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PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

Corrosion and Anodic Oxidation of Copper in 1-Butyl-3-Methylimidazolium Bromide–Copper(II) Bromide Ionic Liquid

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Abstract—Using the gravimetric and polarization methods, the corrosion behavior of copper in 1-butyl-3-methylimidazolium bromide (BMImBr) ionic liquid in its pure state and with additions of $CuBr_2$ (from 0.4 to 1.2 mol kg^{-1}) has been investigated. It is found that the corrosion in naturally aerated BMImBr ionic liquid is accompanied by oxygen depolarization. Copper dibromide in BMImBr–$CuBr_2$ ionic liquid plays the role of an oxidant, and the rate of copper corrosion in this case is higher by about an order of magnitude than for the pure ionic liquid. The method of cyclic voltammetry shows that the anodic dissolution of copper in BMImBr–$CuBr_2$ ionic liquid proceeds via the EC mechanism. It is shown that the chemical-reaction rate of dissolving the surface layer and the rate of copper corrosion (according to gravimetric and polarization data) are comparable. Copper corrosion in the studied ionic liquid is accompanied by the effect of surface polishing, as is confirmed by the atomic force microscopy and profilography.

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INTRODUCTION

Ionic liquids (ILs) or salts that are molten at room temperature are the objects of intense study as liquid-phase materials with a high potential for technological applications. The possibility of the application of ILs in the role of electrolytes in electrochemical devices, such as lithium-ion batteries [1–3] and supercapacitors [4–6], as well as in electroplating [7, 8], is being actively investigated. The greatest attention with regard to possible applications is paid to the study of the fundamental physicochemical properties of these salts, such as electrical conductivity, viscosity, and electrochemical stability [9]. At the same time, the characterization of the corrosion resistance of different metals and alloys, including copper and its alloys, in these electrolytes is essential as well. The results of a number of studies indicate that metals actively interact with ILs, giving rise both to oxidation of the metal and to destruction of the ionic liquid [9]. Corrosion studies have been mainly performed in dialkylimidazolium ionic liquids [9–15]. It was established that the rate of the corrosion destruction of copper and brass is sensitive to the temperature of a corrosive medium. The corrosion resistance of carbon steel and aluminum strongly depends on the chemical structure and nature of the IL cation and anion, as well as on the content of water impurity. The corrosion resistance of stainless steel in nonaqueous ILs and ILs diluted with water is rather high.

The corrosivity of ionic liquids containing metal salts has been studied insufficiently. We have established earlier that the corrosion rate of silver in 1-butyl-3-methylilimidazolium bromide (BMImBr) ionic liquid exponentially increases upon an increase of the concentration of dissolved silver bromide (AgBr) [16], while copper is intensely oxidized in BMImBr in the presence of $CuBr_2$ [17]. The observed phenomena are similar to those characterizing high-temperature ionic melts [18].

The effect of temperature on the kinetics of the corrosion and anodic behavior of copper in 1-butyl-3-methylimidazolium bromide–copper dibromide (BMImBr–$CuBr_2$) ionic liquid is studied in the present work.

EXPERIMENTAL

1-Butyl-3-methylimidazolium bromide ionic liquid (we synthesized and characterized BMImBr in [19]; the water impurity content determined by the Karl Fisher method is 1.8%) and solutions of $CuBr_2$ (chemically pure grade) in BMImBr were used in the present studies. The solutions were prepared by direct mixing of the components in a dry glove box at a constant air humidity of 0.03 mg L^{-1} controlled by the use of preliminarily calcined silica gel. $CuBr_2$ was maintained in BMImBr at a temperature of 70–80°C in an LT-VO/20 vacuum oven until the complete dissolution of a solid phase. Physicochemical characteristics of the binary melt are given in [20].

Electrodes were made of M0b brand copper (oxygen-free, vacuum melting). Prior to the experiment, the studied electrode surface was polished with no. 2 grade sandpaper, washed with distilled water, degreased with ethanol, and dried in air.

Polarization studies were performed using a PI 50-Pro-3 potentiostat controlled with the use of the PS_Pack_2 software in a glass three-electrode thermostatted equilibrated hermetically closed electrochemical cell of special design [16]. The counter electrode and quasi-reference electrode were made of platinum. The potentials of the copper electrode are given with reference to the platinum quasi-reference electrode.

