Changing of mechanical characteristics of Co-based amorphous alloy and Fe-based nano-crystalline alloy in the hydrogenous medium under the influence of impulse electric current

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Abstract. Experimentally established the preliminary influence of hydrogen-containing medium (NACE) in cobalt-based amorphous alloys reduces the temperature of the onset of ductility during annealing. The structure of the surface changes forming in the holding of samples in the NACE medium either separate NaCl crystals or branched crystalline structures on the surface. A layer of oxide appears on the nanocrystalline alloy is preventing in heat exchange between the sample and environment. The passing of the impulse electric current $j = 10^8 – 10^9$ A/m² results increases mechanical stress releases comparing to non-affected samples by the hydrogen-containing medium because of the temperature increase. The amorphous structure proves to be more resistant under simultaneous influence with the impulse electric current to the effect of the hydrogen medium NACE compare to the nanocrystalline one.

1. Introduction
The durability of operation of the products made from amorphous metallic alloys (AMA) or metallic glass (MG) depends on the content of undesirable impurities like hydrogen [1-3]. This chemical element can penetrate the material in the process of manufacturing products and the operation of products lowering down their technological properties. Metal glass has high sensitivity to the embrittlement effect of hydrogen and aggressive medium [4-6].

Under real conditions of application metallic glass is subjected to the simultaneous effect of several factors which can affect considerably the glass performance characteristics [7-9] such as stationary and non-stationary thermal fields [10], pulse and static electric and magnetic fields [11-13] and also oxidation corrosion medium. In this regard, this article is devoted to the combined influence of various factors on the mechanical properties of metallic glass [14-18].

2. Materials & Experimental Methods
The experiments were performed on the band-type Co-based AMA (AMAG 180) and the nanocrystalline Fe-based alloy (AMAG 200) with the same configuration of samples. Sample sizes are $15\times3.5\times0.02$ mm (for the bending tests) and $40\times3.5\times0.02$ mm (for the tensile tests). There were used
hydrogen-saturating medium NACE + 100 mg/l H₂S and NACE + 400 mg/l H₂S. Hold up time was 24
hours. Uniaxial tension of the samples was performed on the electric-mechanical unit ‘Instron-5565’
with simultaneous influenced by the impulse electric current during τ = 5 ms and current density
j = 10⁸ – 10⁹ А/m². The annealing temperature was varied from 500 to 1100 K.

3. Results & Discussion
Patterns of change in ductility characteristics ε [4] of hydrogenated and annealed samples were
investigated during bending tests in initial experiments. Fig.1 is shown specific dependencies of
changing of the plasticity characteristics (plasticity) from the annealing temperature of the samples
being subjected to the effect of hydrogen medium and of the samples in the initial state.
Experimentally established diminishes the plasticity of the amorphous alloy for all the annealing
temperatures at preliminary influence of the hydrogen-saturating medium. At the same time the
temperature of the initiation plasticity reduction decreases at ~ 50 K.

![Figure 1. The dependency on the changing of plasticity characteristic from the annealing temperature for the alloy AMAG 180: 1 – without hydrogen saturation; 2 – the medium NACE+H₂S (100 mg/l). The arrows indicate the initiation of the plasticity reduction.](image1.png)

![Figure 2. The dependency of the percentage change of the plasticity from the annealing temperature (10 minutes) for the alloy Co-Fe-Mn-Si-Cr-B-Ni (AMAG 180); the medium is NACE+H₂S (400 mg/l).](image2.png)

Plasticity of the AMA subjected to the simultaneous influence of the annealing and of hydrogen-
containing medium is lower than the plasticity of the samples subjected only to the annealing. The
reduction of plasticity occurs both in the first stage (up to T = 723 K) as well as in the second stage (up
to T = 822 K). The extent of plasticity drops in the first stage amounted to about 50%, in the second
stage – 20 %. The reduction of plasticity can reach up to 90 % in the temperature range of 500 – 625
K.

There is observed an insignificant increase of plasticity to the values corresponding to the plasticity
values of the samples in the initial state in annealing temperatures over 1000 K. Such a character of
the plasticity changing is related to hydrogen-caused embrittlement. The hydrogen can diffuse quickly
into the materials due to the small size of its atoms. Hydrogen is filling up a free volume which is
typical for the AMAs. Hydrogen belongs to a small group of elements which are able to form
interstitial solid solution [19, 20] with metallic phases of the alloys. While studying the absorption of
the hydrogen by the metal and the behavior of this impurity under various external influences on the
metal (for example in a process of deformation) some specificity appears of hydrogen behaviour about
its ability to show up in metal internal unsoundness as a gaseous molecular phase with forming
flocken. This phenomenon might be one of the reasons for the hydrogen-caused embrittlement.
It is a fact the free volume reduces while annealing of AMA, so hydrogenation is carrying out and hydrogen concentration goes down. This might be a reason of an insignificant growth of the AMA plasticity after the annealing at temperatures above 950 K. At the same time the changing of plasticity depends not too much from the hydrogen concentration at high temperatures (above T = 773 K).

