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Kinetics of Phase Transformations during Selective Dissolution of Cu_5Zn_8

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Abstract

The study determined the kinetics of the selective anodic dissolution of the copper-zinc intermetallic compound Cu_5Zn_8 (gamma-phase) in an acetate buffer solution. Microscopic and X-ray analysis methods demonstrated the selective nature of the corrosive dissolution of Cu_5Zn_8 . The dissolution results in the dezincification of the intermetallic compound and morphological development of its surface accompanied by the formation of the copper phase. A theoretical model of the transition of the electrode surface to the critical state together with the experimental concentration dependencies of the critical potential and critical overvoltage demonstrated that the dissolution of zinc from Cu_5Zn_8 is most probably limited by the non-stationary diffusion mass-transfer in the solid phase of the intermetallic compound. The study also demonstrated that the phase transformation during the overcritical selective anodic dissolution of the gamma-phase of Cu_5Zn_8 in an acetate environment accelerates following the growth of the anodic potential and is controlled by the surface diffusion of adatoms towards the three-dimensional nucleus of the copper phase with instantaneous nucleation.

Keywords: copper-zinc alloy, gamma phase, selective dissolution, phase transformation, surface development, heterogeneous nucleation.

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1. Introduction

Copper-zinc alloys and intermetallic compounds with comparatively high concentrations of electronegative components (>15 at% Zn) are susceptible to selective dissolution (SD) of zinc in aqueous solutions [1]. Dezincification belongs to a large group of processes caused by selective external influence (e.g. chemical, temperature, or laser) on multicomponent materials. In case of solid homogeneous copper-zinc alloys, the preferential dissolution of zinc may be accounted for by the difference in the volatility of Cu and Zn during vacuum evaporation [2–4] or in the rate of atomic diffusion during laser sublimation [5, 6]. The electrochemical

dezincification of brasses, however, is based on the difference in the electrode potentials of the components in the medium [7–9].

Selective leaching of zinc results in the formation of a porous structure with a significantly reduced mechanical strength, as compared to the initial material, and often causes the complete destruction of the initial material [10–13]. In order to protect construction materials based on copper-zinc alloys from dezincification, it is necessary to determine the kinetics and mechanism of selective dissolution of zinc in aqueous electrolyte solutions. Furthermore, knowing the kinetics of the process, we can define the optimal conditions for the synthesis of a SD product, macro- and nanoporous copper [5, 6,

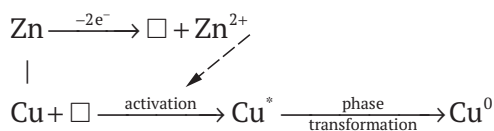
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14–17], which is a promising material that can be used in electrochemical technologies and energy production.

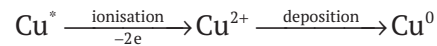
The formation of the porous structure during the SD of a homogeneous Cu–Zn alloy or an intermetallic compound is possible given the following conditions. The initial system must be based on zinc. The ionisation of a certain (critical) amount of zinc results in such an increase in the thermodynamic activity of electrochemically stable copper, that phase transformation (PT) can take place accompanied by the formation of the metallic copper Cu^0 phase. Selective dissolution of Cu–Zn systems with phase transformation was experimentally demonstrated in [18–20]. The increased thermodynamic activity of the electropositive metal during the SD of the binary alloy was theoretically substantiated in [21–23] using the methods of nonequilibrium thermodynamics. Regarding copper-zinc alloys, it can be described as follows. Vacancies \square formed as a result of the dissolution of zinc serve as intermediates for the redistribution of the Gibbs free energy in the highly defective surface layer of the alloy. This results in the thermodynamic activation of copper undergoing phase transformation conjugated with zinc ionisation:



A characteristic feature of selective dissolution accompanied by phase transformation is a substantial morphological development of the surface layer of the alloy. For copper-zinc alloys this was demonstrated using impedancemetry [24] and physical methods of surface investigation [25].

