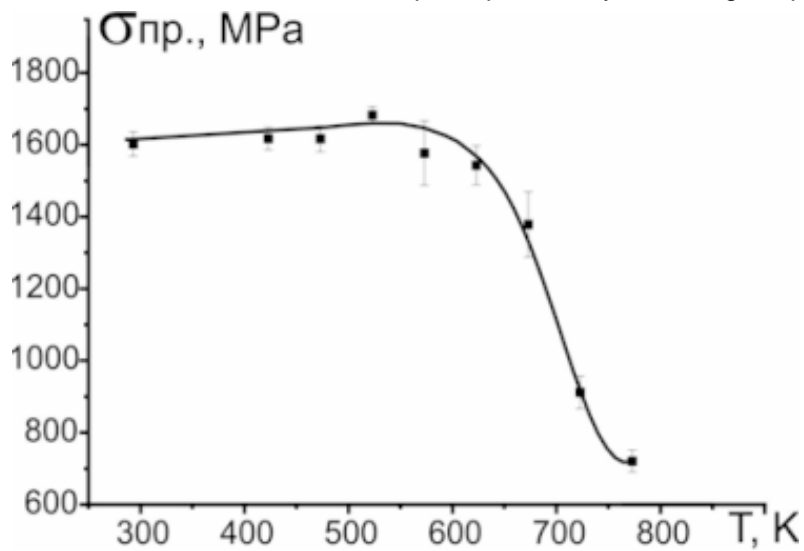


Fig. 9. Behavior of MG strength under thermal processing.

indentation, some laws of MG deformation and destruction were established.

It was found that the MG destruction, characterized by the probability of the cracks formation

and corresponding loadings, can be described with a linear function. It is established that heating of the boundary area of the irradiation zone is equivalent to furnace annealing at $T_{an}=773\text{K}$ for $t=10$ minutes. The straight line for this temperature heat treatment – line 1 in Fig. 6 – is well coordinated with similar linear dependence for laser irradiation – line 2 in Fig. 6.

Thus, the method for determining the cracks formation probability in MG from the loading on indenter allows, – based on comparison of $W(P)$ dependencies, obtained for furnace annealed samples, – estimate equivalent heating temperature for local laser treatment.

The uniaxial static tension showed that due to stretching and subsequent destruction of MG in a material, there were the deformation strips locally located across the length of the sample (Fig. 7). It was assumed that the deformation relief appears on the MG surface after destruction (unloading of samples).

The size, number, and width of strips depend on annealing temperatures. The deformation strips become later possibly the centers of origin of the microcracks, leading to catastrophic destruction of samples. Presence of shift strips point to localized current. With temperature growth the number of such strips decreases (Fig. 8). This is qualitative acknowledgement of the change of deformation character: from localized heterogeneous – to uniform homogeneous. Using uniaxial tension, the dependence of a fluidity limit on temperature of preliminary annealing ($\sigma_c(\tau)$) was discovered (Fig. 9).

The limit of strength weakly depends on temperature in the interval 293–623K, but at reaching $T_{an} = 673\text{K}$ sharp downturn of durability is observed. In free volume model the deformation occurs by nuclear moving along the mechanism of free volume diffusion. With increase of T_{an} , the free volume decreases [9], and, as consequence, the number of deformation strips decreases (Fig. 8). Thus, with annealing temperature growth, one of channels of pressure relaxation on concentrators disappears. Because of that, critical pressure (break pressure) on concentrators is reached at smaller values of the destructive load.

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