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Features of electrochemical and mechanical behavior of cobalt-based amorphous alloys in acidic media with potassium rhodanide additives

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The effect of acidic media with potassium rhodanide additives on the rate of partial electrode reactions in an amorphous cobalt-based alloy has been studied. It is shown that potassium rhodanide is a corrosion inhibitor for the studied alloys. The dependences between the ultimate strength or microhardness of the medium alloy and the acidity are obtained. Morphological features at the destruction of amorphous alloys after exposure to acidic solutions have been established, and occurring as relief, chips and cracks on the fracture surface, which are not typical at the destruction of amorphous alloys in the initial state due to material embrittlement.

Keywords: amorphous alloys, mechanical properties, acidic solutions.

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Amorphous alloys or metallic glasses (MG) due to the features of the structure and chemical composition demonstrate notable corrosion resistance in various media [1,2]. In this case the promising ones are bulk MGs based on Ni [3], which have superb corrosion resistance. At the same time, at the expense of the hot compression, the corrosion resistance of MG $Ni_{55}Nb_{45}$ may decrease, and in alloy $Ni_{55}Nb_{35}Co_5Zr_5$ it increases due to the replacement of Nb for Co and Zr [4]. Specific electrochemical behavior and corrosion resistance of bulk MGs determined their application, for example, as bipolar plates in fuel elements with a proton-exchange membrane [5].

Study of the electrochemical behavior and corrosion properties will make clearer the mechanisms of corrosion and processes happening in MGs at the same time, in particular, in cobalt based, which is a high-demand in application.

The main goal — to study the electrochemical and mechanical behavior of amorphous cobalt based alloys in acidic media xM HCl+$(1-x)$LiCl$\,+\,y$mM KSCN, where $x = 0.05$; 0.1; 0.5; $y = 0.5$; 1.0; 5.0, 10.0.

In the paper we studied corrosion properties of ribbon amorphous soft-magnetic alloys (AMAG) based on cobalt (from 80 to 86% of Co phase) and crystalline cobalt. For this purpose, polarization measurements were made in a fixed cobalt electrode in potentiostatic mode at a complex comprising a frequency response analyzer and potentiostat Solartron 1287. The studies used a three-electrode electrochemical cell from „Pyrex" glass with separate cathode and anode spaces. Polarization curves were taken by potentiodynamic polarization with the sweep speed of 0.66 mV/s [6]. The reference electrode was a saturated water chloride-silver electrode, the potentials were recalculated using a hydrogen scale [7]. Polarization and impedance measurements were made in accordance with the methods described in papers [7,8]. The order reaction for the specified particles was calculated as a derivative of the current density logarithm by particle concentration logarithm at constant potential.

In the first part, polarization studies were done using a crystalline cobalt. Polarization curves recorded at solution 0.1M MC1 + 0.9M LiCl, have specific appearance for the crystalline structures in hydrochloride media: without diffusion control in cathode process and passivation in anode one. As potassium rhodanide is introduced, and its concentration is increased, the trend of the polarization curves does not change significantly (Figure $1,a$). Tafel slopes of the corresponding cathode and anode processes will not change as well, and the corrosion potential moves insignificantly to the anode area. The similar results were obtained in solutions 0.5M HC1 + 0.5M LiCl, containing various concentrations of potassium rhodanide.

In the second part we studied the amorphous Co-based alloy AMAG-180. Cathode and anode branches of polarization curves recorded from amorphous alloy in solutions 0.1M HC1 + 0.9M LiCl with various concentrations KSCN, change their trend as the additive is added, and its concentration increases (Figure $1,b$). Therefore, for example, when adding the maximum quantity of the additive (10 mM KSCN), compared to the background solution, the corrosion potential moves to the anode region by 0.3 V, and the value of the Tafel slope on cathode curve (b_k) changes from -0.120 V to -0.180 V: the Tafel slope of the anode curve (b_a) for various concentrations of potassium rhodanide varies insignificantly and stays in the interval of 0.040–0.060 V. Note that rhodanide ionic reaction orders of cathode and anode processes turn out to be negative and make from -0.6 to -0.3 of the unit, which specifies the