In our research, we studied the dezincification of Cu–Zn systems accompanied by phase transformation of the alloy using industrially manufactured high-temperature copper-zinc solder PMTs-36. The chemical composition of this intermetallic system includes ~36 at% of copper. The intermetallic system is the gamma phase of Cu–Zn. PMTs-36 solder was chosen as the material for the study of the PT, because the probability of copper ionisation/deposition

(a process alternative to phase transformation) during the anodic dissolution of this solder is low



The fact is that anodic potentials during the electrochemical dealloying of zinc-rich alloys are negative, which means that copper does not get dissolved. Furthermore, to study the kinetics of the selective dissolution of PMTs-36 the sample was put into an acetate buffer solution. According to [9], in this medium the soluble corrosion products of the γ -phase of Cu–Zn are zinc ions Zn^{2+} , the insoluble product is metallic copper Cu^0 , and copper oxides are not formed. In other words, the anodic process involving the studied alloy is the selective dissolution proper. Therefore, the total anodic current equals the partial current of zinc ionisation.

We also took into account the fact, that the beginning of the phase transformation and morphological development of the surface of the Zn-based Zn–Cu alloy undergoing selective dissolution is characterised by certain critical values of the charge q_{cr} transferred through the electrode and the anodic potential E_{cr} [26]. The transition to the critical state is indicated on the polarization curves and chronoamperograms by a rapid increase in the anodic current i . According to the theoretical model of transition to the critical potential [27], the values E_{cr} for the copper-zinc alloy in the media with various activity levels of Zn^{2+} ions can be used to determine the kinetics of selective dissolution and the partial rates of SD and PT.

The aim of this paper was to determine the kinetics of the selective anodic dissolution of the copper-zinc intermetallic system (γ -phase) in an acetate buffer solution.

In order to achieve this we needed to complete the following tasks.

To determine the critical parameters for the development of the electrode surface during the selective anodic dissolution of the copper-zinc system (γ -phase) in an acetate buffer solution.

To determine the rate of partial electrode processes involving the components of the copper-zinc intermetallic system (γ -phase) (zinc ionisation and phase transformation of copper) and define the nature of the limiting stage of copper recrystallization.

2. Experimental

The study was carried out using polycrystalline metals (Cu, Zn) and an industrially manufactured copper-zinc solder, PMTs-36 (atomic fraction of copper – 0.36). According to the phase diagram and the results of X-ray diffractometry, the system was an intermetallic compound Cu_5Zn_8 . To make the electrode, the metallic sample was cut, sanded, and mounted in polymerizable epoxy resin. The standard preparation of the surface of the electrode for the experiment included polishing with abrasive paper of decreasing grade, mirror-polishing with suede leather and an MgO alcohol-based suspension, washing, degreasing with isopropyl alcohol, and drying with filter paper.

The following solutions were used: 0.05 M $\text{CH}_3\text{COONa} + 0.05 \text{ M CH}_3\text{COOH} + x \text{ M ZnSO}_4$ ($x = 10^{-4} \div 10^{-2}$) and an acetate buffer solution 0.05 M $\text{CH}_3\text{COONa} + 0.05 \text{ M CH}_3\text{COOH}$ prepared using bidistilled aqueous solution and AR grade reagents. The solutions were also preliminary deaerated with chemically pure argon for 1.5 hours. The experiment was conducted on unstirred solutions.

The study was performed using a three-electrode glass cell with the working and the auxiliary (platinum) electrode being in the same compartment. A silver chloride reference electrode was placed in a separate container linked to the electrolytic cell by a salt bridge with a potassium nitrate saturated solution. The potential values E are given according to the standard hydrogen electrode (SHE) scale. The current i was calculated for the visible geometric area of the electrode S_{geom} .

The measurement and control of the electrode potential and the registration of the polarization curves was performed using an IPC-compact computer-aided potentiostat. A prepared electrode was put into the cell filled with a deaerated solution and held until the open-circuit potential reached quasi-stationary values. During the potentiodynamic measurements, the potential scan rate V was set and the i, E -dependency was recorded. During the chronoamperometric measurements, the potential $E = \text{const}$ was set and the i, t -dependency of the current decay over time was recorded for 15–20 minutes.

The morphology of the surface of the alloy was studied using scanning electron microscopy (SEM) (JSM-6380LV microscope). The chemical composition of the surface layer was determined by means of energy dispersive X-ray spectroscopy (EDX) (INCA 250 system), and the phase composition was determined using X-ray diffractometry (ARL X'TRA diffractometer). The results of the SEM, EDX, and X-ray diffractometry studies were obtained using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University (<http://ckp.vsu.ru>).

