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Anodic behaviour of copper during electrorefining using a rotating ring-disc electrode

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The anodic dissolution of copper during electrorefining has been studied by a rotating ring-disc electrode technique. The influence of temperature, some additives (Cl^- ions and polyethylene glycol) and the anode-alloying element (phosphorus) on the polarization curves was examined. It was shown that at certain conditions the concentration of Cu^+ ions on the ring electrode decreased. As a result, a reduction of powdered copper in the electrolyte due to the disproportionation of cuprous ions may be expected.

1. Introduction

The anodic dissolution of copper in sulphuric acid/sulphate electrolytes used for plating has been studied by many authors [1–7]. There have been a number of studies which address the passive state of copper [8], the effect of Cl^- ions [9–12] and some surface active agents [13–19] upon the anodic behaviour of this metal. It has been shown that Cl^- ions and some surface active agents form complexes with Cu^{2+} and Cu^+ ions [18, 20]. Several authors have investigated the electrolytic dissolution of phosphorus-containing copper [21–26].

The anodic behaviour of copper during electrorefining has attracted the attention of relatively few authors. Regardless of the fact that copper electrorefining was one of the first electrometallurgical processes to be used in industry, the mechanism of anodic oxidation is still insufficiently studied and several practical and fundamental problems of a purely electrochemical nature remain to be solved. One of the most important issue is anodic passivation and relatively more investigations have been devoted to this problem [27–32]. Numerous hypotheses about the mechanism of anodic passivation during the electrorefining of copper have been proposed, but a comprehensive solution is still lacking. However, it has been proved that the high acidity of the electrorefining electrolyte renders the copper anodes more prone to passivation and this is due to the formation of a surface layer of crystallized copper sulphate.

Another issue in copper electrorefining is slime formation, a problem relatively rarely investigated [33, 34]. It is well known that in copper electrorefining undissolved metals, oxides and chemical compounds form a so-called anodic slime. This slime contains mainly Ag, Au, Se, Te, Pb and deposits on the bottom of the electrolytic cell. The compounds of some other elements (As, Sb, Bi) form the so-called floating slime which is finely dispersed in the electrolyte and may contaminate the cathodic copper [34]. Another deleterious phenomenon is the formation of powdered copper in the electrolyte, that results from cuprous ions disproportionating according to the reaction:

$$2Cu^+ \Longleftrightarrow Cu^{2+} + Cu \qquad (1)$$

The sedimentation of this type of slime is very difficult and it may contaminate the copper deposit with impurities. The powdered copper also participates in the formation of the slime layer on the anode (with lead sulphate and cemented silver), that promotes precipitation of copper sulphate on the anode and accelerates the passivation process. The problem is more complicated since many refining plants apply current reversal, which further increases this type of slime in the electrolyte [20].

Some of the oldest methods for reducing slime formation and its negative effect are: use of optimum electrolyte circulation rates [35] and filtering of the solution [36], but these techniques have several shortcomings. Some novel approaches are also proposed: e.g. the use of bipolar electrodes [37]. Some authors suggest the use of special surface active agents to enhance the coagulation of slime [38].

In the present work model studies of the anodic behaviour of copper during electrorefining are described, with special stress on the electrochemical characteristics of cuprous ions when acting as a source for powdered copper slime formation according to the disproportionation reaction. The investigations are directed toward the determination of the factors affecting the concentration of cuprous ions, in an effort to decrease their amount in the electrolyte.

The experiments were performed using a rotating ring-disc electrode (RRDE) technique [39]. The advantages of the RRDE for the study of a copper system have been elegantly demonstrated [40–44]. The ring can detect any Cu^+ ions which are formed during copper oxidation (disc). Thus it is possible to evaluate the effect of various parameters on the ring current.

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2. Experimental details

The electrorefining electrolyte contained 0.8 M $CuSO_4 \cdot 5H_2O$ and 1.7 M H_2SO_4. All reagents were of analytical grade. The additives used were NaCl and polyethylene glycol with molecular weight 3000 (PEG) or combinations of both compounds.