Quantitative determination of the corrosion rate parameters was carried out by the gravimetric method using a Sartorius analytical balance (ME215S model, weighing precision1 × 10^{-5} g).

The surface topology of the copper samples after exposure in the binary copper-containing melt was analyzed on the basis of microimages obtained using a Nova SPM Solver P47H-PRO atomic-force microscope.

The surface roughness of the copper electrode before and after exposure in ionic liquids was measured using a 170622 profilometer (the measurement accuracy of mean profile deviation R_a of the studied surface is $\pm 0.75 \times 10^{-3}$ μm).

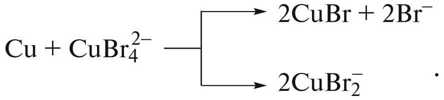
RESULTS AND DISCUSSION

It is known [21–26] that the dissolution of metal salts in halide ionic liquids with identical anions is accompanied by the formation of metal-containing complex anions in the melt. Their composition is determined by the molar ratio of components in the mixture; specifically, if the metal salt content of does not exceed 50%, then predominantly mononuclear complex anions ($[FeCl_4]^-$, $[InCl_4]^-$, $[ZnCl_3]^-$, $[CuCl_2]^-$, $[NbF_6]^-$, $[TaF_6]^-$, etc.) are present, while an increase of the metal salts content to more than 50% gives rise to the formation of polynuclear complex particles ($[Fe_2Cl_7]^-$, $[Zn_2Cl_5]^-$, $[Zn_3Cl_7]^-$, etc.). The dissolution of $CuBr_2$ (up to 30.5 mol %) in BMImBr under the conditions of this experiment is also accompanied, apparently, by the formation of a mononuclear $[CuBr_4]^{2-}$ complex ion [27]. Hence, the studied ionic liquid is composed of the two types of anions: Br^- and $[CuBr_4]^{2-}$.

Corrosion of Copper in BMImBr and BMImBr–$CuBr_2$ Ionic Liquids

Stationary (corrosive) potential E_{st} of copper in BMImBr at 20°C is –0.71 ± 0.02 V. Small amounts of copper dibromide significantly shift the potential to the negative region. However, upon an increase in the concentration of $CuBr_2$ from 0.1 to 2.0 mol kg^{-1} of BMImBr (equivalent to changing the copper dibromide concentration from 2.2 to 30.5 mol %), the E_{st} value of the copper electrode increases from –0.91 to –0.77 V [17]. The concentration dependence of E_{st} is nonlinear, which is typical for metals corroding in ionic melts under the stationary conditions [18].

BMImBr–$CuBr_2$ ionic liquid shows marked oxidizing properties. The same as in aqueous solutions, in which Cu(II)-containing ions play the role of an oxidant in the corrosion process, being reduced to Cu(I) ions [18, 28], the interaction of Cu with Cu(II) in the investigated IL is possible by the following scheme [18]:



$$Cu + CuBr_4^{2-} \begin{cases} \rightarrow 2CuBr + 2Br^- \\ \rightarrow 2CuBr_2^- \end{cases}.$$

The Cu(I) ions can be oxidized by dissolved oxygen to Cu(II) ions.

The results of gravimetric determination of corrosion rate mass index V_k of copper in BMImBr and BMImBr–$CuBr_2$ ionic liquids, as depending on the contact time of the sample with a corrosive medium and on the temperature, are given in Table 1.

As is seen from Table 1, the corrosion rate of copper in the initial IL significantly increases with an increase in temperature. Upon the addition of $CuBr_2$ in a concentration of 0.4 mol kg^{-1} of BMImBr, the mass index of the corrosion rate increases by an order of magnitude. An increase in the concentration of $CuBr_2$ leads to corrosion intensification. Hence, copper dibromide is directly involved in the corrosion process as an oxidant. The corrosion rate of copper in the studied ILs is high and comparable with that in an aqueous solution of sulfuric acid with additions of $CuSO_4$ [29]. When the time of contact of metal with a corrosive medium is increased, the V_k value is decreased and, subsequently, stabilized. The observed shift of the corrosion potential toward more positive values is small and equals 20–30 mV (20°C). The formation of a film of copper oxidation products weakly adhered to the surface may be a reason for a decrease in the V_k value [30]. It is obvious that this film is porous and has poor protective properties. The inhibition of the corrosion is most largely expressed in starting IL (BMImBr) at 70°C. To the greatest extent, the corrosion inhibition in BMImBr at this temperature is apparently determined by a decrease in the oxidant concentration, i.e., dissolved oxygen. The solubility of O_2 in ILs containing the 1-butyl-3-metilimidazolium

