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## Features of electrochemical behavior of an amorphous iron-based alloy in acidic solutions containing potassium rhodanide

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**Abstract.** Impact of acidic solution with potassium rhodanide on partial electrode reactions was studied in AMAG-200 metallic glass (MG). Increase of acidity leads to growth of electrochemical reactions. With (mol/l) growth of potassium rhodanide in hydrochloric solution, radius of a circular Nyquist diagram increases that testifies to better corrosion resistance of AMAG-200 MG in mentioned environment. Surface coverage ratio of rhodanide-ions increases up to the 0.9–0.99 maximum with adding of potassium rhodanide. Because of the physic-mechanical features of the solution, surface co-adsorption of rhodanide-ions, Cl<sup>-</sup>, H<sub>3</sub>O<sup>+</sup> ions, and HSCN, H<sub>2</sub>O molecules is possible that can lead to competitive adsorption, noticing in diagrams.

Keywords: potassium rhodanide, electrochemistry, acidic solutions

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## Особенности электрохимического поведения аморфного сплава на основе железа в кислых растворах, содержащих роданид калия

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Аннотация. Изучено влияние кислотности среды и добавок роданида калия на скорость парциальных электродных реакций на аморфном сплаве АМАГ-200. Рост кислотности среды приводит к увеличению скоростей электродных реакций. При увеличении содержания роданида калия в солянокислых растворах радиус полуокружностей годографов возрастает, что указывает на повышение коррозионной стойкости АМАГ-200 в изученных средах. Степень заполнения поверхности роданид ионами увеличивается с ростом концентрации добавки и достигает значения 0,9–0,99 при максимальной концентрации роданида калия. Исходя из физико-химических особенностей состава раствора следует вероятная соадсорбция поверхностно-активных роданид — ионов и молекул HSCN, H<sub>2</sub>O, а также ионов Cl<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>, что приводит к конкурентным процессам адсорбции и может в определенной степени объяснять наблюдаемые зависимости.

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Ключевые слова: роданид калия, электрохимия, кислые растворы

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#### Introduction

Broader usage of amorphous metallic alloys (AMAs) or metallic glasses (MGs) stimulates practical study their corrosion resistance. Iron based AMAs resist stronger to corrosion compare with their crystalline analogs [1] that is caused by absence of typical crystalline defects in a disordered structure [2]. Corrosion resistance can be increased with structural relaxation that caused by less residual stress, probable growth of activation energy and surface atomic restructure [3] with less potential of corrosion zones [4]. By study of reaction between Ringer's solution and Fe-based ribbon MGs, substantially better corrosion resistance was shown at higher concentration of niobium [5]. In Mo-doped alloy, partial replacement by niobium also improves corrosion resistance [6]. Moreover, the dope elements such as tungsten, yttrium, manganese and nitrogen [7] are used in Fe-based alloys with molybdenum phase, and it provides more corrosion resistance because of additional oxides and nitrogen bonding in the passivation layer. Impact of molybdenum doping on corrosion parameters in Fe-based MGs also depends on the ambient acidity [8, 9]. Amorphising dopants also affect corrosion resistance. For example, phosphorus is more effective than boron as anticorrosive agent. The presence of carbon in bulk MGs accelerates their dissolution [10], but silicon improves corrosion resistivity [11, 12]. Thus, corrosion behaviour of Fe-based AMAs is not fully studied because of multicomponent chemical reactions.

The main goal is studying the impact of ambient acidity and potassium rhodanide (KSCN) on electrochemical and adsorption processes in Fe-based metallic glasses.

#### Materials and Methods

For estimation of the rates in partial electromechanical reactions, we used polarization methods. The measurements were carried out with Solartron 1287 potentiostat, static electrode and harmonic analyser. Acidic solutions of xM HCl + ymM KSCN with x = 0.05; 0.1; 0.5; y = 0.5; 1.0; 5.0, 10.0 were used in the estimation of corrosion resistance and electrochemical behaviour of Fe-based metallic glasses. KSCN was injected for the study of surface active rhodanide-ion adsorption in amorphous structure. The working electrochemical electrode of 0.5 cm<sup>2</sup> active surface area was preliminary degreased with acetone and then preset in insulating epoxy base. For electrochemical etching, a three-electrode "Pyrex" glass cell with the separated anode and cathode terminals was used. A silver chloride electrode was used for control and auxiliary one was made of Pt. Measured potentials were converted by the standard hydrogen scale. The experiments were carried from cathode to anode space by the potentiodynamic polarization with 0.66 mV/s scan rate.