3. Results and discussion

The results of the EDX proved that the dissolution of the copper-zinc alloy PMTs-36 in the acetate buffer solution is selective: after 400 days of incubation the concentration of copper increased from 36 to 76 at.% on average, which indicates deep dezincification of the system. The corrosion process is accompanied

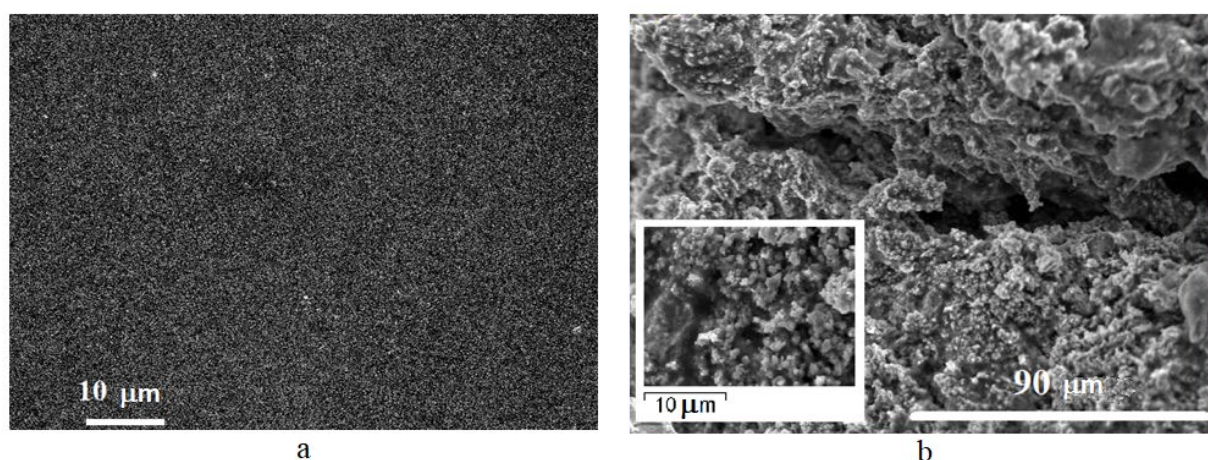


Fig. 1. SEM photographs of the surface of the PMTs-36 alloy before (a) and after (b) 400 days of immersion in a 0.05 M $\text{CH}_3\text{COOH} + 0.05 \text{ M CH}_3\text{COONa}$ solution

by a substantial morphological development of the surface (Fig. 1). The results of the X-ray diffractometry indicate the formation of the copper phase during corrosive dissolution of the PMTs-36 alloy in the 0.05 M $\text{CH}_3\text{COOH} + 0.05$ M CH_3COONa solution (Fig. 2). Indeed, the initial sample was the intermetallic compound Cu_5Zn_8 . However, after the PMTs-36 alloy was held in the acetate buffer solution for a long time, the X-ray diffraction pattern demonstrated peaks corresponding to metallic copper. Therefore, corrosion of PMTs-36 in the studied solution is selective. It is accompanied by the phase transformation of $\text{Cu}_5\text{Zn}_8 \rightarrow \text{Cu}$.

In order to determine the kinetics of selective dissolution of the intermetallic compound Cu_5Zn_8

we need to analyse the anodic behaviour of the studied copper-zinc alloy PMTs-36 in the acetate solution using the corresponding polarization curves (Fig. 3). We can see that the dissolution of the alloy proceeds at significantly more positive potentials than the dissolution of pure zinc. Judging by the position of the polarization curve of copper, we can suggest that within the studied range of potentials copper is electrochemically stable and does not dissolve.

Upon reaching a critical potential E_{cr} the polarization curve of the alloy demonstrates a region of rapid increase in the anodic current density. This increase might indicate the beginning of phase transformation and surface development, because other electrochemical processes, such as

