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EFFECT OF PULSED ELECTRIC CURRENT ON DEFORMATION OF AMORPHOUS AND NANOCRYSTALLINE METALLIC ALLOYS AGED IN ACIDIC ENVIRONMENTS

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Abstract. Specific features of deformation of amorphous and nanocrystalline metallic alloys influenced by pulsed electric current were studied. It has been discovered that passing pulse electrical current causes a momentary relief of mechanical stresses in loaded samples with its subsequent reduction. The effect of aggressive media (20 % solutions of H_2SO_4 and HNO_3) on the value of mechanical stress drop in samples of amorphous cobalt-based alloys and nanocrystalline iron-based alloy was also investigated. It depends on the tensile stess – tensile strain and occurs when electric current pulses are passing. The paper determines dependence of the mechanical stress value in tested materials on the density of pulsed electric current. It also investigates the structural and morphological state of the alloy surface after its exposure to aggressive media of different concentration.

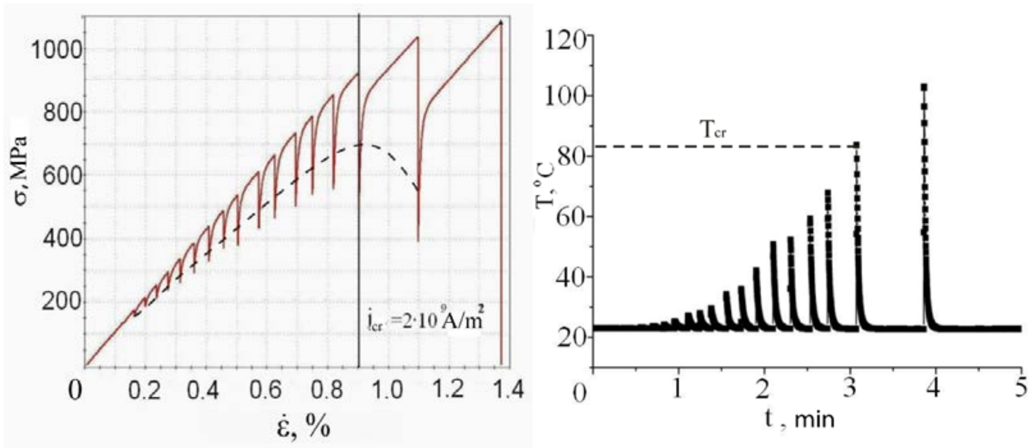
1. Introduction

It is known [1] that amorphous metal alloys have structural relaxation that leads to a change in physical properties of materials and their products. Structural relaxation apparently also occurs when amorphous alloys are heated by pulsed electric current. Expanding the range of application of amorphous and nanocrystalline alloys sets targets for study structure and properties of these materials after exposing them to various influences. These may be both stationary and non-stationary thermal fields, pulse and static electric and magnetic fields, and different media leading to oxidation and corrosion. Metallic glasses that have a high level of corrosion resistance show a significant sensitivity to the effects of hydrogen and corrosive environments, resulting in embrittlement of these materials [1]. Consequently, the study of the effect of pulsed currents and exposure to corrosive environments on the deformation and structural state of amorphous and nanocrystalline alloys is an urgent task.

2. Results and discussion

The following alloys were chosen for testing: amorphous cobalt-based metal alloys (AMAG-172–186) and nanocrystalline Fe-based alloy (AMAG-200) obtained by melt spinning. Sample dimensions: ~ 3.5 × 0.02 × 40 mm. The uniaxial stretching experiments were performed on the electromechanical machine for static testing Instron-5565. The current density (j), passing through the samples ranged from $1\ 10^8$ to $5\cdot10^9$ A/m^2. Pulses of duration τ_1 ~ 2.5 ms and τ_2 ~ 5 ms were used. Heating the samples during the whole process of deformation was controlled by the laser thermometer Testo-845 at the rate of 10 sec^{-1}. The phase composition of the samples was determined by X-ray methods using the X-ray diffractometer ARL X'TRA. 20 % solutions of sulfuric and nitric acids served as corrosive media. The samples were incubated for 40 minutes.

