Inhibition of pitting formation on copper by microadditives of halide ions in alkaline glycinate media

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Abstract

Using a complex of physicochemical methods: voltammetry, chronoamperometry, scanning electron microscopy, X-ray spectroscopic analysis, it was shown that in alkaline glycinate solution in the presence of microadditives of Br- or F- ions, copper is subjected to local depassivation accompanied by an antagonistic effect of activators. This effect is expressed as the suppression of local activation (LA) caused by the addition of amino acids and micro quantities of halide ions. Indeed, the hysteresis loop was not detected on cyclic voltammograms of copper in the solutions studied, which indicates the suppression of pitting formation processes in the presence of microadditives of inorganic anions of the copper electrode where local damages have the form of a few little pits in media with halide ions, in contrast to the alkaline glycinate electrolyte where the surface damages are more significant. It has been found that the process of pitting formation in alkaline glycinate-halide systems occurs by the nucleophilic substitution mechanism of dissociative type. At the same time, the inhibitory effect of inorganic anions is manifested in a wider range of concentrations from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M as compared with that for chloride ions. The values of the potential of LA (E_{LA}) in the media studied exceed the value of E_{LA} in an alkaline glycinate solution. In NaBr solutions, an increase in its concentration results in improved copper resistance to LA and ennoblement of E_{LA} to 0.360 V for the solution containing $1 \cdot 10^{-3}$ M NaBr. For alkaline glycinate-fluoride systems in the indicated concentration range of NaF, the above-noted tendency of E_{LA} ennoblement remains, but there is no dependence on the F⁻ content $(E_{LA} \sim 0.360 \text{ V})$. The established suppression of pitting formation in alkaline glycinate media with additions of halide ions may be due to the fact that small concentrations of halide ions (especially Br⁻) force water molecules out of the adsorbed amino acid complex on the metal. As a result, the surface complex becomes more hydrophobic and its solubility decreases. This complicates copper activation due to blocking of a fraction of active centers. Comparison of the results with data on the behavior of copper in alkali-glycinate-chloride solutions shows that as the corrosivity of inorganic activators decreases in the Cl⁻, Br⁻, F⁻ series, the range of concentrations in which they inhibit LA caused by the organic activator (glycine) expands.

Key words: copper, alkaline media, organic and inorganic additives, passivity, local activation, inhibition.

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Introduction

Development of new technologies in the areas of biomaterials, biosensors and biocatalysis increases the need to study the interactions in the systems biologically active substances (especially amino acids) / inorganic activator anions / metal. Earlier in [1–3] it was shown that microadditives of inorganic depassivators are able to cause inhibition of local damages of the metal surface in media containing organic and inorganic depassivators. Thus, according to [2, 4], local copper damage at a potential of 0.100 V in an alkaline electrolyte caused by glycine ($5 \cdot 10^{-3}$ M) is suppressed by introducing ($1 \cdot 10^{-6} - 1 \cdot 10^{-4}$ M) NaCl. The difficulty of copper depassivation is confirmed by the increased potential of pitting formation. The inhibition of the local activation process with small amounts of Cl⁻ ions is explained, firstly, by a decrease in the solubility of the adsorbed copper(II) amino acid complex due to replacement of water molecules by Cl⁻ ions in its hydration shell and, secondly, by the possible formation of poorly soluble neutral CuCl.

In continuation of previous research [2, 4], this work deals with possible suppression of the copper depassivation process in alkaline solutions containing an amino acid (glycine (Gly)) with small amounts ($c = 1 \cdot 10^{-6} - 1 \cdot 10^{-3}$ M) of inorganic activators (bromide and fluoride ions). The work also deals with finding the inhibitory effect of inorganic anions and revealing the general patterns and specific features of interaction between halide ions, glycine and local activation of copper.

Experimental

The research subject was copper (99.9%). The study was performed in working solutions with addition of activating inorganic anions: $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly + X M NaBr and $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly + X M NaF (where X is an inorganic additive with concentration ranging from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M, pH 12). The experiments were carried out on a stationary electrode using a classical three-electrode electrolytic cell with free air access at a temperature of $20\pm 2^{\circ}$ C.