A thermostated three-compartment electrochemical cell, containing a saturated calomel electrode (SCE) as reference and a platinum wire counter electrode, was used. The electrochemical measurements were carried out with a voltammetric system CBA-1, comprising the following main parts: electric motor, control unit for the pretreatment of the electrode, control unit for the electric regime, generator for scanning the potential according to a predetermined programme and a bipotentiostat. The potentiodynamic measurements were recorded with two X–Y chart recorders.

The working electrode – Cu/Pt RRDE ($r_1 = 2.5$, $r_2 = 2.75$, $r_3 = 3.75$ mm; disc area: 19.625 mm^2) – was polished with fine emery paper, cleaned with ethanol and amply rinsed with distilled water. In most of the experiments, the anodic dissolution of copper was carried out with coatings freshly deposited from acidic plating electrolytes. During the experiments and 30 min before starting, argon was bubbled through the cell.

3. Results and discussion

3.1. *Effect of temperature*

Figure 1 shows the polarization characteristics of the disc and the ring, obtained simultaneously at constant temperature of 25° C. The scan rate of all the experiments was 120 mV min^{-1} within the range 0 to +0.8 V at constant ring potential of $E_R = +700$ mV vs SCE, which corresponds to the potential of the limiting oxidation current of Cu^+ on the ring.

The anodic polarization characteristic of the disc shows an exponential increase of current with potential up to the maximum, and this region corresponds to the active dissolution of copper. The current maximum is followed by a current minimum, after which a plateau is reached representing the passivation region of the electrode.

The recording of the ring current, I_R, during anodic scanning of the disc potential provides evidence that the anodic dissolution of copper under these conditions is a two-stage process. In addition it may be concluded that the main product of the anodic copper dissolution is Cu^{2+}. Cu^+ ions are an unstable intermediate species, and although their stability within the anodic potential region is considerably higher [20], only a small portion of Cu^+ fails to participate in the second electron transfer step.

As the temperature increases from 25 to 55° C, the following effects appear on the polarization characteristics of the disc and ring electrodes:

In the case of the disc (Fig. 2), the increase in temperature leads to a shift in the current maximum towards more positive values, i.e. passivation is retarded. In addition, the value of the maximum polarization current increases at elevated temperatures. This reflects the increased solubility of $CuSO_4$

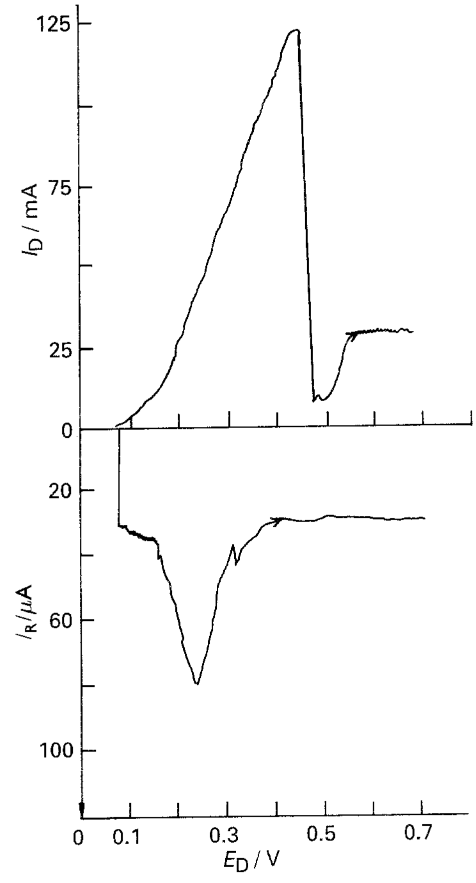

Fig. 1. Potentiodynamic curves $I_D = f(E_D)$ and $I_R = f(E_D)$ at 25° C in the base electrolyte; potential scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.