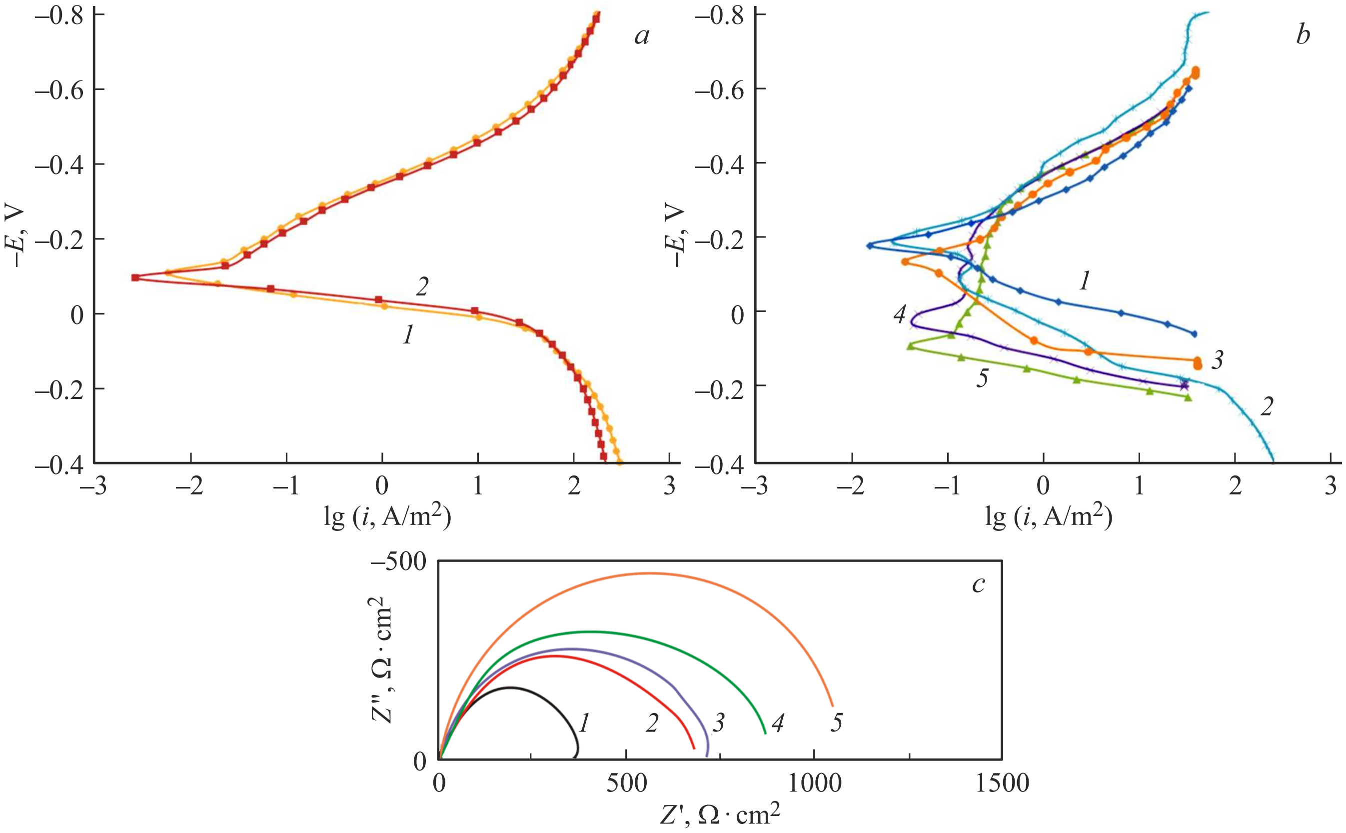

Figure 1. Polarization curves taken: (*a*) — on crystalline cobalt in solution 0.1M HC1 + 0.9M LiCl, containing 1 mmol (1) and 10 mmol (2) KSCN; (*b*) — on amorphous AMAG-180 Co-based alloy; (*c*) — Nyquist diagrams for AMAG-180 alloy. Solutions: *1* — 0.99M HCl + 0.01 LiCl; *2* — 0.5 mmol KSCN; *3* — 1 mmol KSCN; *4* — 5 mmol KSCN; *5* — 10 mmol KSCN.

inhibiting action of potassium rhodanide as AMAG-180 is dissolved in acid media with constant ionic strength.

Therefore, the largest inhibiting effect is provided by potassium rhodanide at AMAG-180 compared to the crystalline cobalt, especially at minimum and maximum acidities of the medium. Tafel slopes of partial electrode reactions vary insignificantly, which means absence of the change in cathode and anode partial reactions.

In the crystalline cobalt such processes were not observed due to the less developed surface, which substantially impacts the adsorption of rhodanide-ions, occurring to a lesser extent vs. on the amorphous material. At the same time all processes typical for AMAG-180 make less sense. The surface maturity was detected with the switch from surface irregularities into a single line.