Impedance measurements were also conducted in the same three-electrode cell with a specimen of AMAG-200 MG as a planar electrode. Frequency was varied from 0.05 to 10 kHz with voltage amplitude 10 mV. The electrode was etched in solution at 900 seconds for the exception of transient response.

Measured hodographs were processed with a ZView 3.0a software, which offers many equivalent electric schemes (and their voltage-current values) up to 20 circuit elements after coefficient selection by a simplex method. Values in similar schemes were averaged for several

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typical experiments. Only data with the less 5% calculated error were used.

Surface coverage ratio  $\Theta$  was measured by the equation [13]:

$$\Theta = \frac{C_0 - C_j}{C_0 - C_\infty} \tag{1}$$

where  $C_0$ ,  $C_j$  are electrode capacity of clear and doped solvent,  $C_{\infty}$  is constant capacity at higher solvent concentration.

### **Results and Discussion**

## A. Impedance measurements with AMAG-200 in acidic aqueous solutions doped by KSCN.

Impedance hodographs with non-zero corrosion potential in the aqueous solutions have a circle form deformed in the low-frequency spectrum both with KSCN doping and without it. Equivalent electric scheme [14] with AMAG-200 electrode consists of  $R_s$  (electrolyte) and  $R_1$  (anodic current) resistivity with adsorption  $C_a$  (capacity) and  $R_a$  (resistance) of transition bonds in anode reaction. To the cathode restorative process of proton donors and dissolved oxygen, the series coupling of  $R_2$  (cathode current) and  $Z_D$  (diffusion impedance) is corresponded. As seen from experimental and model curves (Fig. 1), the proposed schemes describe well boundary processes between the electrode and solution.



Fig. 1. Nyquist diagram for AMAG-200: (*a*) 0.05M HCl (base); (*b*) base solution with 0.5 mM of KSCN. Z' and Z" are calculated in Ohm·cm<sup>2</sup>; the 1st curve corresponds to experiment and the 2nd one corresponds to calculation

Table 1

Parameters of equivalent scheme with AMAG-200 electrode in 0.05M of
HCl and different concentration of KCNS. Listed values have quite other SI
units despite their symbols and titles in the text, but they better describe the
surface dynamics and are common in electrochemistry by these names

Solution Element	0.05M HCl (base)	0.05M HCl + 0.5 mmol/l KSCN	0.05M HCl + 1 mmol/l KSCN	0.05M HCl + 5 mmol/l KSCN	0.05M HCl + 10 mmol/l KSCN
$R_{\rm s}$ ,Ohm·cm <sup>2</sup>	10	10.65	15.5	10.6	9.7
$R_2$ ,Ohm·cm <sup>2</sup>	2.8952.10-5	7.8159·10 <sup>-8</sup>	12.37	83.5	21.04
$Z_{\rm D}(R)$ ,Ohm·cm <sup>2</sup>	1033	1705	42146	102730	91815
$Z_{\rm D}(T)$ ,Ohm·cm <sup>2</sup>	0.18804	0.40875	19.99	40.99	27.17
$Z_{\rm D}(P)$ ,Ohm·cm <sup>2</sup>	0.40438	0.41997	0.71315	0.785	0.722
$R_1$ , Ohm·cm <sup>2</sup>	426290	112780	2434	8390	3755
$C_{\rm a} \times 10^{-5},  {\rm F/cm^2}$	3.6605	5.2542	2.4835	1.9671	2.7802
$R_{a}$ , Ohm·cm <sup>2</sup>	9.714	5.575	840.9	12.17	1305
$C_{\rm dl} \times 10^{-5},  {\rm F/cm^2}$	3.2151	2.9774	1.3313	1.5052	0.78702

With increasing of KSCN concentration, radius of the semi-circle increases. The similar curves are received to HCl solutions with 1.0; 5.0 and 10.0 mM of KCNS doping, where radius increases at higher dopant concentration.