Experimentally established that the passing of electric current through the belt sample of amorphous alloys follows by a release of mechanical stress which is fixed on loading diagrams (look Fig. 3, 4) [9, 14] and apparently is conditioned not only by the thermal dilatation but also by the initial reversible stage of the directed structural relaxation. The influence of aggressive media on the behavior of materials during electric impulse exposure has not been previously considered.

**Figure 3.** A diagram $\sigma(\varepsilon)$ of the Co-based amorphous alloy with releases of mechanical stress $\Delta\sigma$ at the moment of electric current impulses transmission. $\tau=5$ ms; $j = 10^8$ A/m$^2$

**Figure 4.** The heating thermal discontinuity of the deformed samples of the Co-based amorphous alloy during electric current impulses transmission (Fig.3).

In the second part of the article there is shown for the first time that the kind of dependency $\sigma(\varepsilon)$ of the AMA samples held in the NACE solutions is not different from the kind of dependency $\sigma(\varepsilon)$ of the samples in the initial state under simultaneous influence of the load and impulse electrical current.

At the same time the influence of the NACE solutions results in the increase of the mechanical stress release value in the nano-crystalline Fe-based alloy (this stress has been caused by the passed impulse current of density $j \geq 10^9$ A/m$^2$) by $\Delta\sigma \approx 10\%$ in relation to the samples of the same alloy which have not been held in the NACE solutions (Fig. 5).

The value of mechanical stress release in the nano-crystalline samples does not depend on the concentration of the NACE solutions in our investigation. It has been noted that after the combined influence of the NACE solutions and electric current impulses the ultimate ratio is changed. For example no changes are observed in the Young modulus for practically all the studied samples whereas the ultimate strength decreases by $\approx 40\%$ after the combined application of the NACE solutions and 4 impulses of the electric current of density $\sim 10^9$ A/m$^2$.

The carried-out X-ray diffraction studies and electronic microscopy investigations of a surface of the samples and their structural condition have been shown that the NACE medium initiates oxidation reactions on the surface of the nano-crystalline alloy; due to these reactions there are formed Ferrum oxides (as layers of $\sim 1$ µm thickness, Fig. 6) whereas on the surface Co-based alloy there are noticed salt crystals of the Euclidean geometry (Fig. 7) and fractal geometry (Fig. 8).
Figure 5. The dependency of the mechanical stress release value from the current density influencing on the alloy AMAG 200: 1 – for samples held in the solution NACE + H₂S (100 mg/l); 2 – for samples non-affected by the NACE medium.

Figure 6. The layer of oxide on the surface of the nano-crystalline alloy AMAG 200.

The layer of oxide which has formed on the surface of the nano-crystalline alloy due to the holding of the samples in the NACE solutions is the reason for the reduction of the heat emission in material. As a result of this the impulse current transmission leads to the excessive heating of the samples, thus mechanical stress goes down which is conditioned by the thermal dilatation. Such a layer is not observed on the surfaces of amorphous alloys after holding the samples in the NACE medium. Because of that the sample heating is not changed and the rate of mechanical stress release remaining the same conditioning by the thermal dilatation and initial reversible stage of structural directed relaxation processes [21].

Figure 7. NaCl crystals on a surface of the alloy AMAG-180.

Figure 8. Dendrite-shaped branches of NaCl crystals on the surface of AMAG-180.

4. Conclusion
Thus it’s been established new regularities of preliminary influence of hydrogenous medium on plasticity of annealed amorphous metallic alloys and on the temperature of initiation of plasticity decrease during the annealing. The changing of the AMA properties while the hydrogen saturation is connected with the existence of free volume where hydrogen can accumulate and with the change of hydrogen concentration depending on the temperature of the AMA annealing. It was determined the
values of the decrease of the mechanical stress of hydrogen-saturated samples in a process of electric current impulses transmission depending on the structural condition of alloy surface being formed in a process of hydrogen saturation.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (project no № 18-01-00513_A).

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