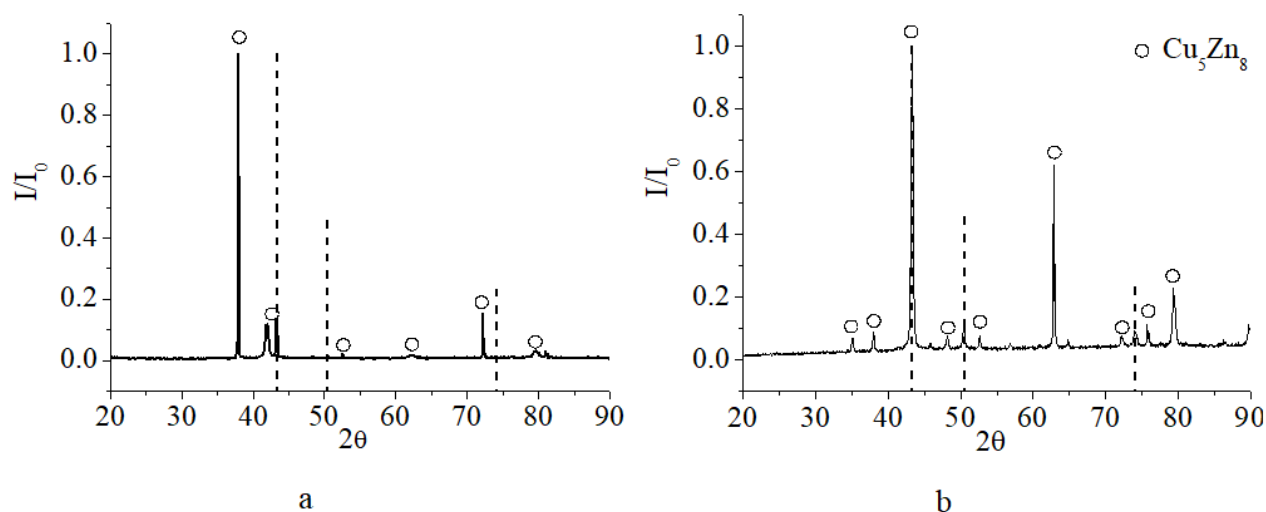


Fig. 2. X-ray diffraction patterns of the surface of the PMTs-36 alloy before (a) and after (b) 400 days of immersion in a 0.05 M $\text{CH}_3\text{COOH} + 0.05$ M CH_3COONa solution. The peaks of the polycrystalline copper are marked with dotted lines [28]

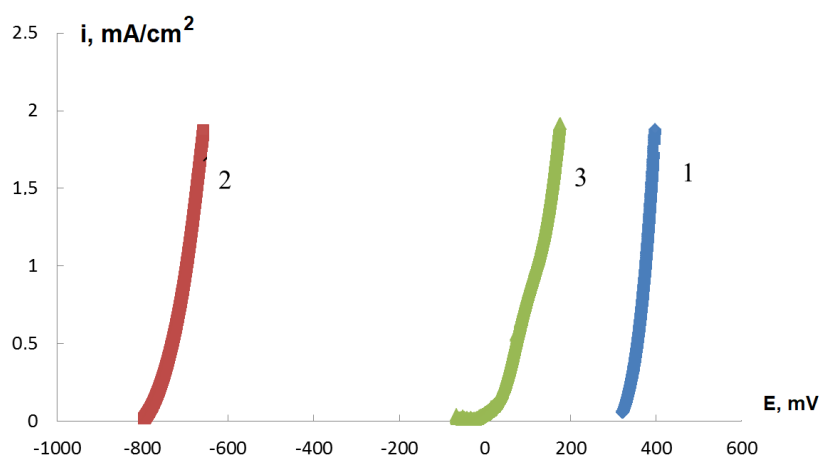


Fig. 3. Anodic polarization curves of Cu (1), Zn (2), and PMTs-36 (3) in a 0.05 M $\text{CH}_3\text{COOH} + 0.05$ M CH_3COONa solution with $V = 0.5$ mV/s

copper dissolution or oxygen evolution, take place at significantly more positive potentials. Values E_{cr} were determined by means of tangents to the high-current region of the i, E -curve [26]. The difference between E_{cr} and the open-circuit potential $E(0)$ of the electrode in the solution was used to calculate the critical overpotential η_{cr} for the selective dissolution of PMTs-36. It appeared that the activity level of Zn^{2+} ions in the solution does not effect anodic polarization curves. However, an increase in ion activity is accompanied by a significant increase in E_{cr} . Within the studied concentration range, the dependency of E_{cr} on $a_{\text{Zn}^{2+}}$ is linearized with the slope being $\sim 42 \pm 2$ mV (Fig. 4a). According to the theoretical model of E_{cr} [27], this indicates the fact that the diffusion process is hindered mainly in the solid phase. In turn, the critical overpotential η_{cr} alters unsystematically with various $a_{\text{Zn}^{2+}}$ (Fig. 4b). This is another proof that in the vicinity of the critical potential the system PMTs-36 undergoes solid-phase-diffusion, because according to [27] $d\eta_{\text{cr}}/d \lg a_{\text{Zn}^{2+}} = 0$ under these conditions.