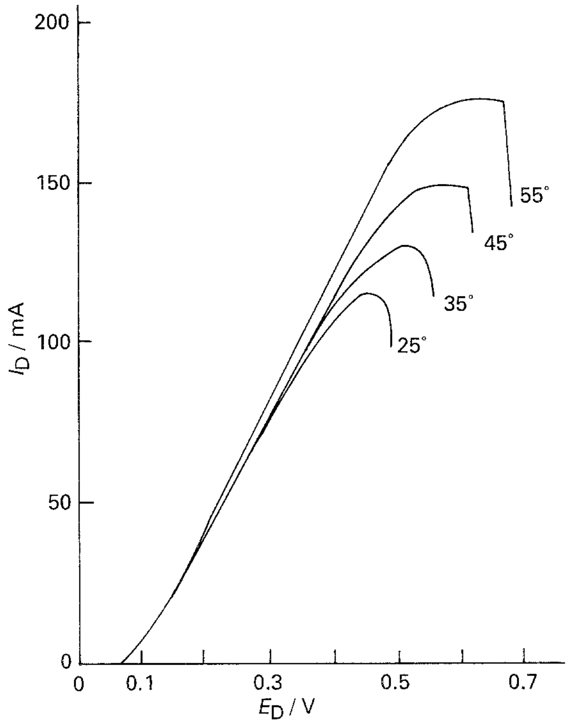

Fig. 2. Potentiodynamic curves traced in the base electrolyte at various temperatures (25, 35, 45 and 55° C); potential scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.

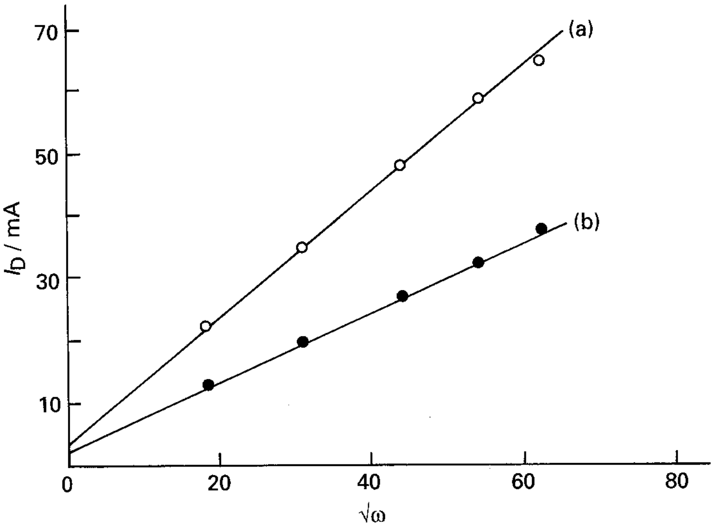

Fig. 3. The anodic current of the disc as a function of the square root of r.p.m. ($I_D = f(\sqrt{\omega})$ at constant disc potentials (a) 200 and (b) 150 mV; base electrolyte at 45° C.

at elevated temperatures and slowing down of the passivation mechanism. This agrees with data of Kish *et al.* [8] for the anodic behaviour of copper at elevated temperatures (up to 38° C) in copper plating electrolytes.

The curves obtained under optimum electrorefining temperature (45° C) show, by increasing the rotation speed of the electrode, that the current at a certain potential (including the critical passivation current) increases considerably within each region of the active branch of the polarization curve. This fact suggests that diffusion plays an important role in the kinetics of the process. Figure 3 shows the relationship between the disc current and rotation speed at potentials of 150 and 200 mV vs SCE. The plots indicate diffusion control of copper dissolution.

The effect of temperature on I_R is shown in Fig. 4. During these measurements the disc potential was kept constant (150 mV), corresponding to the active copper dissolution region in which electrorefining takes place. With increase in temperature, I_R (Cu^+ concentration) increases sharply. The results of these measurements provide evidence that the role played by Cu^+ ions under electrorefining conditions is significant since their concentration in the vicinity of the anode is increased, thus creating favourable conditions for the disproportionation reaction and abrupt increase of powdered copper in the electrolyte.

3.2. *Effect of Cl^- ions and polyethylene glycol*

The potentiodynamic measurements $I_D = f(E_D)$ and $I_R = f(E_D)$, presented in Figs 5 and 6, respectively, show the effect of Cl^- ions at 45° C. As observed in Fig. 5, the peak of I_D decreases markedly and the corresponding potential shifts to more negative values upon addition of Cl^- ions to the electrolyte. Therefore, a certain acceleration of passivation is expected. This phenomenon has been confirmed and explained in the case of copper electrorefining with a cuprous chloride layer adsorbed on the anode causing a general decrease of its active surface and anodic current density [45].