Table 1. Corrosion rate mass index of copper in BMImBr and BMImBr–$CuBr_2$ ILs as depending on the time of contact with a corrosive medium at different temperatures

$CuBr_2$ content, mol kg^{-1} of BMImBr	t, °C	Corrosion rate mass index $V_k \times 10^4$, g(cm^{-2} h)				
		0.5 h	1 h	1.5 h	2 h	3 h
0	20	0.31	0.19	0.21	–	–
	30	–	0.67	–	0.46	0.54
	70	6.51	1.25	1.00	0.55	–
0.4	20	4.1	1.92	2.05	2.02	–
	30	–	3.32	–	2.64	1.49
	70	12.52	9.38	10.81	9.38	–
1.2	70	16.71	10.02	11.72	8.86	–

cation is extremely low. In the temperature range from 20 to 100°C and at atmospheric pressure, it equals from 0.02 to 0.03 mol kg^{-1} of IL and decreases upon an increase in the temperature [31]. In contrast, the oxidant concentration in BMImBr–$CuBr_2$ ionic liquid is high, and its activity increases with an increase in the temperature.

Polarization diagrams of the copper electrode in BMImBr and BMImBr–$CuBr_2$ ionic liquids at 30°C are shown in Fig. 1. As is seen from Fig. 1 (diagrams 1–3), a plateau corresponding to the limiting oxygen diffusion current in a natural aerated unstirred BMImBr is observed on the cathodic polarization curve in the absence of Cu(II). It should be noted that the order of magnitude of the molecular oxygen diffusion coefficient in IL containing 1-butyl-3-metilimidazolium cation is 10^{-6} cm^2 s^{-1} [32]. The limiting diffusion current density does not change in time and does not depend on the exposure of the sample in IL, and remains within a range from 39 to 41 μA cm^{-2}. Tafel slope b_a of the anodic polarization curves is 0.24 ± 0.02 V. Such b_a values are seemingly determined by the formation of a corroding surface film of copper oxidation products. The film not passivates metal but influences the kinetic of the anodic process.

In line with general notions about the corrosion of metals with oxygen depolarization, the corrosion current, j_{cor}, is determined by the limiting oxygen diffusion current [33]. In order to compare the j_{cor} values obtained from the results of polarization and gravimetric data, the corrosion current density of copper was calculated by the following equation [33]:

$$j_{\mathrm{cor}} = \frac{\Delta m}{S \tau A} z F,$$

where Δm is the change of the sample weight after corrosion testing, S is the surface area of the tested sample, τ is the corrosion testing time, A is the atomic weight of metal, z is the oxidation number of metal ($z_{Cu} = 2$), and F is the Faraday constant. The calculation results are given in Table 2 in comparison with the data obtained from the polarization diagrams.

As is seen from Table 2, the values of the limiting current density of oxygen diffusion and corrosion current density of Cu in BMImBr are equal. Thus, the corrosion rate of copper in 1-butyl-3-metilimidazolium bromide is controlled by the oxygen diffusion to corroding metal, which is determined by the experimental conditions (natural aeration and unstirred).