Impedance measurements were made together with Nyquist diagrams in the absence of the main electrode polarization (at the -0.1 V corrosion crystalline cobalt potential and AMAG-180 about -0.2 V) in aqueous solutions, both in absence and in presence of KSCN. The experiment procedure and the equivalent scheme are described in [7]. Impedance curves look like semi-circles distorted in low-frequency region (Figure 1, *c*). Distortion of the circles in the low-frequency region is a result of the secondary and competitive adsorption. As the concentration of KSCN grows, the semi-circle radius increases, which corresponds to the resistance of the system to direct current [9]. Similar dependences are obtained in HCl solutions containing 1.0; 5.0 and 10.0 mM KSCN, where the trend to increase the radius of the semi-circle with the growth of the potassium rhodanide additive concentration preserves.

According to the values of electrochemical parameters (see table), the charge transfer resistance in the cathode process R_2 increases with the growth of the potassium rhodanide concentration. Therefore, as the additive concentration increases, the radii of semi-circles and the charge transfer resistance in the cathode and anode processes increase symbasically (R_2 and R_1, consequently). In this case rhodanide-ions inhibit dissolution of the Co-based amorphous alloy in acid chloride centers, which may be explained by high energy of rhodanide-ion adsorption in active centers on amorphous alloy surface, and by secondary adsorption.

Using the capacitance of a double electric layer (C_{dl}) for all the inhibitor concentrations, the curve was built in $C_{\mathrm{dl}} = f(1/C_{\mathrm{inh}})$ coordinates, and $1/C_{\mathrm{inh}}$ is opposite molar inhibitor concentration, whose extrapolation to the crossing with the vertical axis allows to determine the capacitance

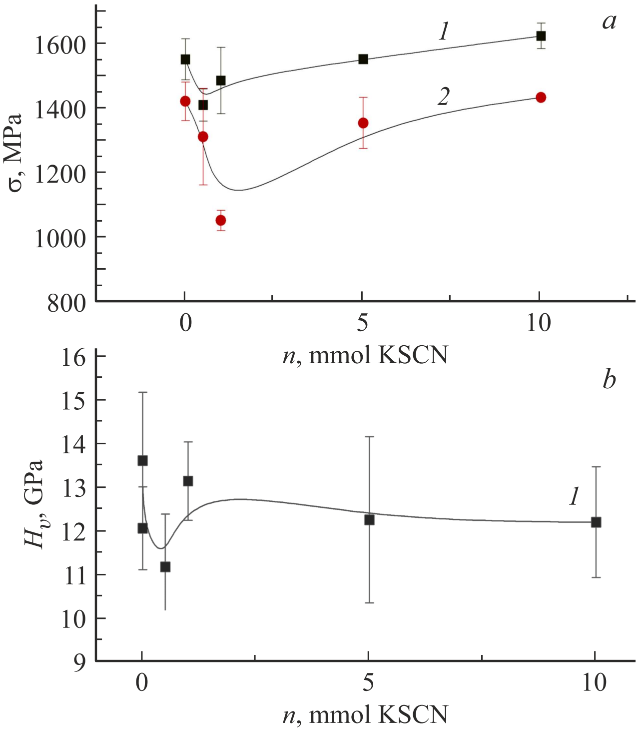

Figure 2. Dependences of limit strength (*a*) and microhardness (*b*) for AMAG-186 alloy after exposure to the medium: *1* — 0.1M HCl + 0.9 LiCl, *2* — 0.5M HCl + 0.5 LiCl and various concentrations of potassium rhodanide.

of the double electric layer (C_∞) at the limited electrode surface filling with surfactant particles.

As it follows from the table, introduction of SCN^- in the system causes rather high values of the surface filling with rhodanide ions (Θ_{SCN^-}) on amorphous cobalt electrode, however, as the concentration increases, (Θ_{SCN^-}) rise is uneven. This fact may be explained, on the one hand, by competitive adsorption of dissolvent molecules, chloride-ions and particles SCN^-. On the other hand, according to the preliminary studies, adsorption of added particles under the specified conditions is poly-layer, and filling acquires rather relative or even blurred nature, since the number of active centers in this case will be a rather quickly changing value, and accordingly, (Θ_{SCN^-}) is practically impossible to compare for the case at monolayer and polylayer filling. Besides, large complications are introduced by the adsorption of atomic hydrogen, and it is possible at already adsorbed additive particles, with the absence of the fully filled monolayer. This was indicated earlier in paper [10] when the kinetics of the hydrogen release reaction is studied in aqueous media in presence of meta-nitrophenyl biguadinine.