To determine the kinetics of phase transformation occurring at overcritical potentials parallel to the selective dissolution of zinc from Cu_5Zn_8 in the acetate buffer solution, we need to analyse the results of potentiostatic chronoamperometry presented as the current decay curves replotted in a bi-logarithmic scale (Fig. 5a).

These curves have linear regions which, following the Cottrell equation [29], indicate that the diffusion mass-transfer is the controlling stage of the SD. Combined with the above given data on the concentration dependence of the critical potential, the observed partial rectification of the chronoamperograms in a bi-logarithmic scale is another proof that the solid-phase diffusion SD takes place.

At some point, the current decay becomes less prominent, or the current begins to grow. The nonlinearity increases with higher anodic potential, which may be accounted for by the phase transformation taking place parallel to the SD. Indeed, the phase transformation allows the electrolyte to penetrate into the deeper layers of the alloy dissolving larger amount of zinc and thus increasing the rate of the SD [27].

Let's assume that the nonlinearity of the bi-logarithmic chronoamperogram is determined by two non-stationary processes: selective dissolution of Zn during the slow non-stationary diffusion mass-transfer at the rate $i_{\text{diff}}(t)$ and phase transformation involving Cu at the rate $i_{\text{nucl}}(t)$. Then the current transient of the PT $i_{\text{nucl}}(t)$ can be calculated [27] as the difference between the total (registered in the experiment) current density $i(t)$ and the diffusion current density calculated using the Cottrell equation:

$$i_{\text{nucl}}(t) = i(t) - i_{\text{diff}}(t),$$

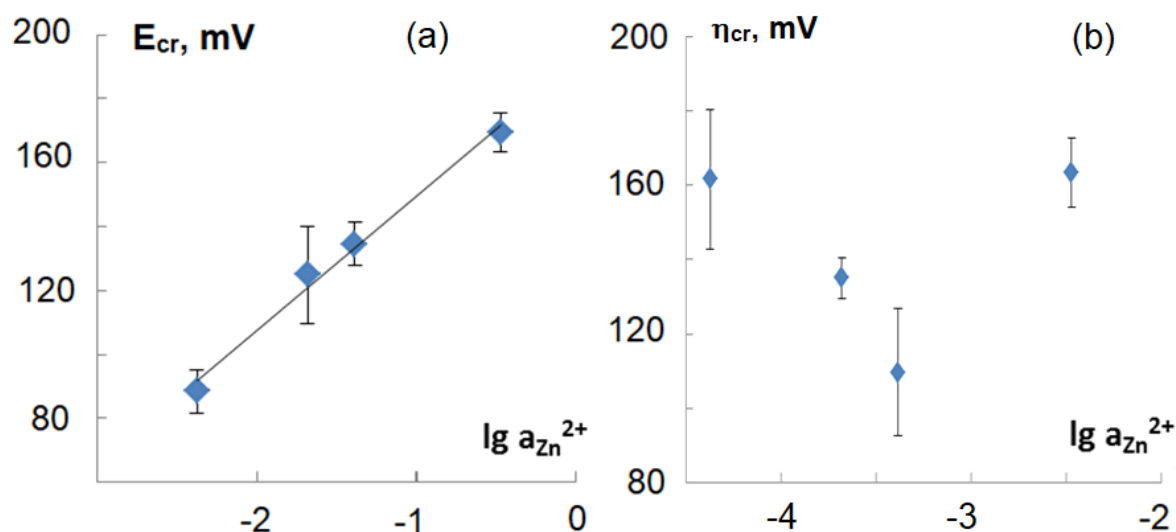


Fig. 4. Dependence of the critical potential (a) and critical overpotential (b) of the development of the PMTs-36 surface on the ion activity Zn^{2+} in the acetate buffer solution 0.05 M CH_3COOH + 0.05 M CH_3COONa with various concentrations of zinc ions