At the same time, a noticeable decrease of I_R was observed (Fig. 6), indicating a decrease of Cu^+ concentration in the presence of Cl^- ions in the electrolyte; a more expressed effect at 0.3 g dm^{-3} Cl^- ions (a change in the shape of the curves) was also observed. The effect of Cl^- ions is a result of the binding of Cu^+ into CuCl, and it is considered favourable with respect to copper slime formation.

Recent years have shown an increasing use of PEG as additive in copper electrorefining electrolytes. The role of this additive as brightening and levelling agent for copper plating is well documented [46–49]. In addition, PEG has been also used as a corrosion inhibitor. This action is a result of the ether oxygens forming surface bonds with Cu, Cu^+ and/or Cu^{2+} ions [50, 51].

The potentiodynamic relationships $I_D = f(E_D)$ at 45° C (Fig. 7) demonstrate that the peak of I_D decreases in the presence of PEG and the potentials of copper electrooxidation become more positive.

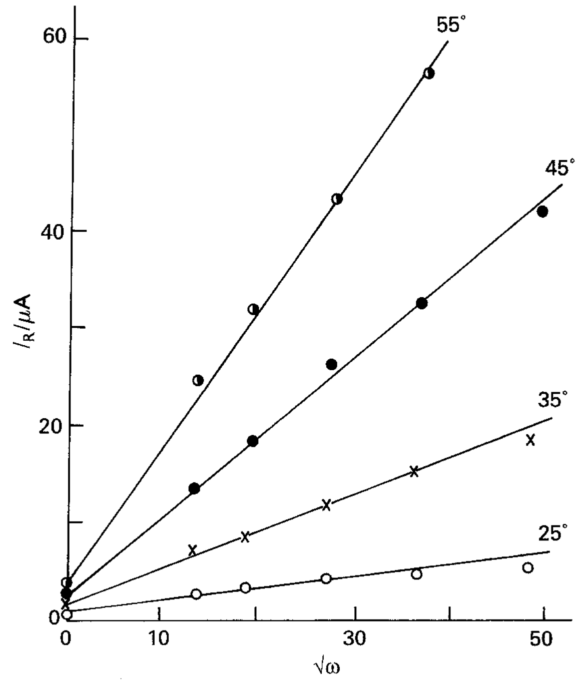

Fig. 4. The effect of temperature (25, 35, 45 and 55° C) upon the oxidation of Cu^+ on the ring (I_R).

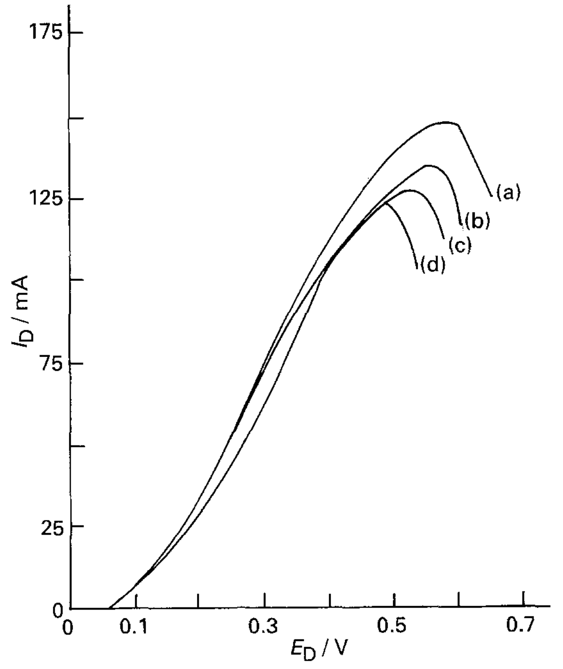

Fig. 5. Potentiodynamic curves $I_D = f(E_D)$ obtained at (a) base electrolyte; (b) base electrolyte containing 0.1 g dm^{-3} Cl$^-$; (c) 0.2 g dm^{-3} Cl$^-$ and (d) 0.3 g dm^{-3} Cl$^-$; scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.; $T = 45°$ C.