In the third part we studied the dependence between the limit strength of the alloys and the initial solution concentration. The specimens were soaked for 2 hours in the solution and then tested with an Instron-5565 machine. It is found that with growth of HCl concentration in the working

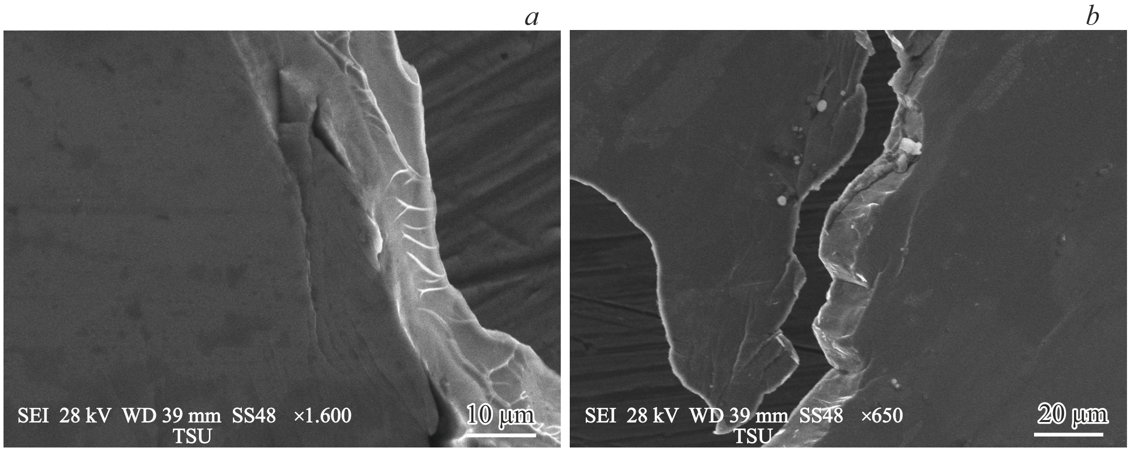

Figure 3. Damage of AMAG-186 alloy without pre-treatment (*a*) and after exposure to 0.1M HCl + 0.9 LiCl + 10 mmol KSCN medium (*b*).

Electrochemical parameters for AMAG-180 in solutions 0.99M HCl + 0.01M LiCl, containing different quantity of KSCN

Parameter	Solution				
	0.99M HCl + 0.01M LiCl (background)	Background + 0.5 mmol KSCN	Background + 1 mmol KSCN	Background + 5 mmol KSCN	Background 10 mmol KSCN
R_2, $\Omega m \cdot cm^2$	1.549	419.2	511.2	636.2	649.8
R_1, $\Omega m \cdot cm^2$	363.7	809.4	861.7	948.9	989.2
$C_{dl} \cdot 10^{-5}$, $1/cm^2$	8.886	2.8587	2.4021	1.7128	1.3585
C_{o-ffbg}, mM	–	0.798	0.858	0.950	0.993

solution limit strength decreases. Addition of potassium rhodanide in small concentrations reduces the limit strength with its subsequent recovery to the initial values as KSCN concentration increases (Figure 2, *a*). Microhardness values at the specified actions have certain correlation with the trend of the limit strength dependence (Figure 2, *b*).

Study of break surfaces demonstrated that the exposure to acid media with KSCN additives leads to dents, cracks and relief that are not specific to the damage of amorphous alloys in the initial state (Figure 3). This is related to embrittlement of alloys due to the adsorption of the atomic hydrogen.

Therefore, addition and growth of the potassium rhodanide concentration into hydrochloride media with crystalline cobalt practically will not change the trend of polarization curves. For amorphous Co-based AMAG-180 alloy in similar media, the orders of reaction by rhodanide ions at cathode and anode processes turn out to be negative and make from $-0.6\,\mathrm{V}$ to $-0.3\,\mathrm{V}$, which specifies the inhibiting action of potassium rhodanide as AMAG-180 is dissolved in acid media with constant ionic strength. Inhibiting effect of KSCN is indicated with impedance measurements, according that surface filling by rhodanide-ions increases as with growth of the additive concentration, as well as the resistance to charge transfer in cathode process.

The observed changes of the limit strength and microhardness under medium acidity variation are due to the adsorption processes on the investigated surface, in particular, the additive particles and further adsorption of atomic hydrogen adsorption on these particles, which causes alloy embrittlement.

Conflict of interest

The authors declare that they have no conflict of interest.

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