A set of the following physicochemical methods were used to obtain reliable results: voltammetry, chronoamperometry, optical and scanning electron microscopy (SEM) with subsequent X-ray spectroscopic analysis of the passive layer on copper.

Before experiments, mechanically polished electrodes were subjected to cathodic prepolarization in a working solution at a potential of -1.000 V for 10 minutes to restore the natural oxides and achieve reproducibility of the initial state of metal surface. Subsequently inverse and cyclic voltammograms (IVA and CVA, respectively) were recorded in the potential range from -1.000 V to +1.000 V. The copper electrode potentials were measured relative to the potential of a silver chloride electrode and recalculated into the normal hydrogen electrode scale.

Results and discussion

Analysis of the experimental data showed that introduction of small amounts of NaBr or NaF $(1 \cdot 10^{-6} - 1 \cdot 10^{-3} \text{ M})$ into the background alkaline glycinate electrolyte [2] changes the shape of copper CVA: three anodic and two cathodic peaks are preserved, while there is no hysteresis loop on the CVA (Figure 1).



Figure 1. CVA of copper in solutions: 10^{-2} M NaOH + $5 \cdot 10^{-3}$ M Gly (a), 10^{-2} M NaOH + $5 \cdot 10^{-3}$ M Gly + $1 \cdot 10^{-3}$ M NaBr (b), 10^{-2} M NaOH + $5 \cdot 10^{-3}$ M Gly + 10^{-3} M NaF (c), where A1/C1 - Cu/Cu₂O, A2/C2 - Cu₂O/CuO, Cu(OH)₂, A3 - CuGly⁺, Cu(Gly)₂.

The presence of peaks on the polarization curves is associated with the formation of compounds: $A1/C1 - Cu/Cu_2O$, $A2/C2 - Cu_2O/CuO$, $Cu(OH)_2$, $A3 - CuGly^+$, $Cu(Gly)_2$ [4, 5]. These substances take part either in the formation of the passive layer (copper oxides and hydroxides) or in the process of local activation (LA) of the surface (copper glycinate complexes). The absence of a hysteresis loop is evidence of the suppression of pitting formation in the presence of small amounts of inorganic anions in alkaline glycinate

media. Indeed, microscopic observations reveal local damages on the surface of a copper electrode as a small number of small pits in alkali–glycinate–halide media, unlike the background electrolyte in which the surface is damaged more significantly (Figure 2).



Figure 2. Photomicrograph of copper surface after IVA (×2000) in solutions: $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly+X M NaBr (X = 0 (a); $1 \cdot 10^{-3}$ (b) and $1 \cdot 10^{-2}$ M NaOH+ $5 \cdot 10^{-3}$ M Gly+ 10^{-4} M NaF (c).

The results of X-ray structural microanalysis of the copper surface after IVA in solutions with addition of NaBr and NaF show that the film on the electrode surface consists of oxygen compounds of copper. This is evidenced by the elemental composition of the film, including Cu and O (Table 1). The absence of such elements as Br and F confirms that copper complexes CuBr and CuF are not formed. Probably, the suppression of local damages in alkaline glycinate media with addition of halide ions may be due to the fact that halide ions (especially Br⁻) may force water molecules or OH⁻ ions out of the amino acid complex adsorbed on the metal. This increases the hydrophobicity of the complex and reduces its water solubility, which complicates the activation of copper due to the blocking of a fraction of the active centers [2, 4, 6].

Table 1. Quantitative composition of elements in the film on copper surface after IVA in alkaline glycinate media with addition of halide ions according to data of X-ray structural microanalysis.