According to electrochemical data (in Table 1),  $R_2$  increases at higher concentration of KSCN, but 5 mM of KSCN solution does not correlate with this tendency.

It can be caused by the involvement of SCN<sup>-</sup>, Cl<sup>-</sup> and  $H_3O^+$  surface ions in competitive adsorption on active surface centres. Moreover, adsorption of water and HSCN molecules, which forms in hydrochloric environment, must be noted. Similar effect was observed earlier [23, 24].

Deviation of the parameters from 0.05M of HCl solution with 5 mM of KSCN dopant can be explained as follow processes. One side, reaction rate can change non-linear depends on either single ion or co-adsorption with Cl<sup>-</sup>,  $H_3O^+$  ions and  $H_2O$ , HSCN molecules. Other side, coverage of active centres by SCN particles is possible, so that forming of the second monolayer occurs despite the finally unformed first one [15].

As seen from the Table 2, monotonous decrease of  $C_{dl}$  with a higher KSCN concentration happens on the "metal-solution" boundary. Table 2

$C_{\rm KSCN}$ , mM	base value	0.5	1	5	10
$C_{dl}, \mu F$	32.151	29.774	13.313	15.052	7.8702
Θ	_	0.097	0.764	0.693	0.985

Coverage ratio  $\Theta$  and double layer capacity  $C_{dl}$  at KSCN concentration in 0.05M of HCl

This fact testifies to adsorption of doped particles on the amorphous surface. According to Damaskin's and Podlovchenko's calculations of  $\Theta$  [13], its increase for rhodanide-ions on amorphous surface centres occurs at higher ionic concentrations in solution. Note that described surface significantly differs from typical metal one, and it manifests itself first of all in atomic order. Thus, the amorphous surface also contains the active centres, which impact the electrode processes so, in relation between  $\Theta$  and concentration of SCN<sup>-</sup>, coverage only the active centres instead whole surface must be noted.

According to Table 2, coverage ratio is about 0.1 at surface anion adsorption 0.5 mM of KSCN yet, and further doping to 1 and 5 mM of KSCN gives the bend in  $\Theta(C_{\text{KCNS}})$  curve that can be caused by secondary processes (chloride ion co-adsorption, for example). Note that solution 0.05M of HCl with doping 5 mM of KSCN does not fit into tendency by  $R_2$  (see Table 1), and curve bending is observed at the same point (in Fig. 2).



Fig. 2. Adsorption isotherm of SCN<sup>-</sup> ions from solution 0.05M of HCl with different doping of potassium rhodanide in AMAG-200 metallic glass. The curve was plotted in error corridor with respect to one of Langmuir adsorption isotherms

Totally, at a maximal concentration of dopant, coverage of almost all active surface centres happens in MG that is confirmed by  $\Theta = 0.985$  at  $C_{\text{KSCN}} = 10$  mM. For solutions with acidity 0.1 and 0.5M of HCl at doping of potassium rhodanide, the similar

For solutions with acidity 0.1 and 0.5M of HCl at doping of potassium rhodanide, the similar dynamics of Nyquist diagram and  $\Theta(C_{\text{KCNS}})$  preserve. By value of  $\Theta$ , we can conclude about insignificant difference of adsorption isotherms, plotted for SCN<sup>-</sup> ions at 0.05, 0.1 and 0.5 M of HCl in MG. Personal parameters of the isotherms are listed in Table 3.