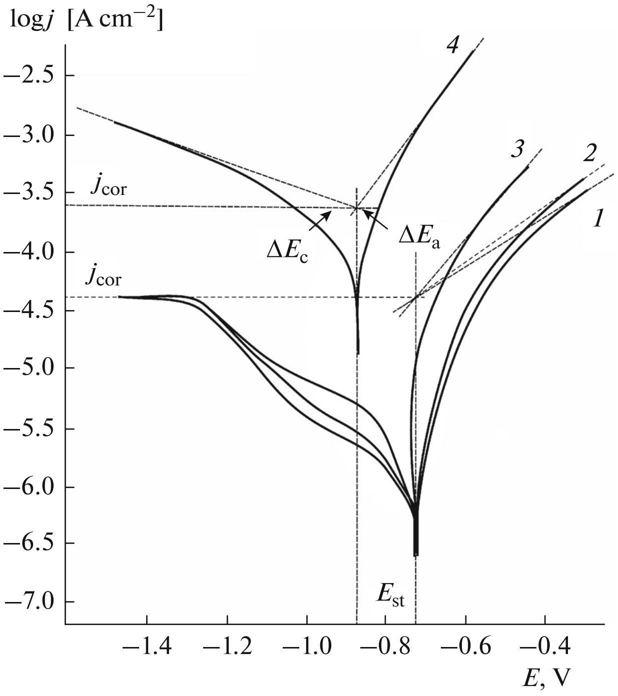


Fig. 1. Polarization diagrams of the copper electrode (*1*–*3*) in BMImBr and (*4*) in IL containing $CuBr_2$ (0.4 mol kg^{-1} of BMImBr) for exposure times of (*1*, *4*) 1, 2 (*2*), and (*3*) h at 30°C and a potential scanning rate of 1 mV s.

Table 2. Corrosion current density of copper in BMImBr and BMImBr–$CuBr_2$ ILs as depending on contact time with a corrosive medium at different temperatures

$CuBr_2$ content, mol kg^{-1} of BMImBr	t,°C	Corrosion-current density j_{cor}, μA cm^{-2}				
		0.5 h	1 h	1.5 h	2 h	3 h
0	20	26.2	16	17.7	4.2	–
	30	–	56	–	39	45
		–	[39]*	–	[40]*	[41]*
	70	549.1	105.4	84.3	47.2	–
0.4	20	345.8	161.9	172.9	170.4	–
	30	–	280	–	223	126
		–	[251]*	–	–	–
	70	1056	791	912	791	–
1.2	70	1409	845	989	747.5	–

* The j_{cor} values obtained from polarization diagrams.

A plateau of the limiting diffusion current of the oxidant, Cu(II)-containing ions, is not observed on the polarization diagram obtained in BMImBr–$CuBr_2$ ionic liquid (Fig. 1, diagram *4*). The concentration of these ions is significantly higher than the concentration of dissolved oxygen. The slope of the anodic polarization curve in the Tafel area of potentials is $b_a = 0.22 \pm 0.01$ V. At j_{cor} $\Delta E_k \gg \Delta E_a$ (where ΔE_k and ΔE_a are the cathodic and anodic polarizations of copper, respectively). Corrosion current density j_{cor} calculated from this diagram is 251 μA cm^{-2}. It is evident that the j_{cor} values obtained by the gravimetric and electrochemical methods are close to each other both for copper in BMImBr–$CuBr_2$ ionic liquid and in pure BMImBr (Table 2).

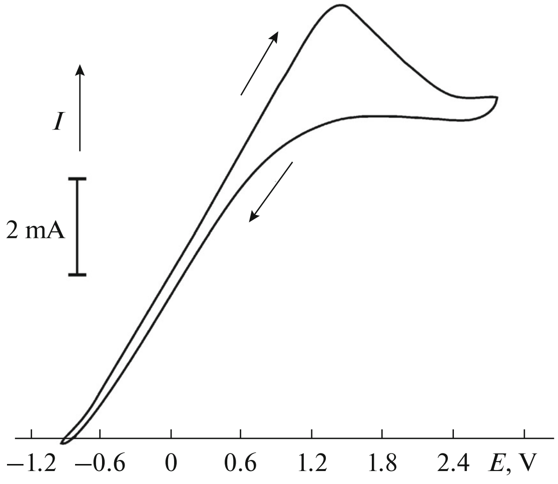


Fig. 2. Cyclic voltammogram of the copper electrode in ionic liquid in IL containing $CuBr_2$ (1.2 mol kg^{-1}) at a temperature of 70°C, a potential scanning rate 20 mV s^{-1}, and an electrode surface area of 0.32 cm^2.