Deformation of amorphous metal alloys together with simultaneous passing of an electric current pulse on load charts is accompanied by a phenomenon similar to an electroplastic effect, which is well-studied for crystal structures [2, 3]. At the time when the current pulse passes, the stress-strain diagrams reveal a short (~1.1 s) mechanical stress relief $\Delta\sigma$ with further complete reduction of variation σ-ε (Fig. 1a). Moreover, the transmission of pulse electric current causes an abrupt short-term increase of the sample temperature (Fig. 1b). It has been noted that at the current density of $j \geq 4 \bullet 10^9$ A/m^2 depending on σ-ε amorphous metal alloys, there is a partially restored stress relief. As for the nanocrystalline alloy, a partially restored stress relief occurs at the current density $j \geq 8 \bullet 10^8$ A/m^2. The non-restorable stress relief is apparently connected with irreversible atomic rearrangements in the materials. The transmission of the pulse current reduces the ultimate strength of materials. Thus, after a series of 10 pulses of electric current at density of $6 \bullet 10^8$ A/m^2 the ultimate strength of amorphous alloys is reduced twice, and that of nanocrystalline alloy by ≈ 40 %.



а) б)

Fig. 1. Stress-strain diagram of an amorphous cobalt-based alloy (a) and the corresponding dependence of heating temperature of a sample on time (b) when exposed to 10 current pulses of duration $\tau \approx 5$ ms.

It has been found that at a given current density the increase of pulse duration causes proportionally greater heating of samples and correspondingly a larger mechanical stress relief. Comparison of stress relief values as a function of current density at a given pulse duration indicates that for the tested amorphous and nanocrystalline metal alloys, dependences $\Delta\sigma(j)$ are similar and can be approximated by the expression

$$\sigma = \sigma_0 + A\, exp\,(-j\,/\,B\,)$$

where A and B are numerical coefficients depending on the alloy.composition. The exponential nature of the dependences shown in Fig. 2 indicates thermoactivated processes occurring in the materials.

When an electric current pulse passes, the temperature of the sample increases due to the Joule heat. Consideration of the thermal effect of a current, which includes accurate measurement of sample heating and assessing the impact of this heating on the deformation of the samples, is an important point in the study of the causes of stress relief. To study this effect, the deformation of the samples was carried out as follows. Initially, the sample was subjected to tension at a constant rate of a grip (0.1 mm / min) at room temperature. Upon reaching the mechanical load corresponding to the time of mechanical stress relief, on diagrams $\sigma - \varepsilon$, after transmitting pulse current, the deformation stopped, but the load was not removed. Then, heating was performed using the thermal machine console Instron-5565. The sample loading was continued at the same strain rate as in the first step, but at an elevated temperature of the sample equal to the heating temperature arising from the pulse current. Experiments on all of the studied alloys have shown that the dependence of mechanical stress $\Delta\sigma$ on the value ΔT is linear. Similar curves were obtained experimentally for the transmission of electrical current pulses. The experimental dependences were approximated by the linear function $\Delta\sigma = k\ \Delta T$, where k is a coefficient showing the amount of stress drop when heated by ΔT = 1 °C.

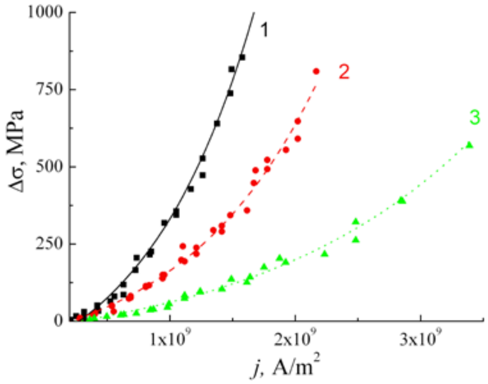


Fig. 2. Dependence of stress relief values on current density at pulse duration τ = 5 ms for alloys: (1) AMAG-180, (2) AMAG-172, (3) AMAG-200

The results of experiments have shown that the mechanical stress drop induced by passing an electric current pulse in the amorphous cobalt-based alloys alloys is ~ 1.5 times larger than the stress relief caused by heating in a furnace (Fig. 3a). It is obvious that the stress relief in the sample is not only due to thermal expansion, but also because of different mechanisms, triggered by the passage of an electric current pulse (Fig. 3, above the dotted line, shows mechanical stress relief caused by heating, below – stress relief resulting from incipient processes of irreversible structural relaxation). Furthermore, magnetostrictive phenomena caused by passing electric current are also excluded, as in amorphous alloys with a high content of Co magnitude of the magneto is practically zero [4].