	Element			
Solution composition	Cu	Ο	Br	F
	Mass.%			
$1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly + $1 \cdot 10^{-3}$ M NaBr	96.76	3.24	_	_
$1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly + $1 \cdot 10^{-4}$ M NaF	96.33	3.67	_	_

The values of LA (E_{LA}) potential in solutions with different NaBr concentrations obtained by the chronoamperometric method show that the $E_{LA} = f(\lg c_{Br^-})$ plot has the form presented in Figure 3. In the concentration range $1 \cdot 10^{-6} - 1 \cdot 10^{-3}$ M NaBr, copper resistance to LA improved, and ennoblement of E_{LA} to 0.360 V was observed in the solution with addition $1 \cdot 10^{-3}$ M NaBr. At the same time, the values of E_{LA} in alkaline glycinate-bromide media exceed the value of E_{LA} in the background electrolyte (0.100 V), which is due to the antagonism of action of two activators – organic (glycine) and inorganic ones (Br⁻). The antagonism is expressed in the suppression of the LA, which is caused by the addition of amino acid, by small amounts of halide ions [2, 4, 6].

The detected changes in E_{LA} of copper are similar to those in systems with chloride ions [2] and are more pronounced. This correlates with the concepts of "hard-soft" interactions during the formation of copper adsorption compounds, since in the $F^- \rightarrow Cl^ \rightarrow Br^-$ series the "hardness" of bases decreases, while copper, as a transition metal, is considered as a soft acid. Thus, the CuBr that is formed will be more stable than similar copper compounds with F^- and Cl^- ions, and it will more actively prevent the adsorption of the amino acid.

In turn, in the series of alkaline glycinate-bromide solutions studied with $c(\text{NaF}) = 1 \cdot 10^{-6} \text{ M} - 1 \cdot 10^{-3} \text{ M}$ the above-noted tendency of E_{LA} ennoblement relative to the background is preserved (Figure 3), but E_{LA} does not depend on F⁻ anion content, that is, $E_{\text{LA}} \neq f(\lg c_{\text{F}})$.



Figure 3. The effect of the concentration of bromide (1) and fluoride ions (2) on the local activation potential (E_{LA}) of copper in solutions of $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly + X M NaHal (X = $1 \cdot 10^{-6} - 1 \cdot 10^{-3}$ M). The dashed line shows the E_{LA} of copper in the solution of $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly [4].

To determine the controlling stage of the LA, the formal kinetic method [7] was used, according to which the rate of the pitting formation process is proportional to $1/\tau_{ind}$:

$$1/\tau_{\text{ind}} = kc_{\text{Hal}^-}^n$$
,

where τ_{ind} is the time of the induction period of the process, c_{Hal^-} is the concentration of halide ions, and *n* is the apparent kinetic reaction order.

The results obtained (Figure 4) show that the reaction rate does not depend on the concentration of Br⁻ ions (n=0) and weakly depends on $c(F^-)$ (n=0.13). Consequently, LA

of copper in the electrolytes studied occurs according to the mechanism of nucleophilic substitution of dissociative type, as noted in [2] for alkaline glycinate solutions containing microadditives of Cl⁻ ions.



Figure 4. The dependence of the rate of copper LA $(1/\tau_{ind.})$ on the concentration of bromide (1) and fluoride (2) ions in solutions: $1 \cdot 10^{-2}$ M NaOH + $5 \cdot 10^{-3}$ M Gly+X M NaHal (X = $1 \cdot 10^{-6} - 1 \cdot 10^{-3}$ M).

The described regularities of local activation inhibition caused by organic depassivator (Gly) and small quantities of Br^- and F^- ions are similar to those in systems with chloride ions [2] but with a wider concentration range of the antagonism of action of two activators.

Conclusions

Thus, the effect of F^- and Br^- ions on the local depassivation of copper in an alkaline glycinate solution has both common and specific features. In both systems, a dissociative type substitution mechanism is realized, and antagonism of the action of activators is manifested. In systems with Br^- ions the E_{LA} potential increases with an inorganic activator concentration, and in the presence of F^- ions there is no such correlation. Comparison of the results obtained with previous data [2] shows that with a decrease in the corrosiveness of inorganic activators in the series Cl^- , Br^- , F^- , the concentration range in which they suppress LA caused by the organic activator (glycine) expands.

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