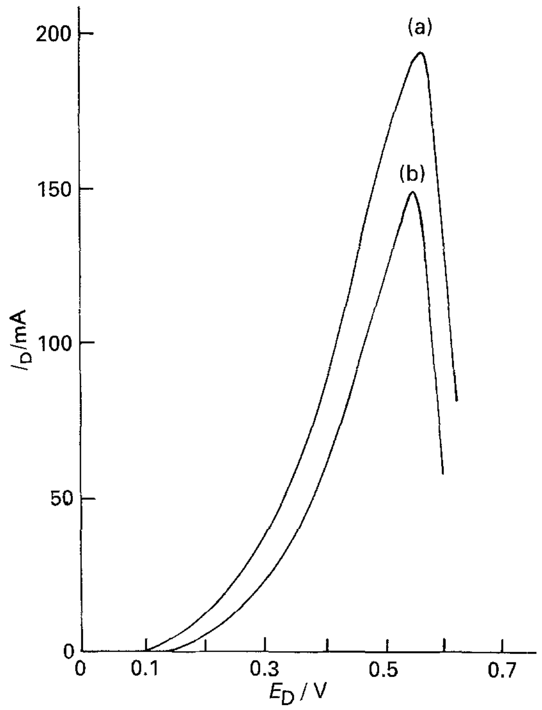

Fig. 7. Potentiodynamic curves $I_D = f(E_D)$ obtained at (a) base electrolyte and (b) base electrolyte containing 0.04 g dm^{-3} PEG; scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.; $T = 45°$ C.

The measurements indicate that this additive effectively inhibits the electrochemical process.

As shown in Fig. 8, the addition of PEG to the electrolyte decreases the ring current and the decrease is proportional to the concentration of PEG. The strongest effect is observed when both PEG and Cl$^-$ ions are present in rather small amounts in the refining electrolyte. (This effect, however, is lower as compared to that in the presence of 0.03 g dm^{-3} Cl$^-$ ions). Therefore, it may be concluded that the combination of PEG and Cl$^-$ ions represents a possibility for suppressing copper slime formation during copper electrorefining. Nonetheless, the combination of PEG and Cl$^-$ polarizes quite efficiently the surface over a broad potential region and the result is a loss in cathode efficiency as reported [20].

3.3. *Effect of the anode-alloying element*

Experiments were carried out using a traditional method for the suppression of copper slime formation, viz the use of P-containing anodes. They were prepared by a special metallurgical processing with the isothermal recrystallization annealing being an

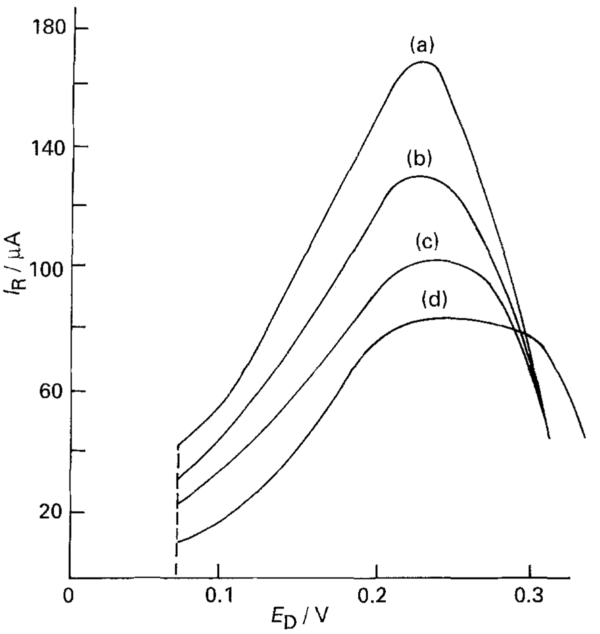

Fig. 6. Potentiodynamic curves $I_R = f(E_D)$ obtained at (a) base electrolyte; (b) base electrolyte containing 0.1 g dm^{-3} Cl$^-$; (c) 0.2 g dm^{-3} Cl$^-$ and (d) 0.3 g dm^{-3} Cl$^-$; scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.; $T = 45°$ C.