Anodic Oxidation of Copper in BMImBr–$CuBr_2$ Ionic Liquid

A typical cyclic polarization curve obtained in the area of anodic potentials for the copper electrode in BMImBr–$CuBr_2$ ionic liquid is shown in Fig. 2. A broad current maximum transitioning into a limiting current plateau is observed on it. The current is not decreased upon changing the scanning direction of the potential and preserves the value close to the limiting current until reaching the potential peak. Similar behavior of the copper electrode during the anodic polarization was observed earlier in aqueous solutions of sulfuric acid and sodium thiosulfate [34, 35]. Maximum current density j_{max} linearly depends on the square root of potential scanning rate V as shown in Fig. 3. The straight lines intersect the j_0 segments on the current density axis, the values of which are close

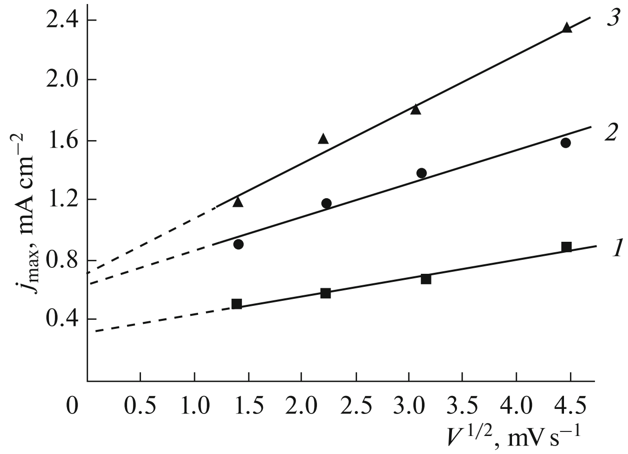


Fig. 3. Dependence of the current maximum of anodic polarization curves of copper in BMImBr–$CuBr_2$ IL (0.4 mol kg^{-1}) on the $V^{1/2}$ value at temperatures of (*1*) 50, (*2*) 60, and (*3*) 70°C.