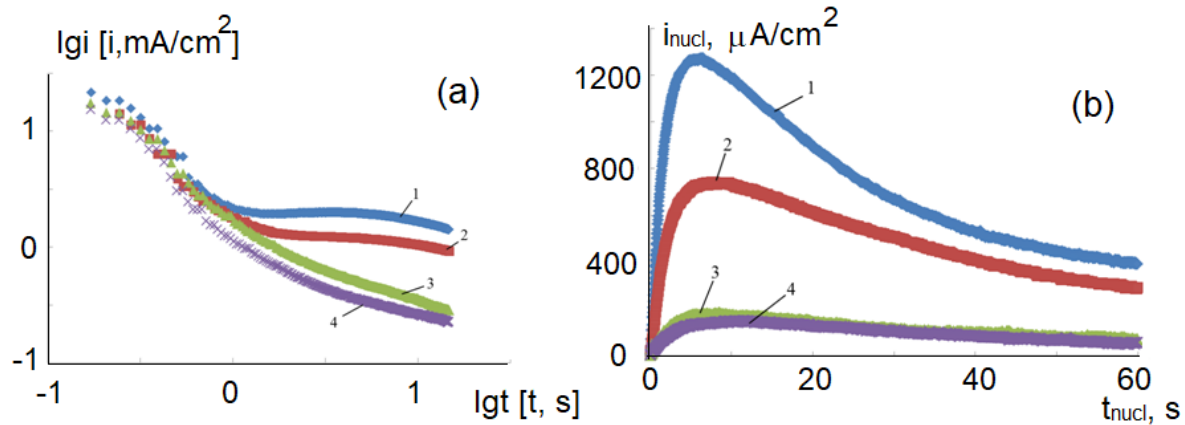


Fig. 5. Anodic chronoamperograms of zinc dissolution (a) and phase rearrangement of copper (b) during SD of Cu_5Zn_8 in a 0.05 M CH_3COOH + 0.05 M CH_3COONa solution with $E = 50$ mV (1), 0 mV (2), -50 mV (3), and -100 mV (4)

The resulting dependence of the phase formation current on time is given in Fig. 5b. We can see that the PT current grows over time. The rate of the growth increases with the growth of the anodic potential, and the chronoamperogram presents a curve with a peak, characteristic of the phase formation process.

To determine the kinetic-limitations to the formation of the Cu phase during selective dissolution of the intermetallic compound Cu_5Zn_8 , the calculated current transients were replotted in the coordinate criterion for various models of heterogeneous nucleation. It appeared

that partial linearisation is only possible over a short period of time during the diffusive mode of three-dimensional nucleation only, provided that the activation of the potential nucleation centres is instantaneous (Fig. 6). The diffusion character of the formation of a new copper phase during the SD of Cu_5Zn_8 is also demonstrated by the comparison of experimental kinetic curves with the model dependencies calculated for various modes of heterogeneous nucleation (Fig. 7).

The quantitative estimation of the effect of anodic potential on the rate of copper PT was performed by analysing the values of the effective

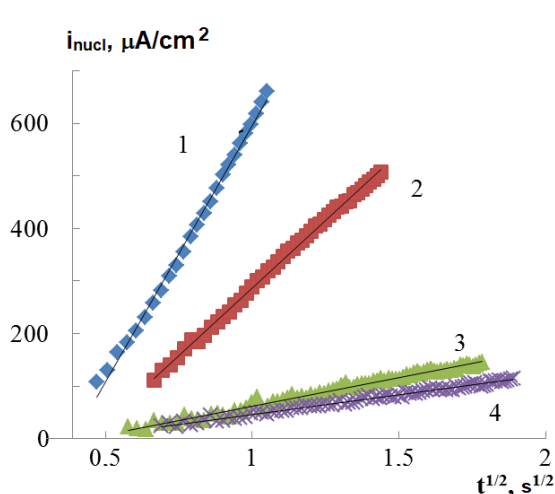


Fig. 6. Linearization of the current transients of PT and SD of the intermetallic compound Cu_5Zn_8 in the coordinates criterion for the instantaneous three-dimensional nucleation during the anodic dissolution in a 0.05 M CH_3COOH + 0.05 M CH_3COONa solution with $E = 50$ (1), 0 (2), -50 (3), and -100 mV (4)