For alloy AMAG-200 the values of mechanical stress reliefs caused by pulse current and heating in a furnace are the same (Fig. 3b) at the same temperature. It may be due to structural features of the material which is more stable than amorphous metal alloys, at least when heated to temperatures of ≈ 100 °C. Consequently, stress reliefs in this alloy can be explained only by thermal expansion caused by passing pulse current.

A comparative analysis of radiographs of unaffected alloys, alloys exposed to current pulses, and alloys annealed at different temperatures was done. It was discovered that: a) amorphous alloys based on Co (AMAG-170–186), after a series of electrical current pulses at density of $10^8 - 10^9$ A/m^2, remain X-ray amorphous. It may be associated with initial stages of reversible atomic rearrangements, which are not sensitive to X-ray methods; b) nanocrystalline alloys based on Fe (AMAG-200), after a series of current pulses and heating not exceeding 100 °C, have shown minor changes on the diffractograms which may be caused by partial drop of quenching stresses. This reduces ultimate stress values, but the values of the coefficient of thermal expansion do not change.

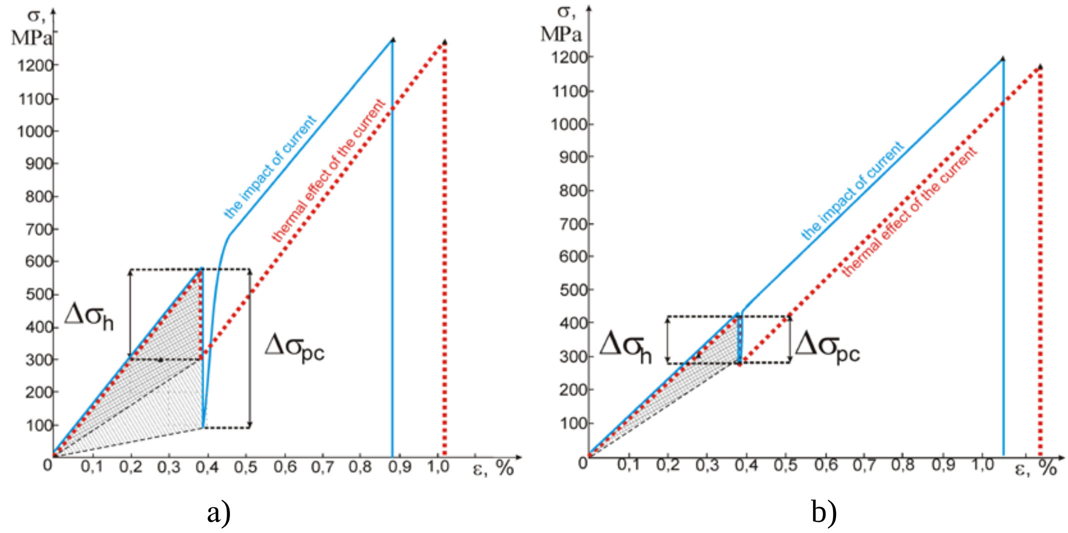


Fig. 3. Stress relief resulting from the passage of pulse current ($\Delta\sigma_{pc}$) and heating ($\Delta\sigma_h$) for alloy AMAG-180 (a) and AMAG-200 (b).

Experiments were done to examine the effect of pulse current on the unloading diagram of tested materials. It has been discovered that the transmission of an electrical current pulse causes mechanical stress relief $\Delta\sigma$ similar to the relief arising in the loading diagrams. In this case, the diagrams of unloading amorphous cobalt-based alloy show that after passing the pulse the recovery of stress is accompanied by load increase (Fig. 4).

The increase of mechanical stress on the unloading chart can be apparently explained in the framework of the directed structural relaxation model [5]. By passing a current pulse, the sample gets heated ($\Delta T \sim$ 10–15 K), which causes directed structural relaxation, which appears to be reversible at initial stages. Its contribution to the total elongation of the specimen is constant for all loads, and the relative contribution value decreases when the load increases. When mechanical loads are > 700 MPa, its contribution is almost invisible.