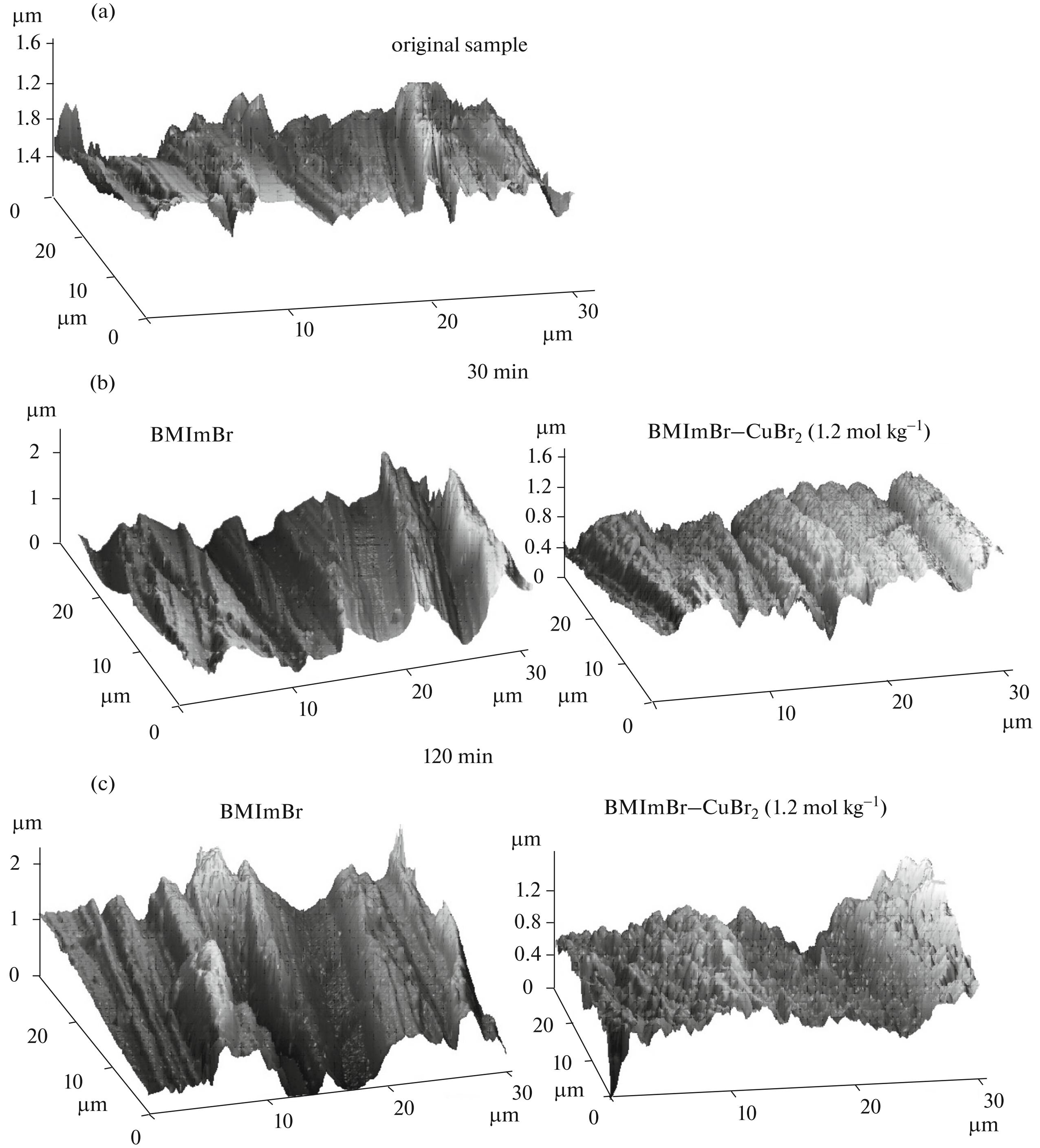


Fig. 4. 3D AFM images of the copper sample surface (a) in the initial state, and after (b) 30- and (c) 120-min exposure in BMImBr ionic liquid and in ionic liquid containing $CuBr_2$ (1.2 mol kg^{-1}) at 30°C.

to the limiting current of the anodic polarization curve at a relevant temperature. Such appearance of the anodic polarization curves and j_{max}–$V^{1/2}$ dependences is typical for the processes of anodic dissolution of metals with the formation of a porous layer of the primary anodic reaction products, which then chemically react with the electrolyte components (EC process) [34–36]. At the same time, the j_0 value expressed in current density units corresponds to the rate of the chemical reaction between the surface-film material and electrolyte. Particularly high j_0 values (i.e., high dissolution rates of films) are observed in the case in

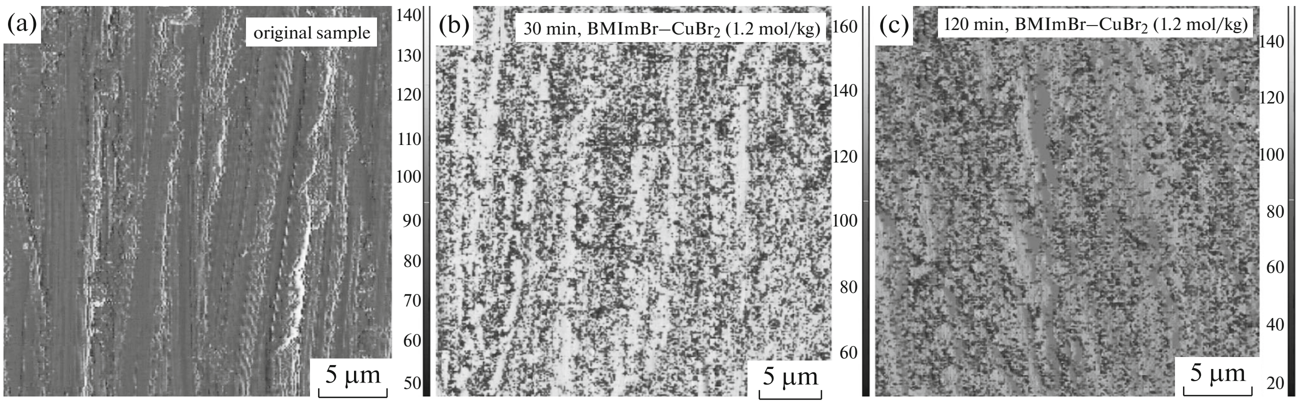


Fig. 5. Surface image of copper in the phase contrast mode (a) before and after (b) 30- and (c) 120-min exposure in a binary melt containing $CuBr_2$ (1.2 mol kg^{-1} of BMImBr) at 30°C.