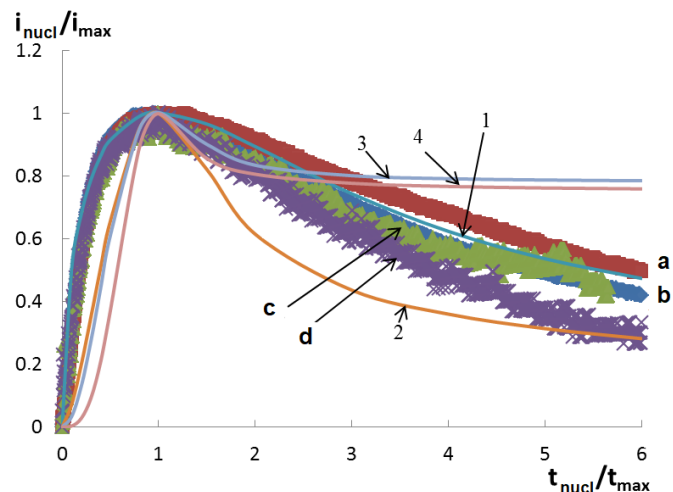


Fig. 7. Dependence of the phase transformation currents during selective dissolution of Cu_5Zn_8 in a 0.05 M CH_3COOH + 0.05 M CH_3COONa solution at various potentials: a, b, c, d – experimental curves; 1 – instantaneous activation, diffusion control; 2 – progressive activation, diffusion control; 3 – instantaneous activation, kinetic control; 4 – progressive activation, kinetic control

rate constant $k_{\text{nucl}} = di_{\text{nucl}}/dt^{0.5}$, determined as the slope of the dependence of PT current density on time in the coordinates criterion for the instantaneous three-dimensional nucleation proceeding in the diffusion mode. Values k_{nucl} are given in Fig. 8. The effect of the anodic potential is obvious, since the shift towards the positive side results in a significant increase in k_{nucl} . This can be explained by the growth of the concentration and rate of the surface diffusion of copper adatoms appearing on the surface during the SD.

4. Conclusions

1. The study determined that corrosion of the copper-zinc alloy PMTs-36, (a single-phase intermetallic system Cu_5Zn_8) in the acetate buffer solution is a selective process. It results in the dezincification of the alloy and is accompanied by morphological development of its surface and phase transformations resulting in the formation of the copper phase.

2. The experiments allowed us to determine the critical potential E_{cr} and the critical overpotential η_{cr} , indicating the beginning of the phase transformation and morphological development in the surface layer of the intermetallic compound Cu_5Zn_8 during its selective anodic dissolution in the acetate buffer solution. Analysis of the dependence of E_{cr} and η_{cr} on the concentration of zinc ions in the solution by means of the theoretical model of transition of the electrode surface to the critical state demonstrated that the dissolution of zinc from Cu_5Zn_8 is most probably limited by the stage of non-stationary solid-phase diffusion.

3. The study determined that the rate and effective rate constant for the phase transformation during the overcritical anodic dissolution of the intermetallic compound Cu_5Zn_8 increase significantly with the growth of the anodic potential. The regression analysis of the nucleation dependencies using several deterministic models of heterogeneous three-dimensional nucleation demonstrated that copper phase formation is controlled by the surface diffusion towards the three-dimensional nucleus of the new phase with instantaneous nucleation.

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The results of the SEM, EDX, and X-ray diffractometry studies were obtained using the

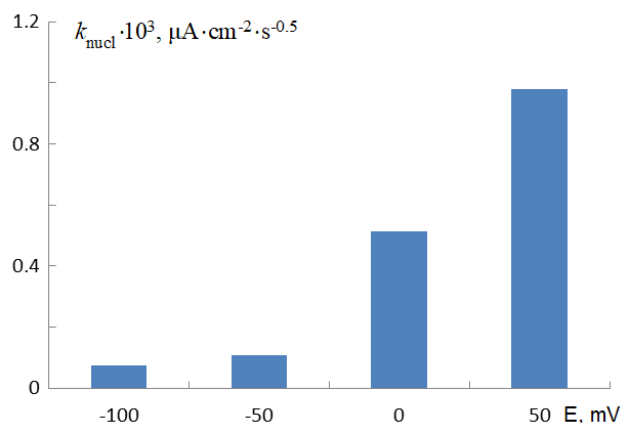


Fig. 8. Dependence of the effective rate constant of the phase transformation during selective dissolution of Cu_5Zn_8 in a 0.05 M CH_3COOH + 0.05 M CH_3COONa solution on the anodic potential

equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University (<http://ckp.vsu.ru>).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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