Table 3

0.1M HCl						
$C_{\rm KSCN}$ , mM	base value	0.5	1	5	10	
$C_{_{\mathrm{dl}}}\mu\mathrm{F}$	47.309	41.587	18.555	18.024	5.987	
Θ	—	0.135	0.681	0.692	0.985	
0.5M HCl						
$C_{\rm KSCN}$ , mM	base value	0.5	1	5	10	
$C_{\rm dl}  \mu F$	35.976	28.869	44.816	8.1645	7.7336	
Θ	_	0.229	0.284	0.871	0.908	

# Relation data for coverage ratio $\Theta$ and double layer capacity $\rm C_{dl}$ at KSCN concentrations in 0.1 and 0.5M of HCl

Table 4

Ratio between HSCN molecules and SCN-ions with respect to acidity of solution

[HSCN]/[SCN]	0.36	0.71	3.57
$[\mathrm{H}^+]$	0.05	0.1	0.5

Dynamics of adsorption isotherm does not change qualitatively but coverage ratio is about 0.9-0.99 at a maximal concentration of potassium rhodanide. Increased acidity intensifies hydrolysis of KSCN salt and rhodanide-ions become partially into HSCN form with less adsorption activity on the amorphous surface, so it can cause lesser  $\Theta_{max}$  (i.e., KSCN + HCl = HSCN + KCl).

In this case, a share ratio between molecular HSCN forms and SCN- ions can be calculated with respect to acidity (Table 4).

Thus, adsorption of HSCN molecules can occur with less heat in compare with SCN<sup>-</sup> rhodanide ions, and it gives less coverage ratio at maximal studied concentrations of potassium rhodanide. Moreover, HSCN and SCN<sup>-</sup> components can impact differently not only in electrode process but also in the solid-phase hydrogen diffusion through amorphous alloy.

From obtained impedance data, we can conclude the change of anode and cathode reactions rates while using rhodanide-ions in Fe-based MG, but it is not always linear and simple process. In all investigated solutions, double-layer capacity decreases with higher concentration of KSCN that testifies about surface adsorption of dopant in amorphous alloy. Adsorption isotherms, plotted by collecting results, have the same form qualitatively. However, for solutions 0.05 and 0.1 M of HCl, data coincide practically at considered content of KSCN, but for 0.5 M of HCl, the maximal coverage ratio is about 0.91 at the most doping of KSCN, and it is 10% less than for solutions 0.05 and 0.1 M of HCl.

B. Electrochemical measurements with AMAG-200 in acidic aqueous solutions doped by KSCN

Polarizing curves of AMAG-200 have a typical form for clean iron and Fe-based alloys. In cathode part, a segment of controlled diffusion absents and passivation is not observed in anode one. Cathode polarizing curves in base solutions 0.1 M of HCl are approximated by linear parts with bc Tafel angle, which is about 0.12 V, and anode plots have a typical view with  $b_a$  one about 0.06 V (Fig. 3 and 4).

Using of minimal doping does not significantly change the polarizing dynamic if only corrosion potential shifts to the anode area. However, there is change both of  $b_c = 0.15$  V and curve in anode area with growth of KSCN concentration up to 1 mM despite the curve slope does not strongly change in compare with solution of 0.5 mM doping. Note that rate of both anode and cathode processes retards at doping 1 mM of KSCN.

Increase of KSCN dopant concentration up to 5 and 10 mM also does not significantly change the dynamics and Tafel angles, but quite balanced the potential and stopped corrosion generally. Compared with [16], polarizing curves have the same form for industrial (polycrystalline) steel.

Mentioned doping is a corrosion stimulus for iron and its alloys, but, in some observed cases, dopant can be inhibitor that is seen from the polarizing curves. Correlation between electrochemical and impedance data can be explained by growth of the surface coverage ratio at higher concentration of KSCN.





Fig. 3. Polarizing curves of AMAG-200 MG in solution 0.1 M of HCl (1); doped by 0.5 mM of KSCN (2); with 1 mM of KSCN (3)

Fig. 4. Polarizing curves of AMAG-200 MG in solution 0.1 M of HCl (1); doped by 5 mM of KSCN (2); with 10 mM of KSCN (3)

## Conclusion

Potassium rhodanide does not obviously change the rates of partial electrode reactions in AMAG-200 amorphous alloy. Analogous relationships were observed in iron (polycrystalline steel) earlier.

For all investigated solutions, surface coverage ratio  $\Theta$  is more than 90% at filling by SCN- ions with respect to impedance measurements.

Ionic adsorption of SCN<sup>-</sup> can be retarded by competitive co-adsorption of  $H_3O^+$ , Cl<sup>-</sup> and HSCN components that can affect the rate of electrode reactions.

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