which the electrolyte anions form complex compounds with the cations of anodically dissolving metal [35]. Consequently, the film of primary products of the anodic oxidation of copper intensely reacts with the studied IL. Nevertheless, this layer is capable of limiting the dissolution rate of metal. The j_0 values in the melt with a $CuBr_2$ concentration of 0.4 mol kg^{-1} of BMImBr at temperatures of 50, 60, and 70°C are 340, 650, and 690 μA cm^{-2}, respectively. The j_0 value equals 1307 μA cm^{-2} at a $CuBr_2$ concentration of 1.2 mol kg^{-1} of BMImBr and a temperature of 70°C. A comparison of the j_0 values with the values of the copper corrosion current density (Table 2) shows that they are of the same order of magnitude.

Smoothing Properties of BMImBr–CuBr$_2$ Ionic Liquid

It is well known that the formation of films (or viscous layers) of metal-dissolution products promotes the creation of favorable conditions for the smoothing (polishing) of its surface [37]. It is important that the produced film (1) does not passivate metal and shows minimal adhesion to the surface, (2) allows oxidant to access the treated surface, and (3) has comparable formation and dissolution rates. As shown above, the studied BMImBr–$CuBr_2$ ionic liquid shows the enumerated properties; therefore, it could be probably used for the chemical polishing of copper.

The performed studies showed that the exposure of the copper sample in BMImBr–$CuBr_2$ ionic liquid melt is accompanied by a visually observable polishing effect. The experiment was carried out in IL with a $CuBr_2$ concentration of 1.2 mol kg^{-1} of BMImBr at 30°C for 30–120 min. By measuring the surface roughness of the copper samples before and after the electrolytic treatment, it is established that the relative change of the electrode profile mean deviation, R_a, decreases is about twofold. An increase in the temperature up to 50°C leads to a more significant decrease in the R_a value of the treated surface.

The surface topology of the copper samples before and after the exposure in copper-containing ionic liquid is studied by the method of atomic-force microscopy (AFM). The results are shown in Fig. 4. A comparison of the AFM images of the copper surface after its corrosion in BMImBr and BMImBr–$CuBr_2$ ionic liquids shows that the pure solvent, in contrast to the Cu(II)-containing melt, has almost no smoothing effect on the microprotrusions on the copper surface (Fig. 4). The surface is most actively polished on the top of bumps, grooves, etc. The corrosion process gives rise to etching of copper on the grain boundaries and to the formation of a new phase, as is rather well seen in Fig. 5. The primary corrosion product (CuBr) can be converted in the two ways: by the dissolution in ionic liquid with the formation of the complex $[CuBr_2]^-$ ion or by the disproportionation with the formation of well soluble $CuBr_2$ and Cu. As a result, the prolonged contact of the copper surface with ionic liquid leads to a noticeable cleaning of the surface layer from a salt phase.

CONCLUSIONS

The study of the corrosion behavior of copper reveals that the corrosion in self-aerated BMImBr ionic liquid proceeds with oxygen depolarization. Copper dibromide plays the role of an oxidant in BMImBr–$CuBr_2$ ionic liquid. The copper corrosion rate is an order of magnitude higher at a $CuBr_2$ concentration in the range from 0.4 to 1.2 mol kg^{-1} of BMImBr. A loose (or viscous) layer of corrosion products is formed on the copper surface upon exposure in such an electrolyte, creating the conditions for the effect of polishing.

It is shown by the cyclic-voltammetry method that the anodic (and consequently corrosive) dissolution of copper in BMImBr–$CuBr_2$ ionic liquid proceeds via the EC mechanism, where C designates the chemical dissolution reaction of the layers of primary products of anodic oxidation of copper upon their interaction with the electrolyte components. It is established that the chemical-reaction rate of dissolution of the surface layer in ionic liquids with additions of $CuBr_2$ and the copper-corrosion rate, which is calculated based on the gravimetric and polarization data, are comparable in value.

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