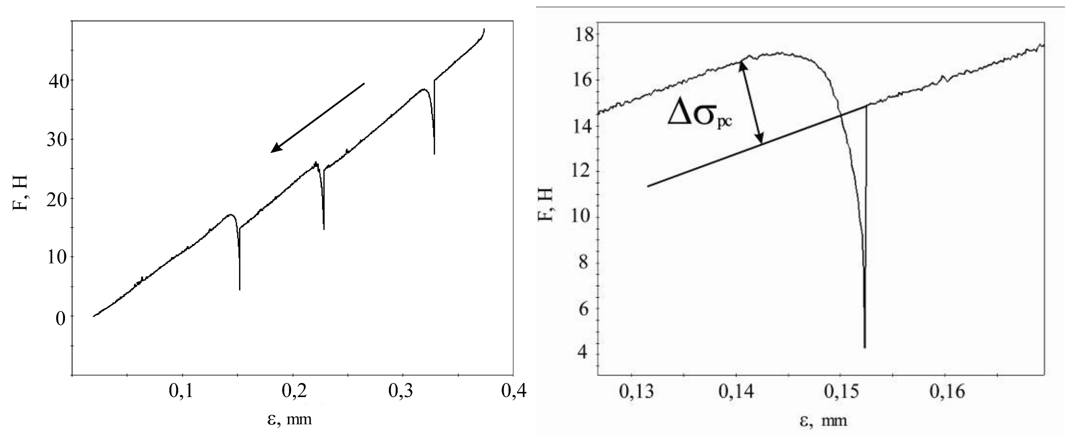
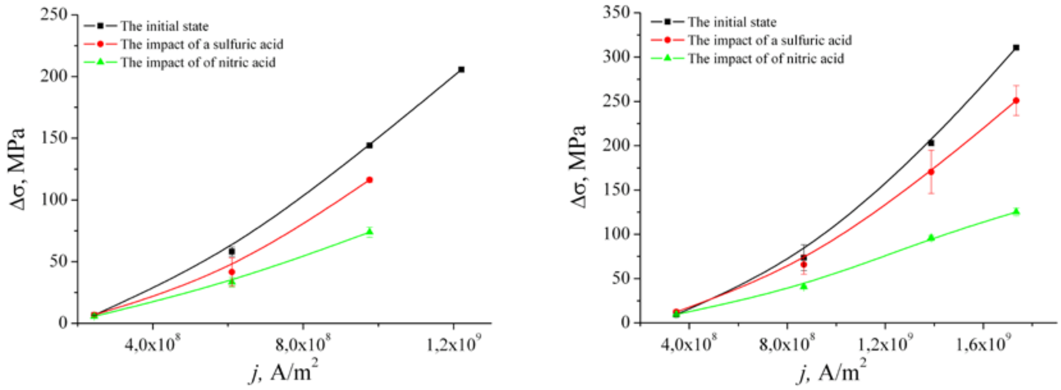


Fig. 4. Unloading diagram for an amorphous cobalt-based alloy (a) when it is influenced by impulse electric current of $\tau \approx 5$ ms.

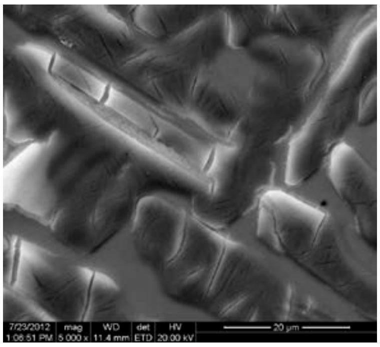
The second part of the investigation dealt with the influence of a 40-minute exposure to 20 % solutions of sulfuric and nitric acids on the values of mechanical stress reliefs caused by passing pulse current. It was discovered that after keeping the samples in a 20 % sulfuric acid solution the value of stress relief falls by $\Delta\sigma \approx$ 20 % as compared with the relief value of the samples at the initial stage (Figs. 3 a, b). Keeping them in a 20 % nitric acid solution reduces the stress relief value by 30 % as compared with the effects of sulfuric acid and by 50 % as compared with the stress relief value at the initial state. Effects of an acidic medium on nanocrystalline Fe-based alloy do not affect the value of mechanical stress drops.

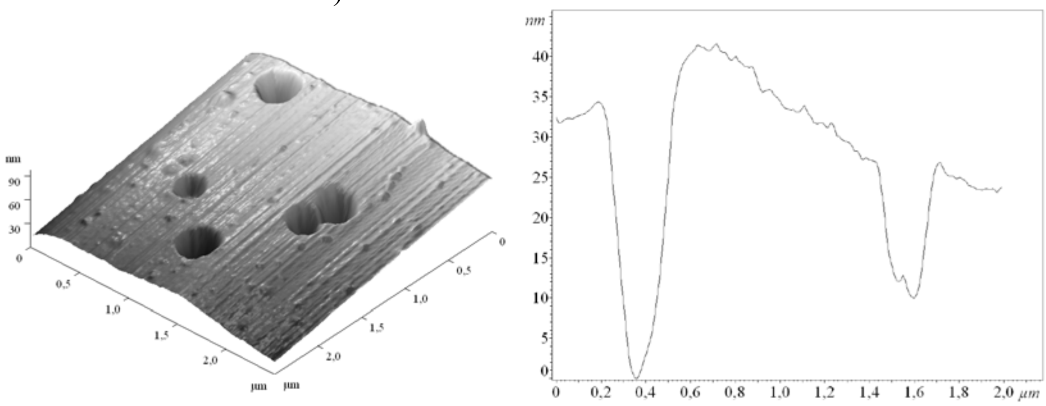
Decrease in the value of stress relief may result from surface phenomena. Figure 6 presents a surface of samples after their aging in an acidic medium. It is seen that the exposure of amorphous materials to an acid medium leads to oxide formations on the surface, which is confirmed by the study of elemental composition. It was found that almost the entire area of the specimen surface was covered with sulfate formations about 3 microns thick.



a) b)

Fig. 5. Dependence of the mechanical stress drop value on current density in an alloy: after exposure to a 20 % solution of sulfuric and nitric acids: a) AMAG-172; b) AMAG-180).

a) 



b)

Fig. 6. Sulfate formations on the surface of AMAG-180 after its exposure to a 20 % sulfuric acid solution (a);
pitting corrosion on the surface of the nanocrystalline alloy AMAG-200 (b).

The oxide film, formed on the surface, reduces the metal section of a sample which leads to the increase in resistance and decrease in current strength acting on the sample. This, accordingly, causes less heating of the sample, which results in decreasing the value of mechanical stress relief caused by passing pulse current [6, 7].

Cobalt is capable of absorbing large amounts of hydrogen [8] without forming compounds of constant composition. Therefore, hydrogen, apparently, does not evaporate but remains in the surface layer of the material, causing its embrittlement, which is observed experimentally.

Keeping a nanocrystalline iron-based alloy in solutions of sulfuric acid leads to the formation of pitting corrosion (Fig. 6 b). A typical size of pitting holes is 300 - 350 nm, ≈ 40 nm deep. In this case, there is a decrease in the values of the ultimate strength of the alloy. Thus, after exposure to sulfuric acid and 4 pulses of current with density of $2 \cdot 10^8$ - $2 \cdot 10^9$ A/m^2 the ultimate strength decreases by 20 %.

3. Conclusions

Passing an electric current pulse of density $j \leq 4 \cdot 10^9$ A/m^2 causes a reversible mechanical stress relief on the loading charts of amorphous alloys. The value of mechanical stress relief in amorphous alloys is determined not only by thermal expansion, but also by incipient structural relaxation.

In a nanocrystalline alloy, the value of critical density of pulse electric current, which does not cause unrecoverable reset, is $j = 8 \cdot 10^8$ A/m^2. The mechanical stress relief is caused by thermal expansion alone.

Exposure to acid forms sulfate compounds on the surface of amorphous alloys, resulting in a marked reduction of the metal section of a sample, which leads to increasing resistance of the material, reducing current strength and consequently, to less heating of the sample, thus decreasing the value of the mechanical load drop.

Nanocrystalline alloys, in spite of pitting corrosion, keep the value of the mechanical stress relief when pulse electric current is passed.

The change in the value of the mechanical load relief caused by pulse current in these alloys after their exposure to aggressive media occurs only due to the change of heating value of the alloys.

Acknowledgements

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