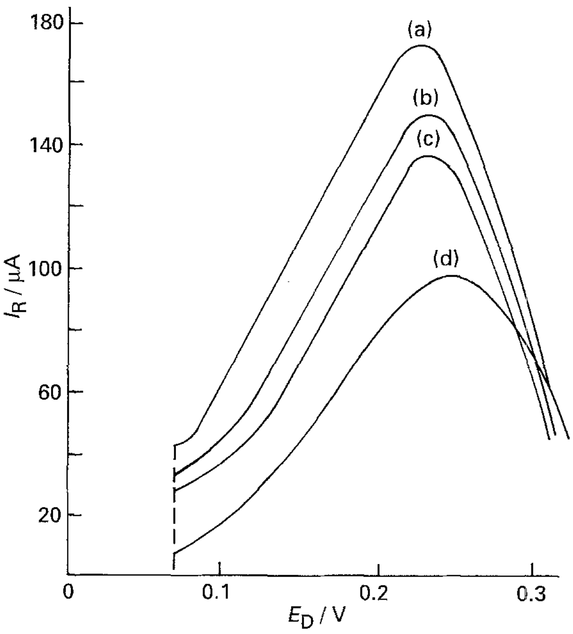

Fig. 8. Potentiodynamic curves $I_R = f(E_D)$ obtained at (a) base electrolyte; (b) base electrolyte containing 0.02 g dm^{-3} PEG; (c) 0.04 g dm^{-3} PEG and (d) 0.1 g dm^{-3} Cl$^-$ + 0.02 g dm^{-3} PEG; scanning rate: 120 mV min^{-1}; rotation speed: 960 r.p.m.; $T = 45°$ C.

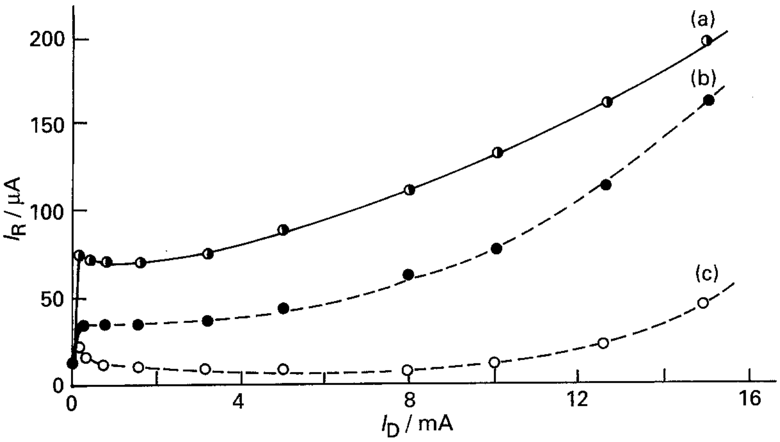

Fig. 9. Relationship $I_R = f(I_D)$ under galvanostatic conditions for the following anode samples: electrolytic copper containing (a) 0% P; (b) 0.02% P and (c) 0.05–0.07% P; rotation speed: 1350 r.p.m.; $T = 45°$ C.

essential part of it [52]. It is well known that P-containing anodes are used in bright acidic copper plating to ensure accelerated, uniform and slimeless dissolution of the anodes. It has been established [26] that the role of phosphorus in the P–Cu system is its predominant concentration along the intergrain boundaries and its bonding with cuprous ions into compounds that are part of the black anodic film. This decreases copper slime formation by eliminating the possibility of selective dissolution along the intergrain boundaries and considerably suppressing the disproportionation of Cu^+. The presence of the film enhances anodic dissolution and the acceleration of the process depends on the crystal structure of the anode, the anodic potential and the temperature of the electrolyte [26].

The relationships $I_R = f(I_D)$ under galvanostatic conditions at 45° C are presented in Fig. 9. Two types of anode used in this case are pure electrolytic copper (99.9%) and P-containing copper with 0.02, 0.05 and 0.07% P. The relationships obtained lead to the conclusion that the presence of P in the anodic metal substantially decreases the I_R values, i.e. Cu^+ concentration. The effect is very pronounced at higher P-additions: 0.05 to 0.07%.

It may be expected that the alloying of anodes with P would contaminate the electrolyte and the cathodic copper. It is well known that even tiny amounts of P abruptly decrease the electrical conductivity of copper [53]. Therefore we carried out semiquantitative analyses by spectral emission for the determination of the P content in the electrolyte and cathodic copper. It was established that the electrolyte was contaminated by trace amounts of P, while the copper deposits were completely free of P.

4. Conclusion

It has been established by ring-disc measurements that at the elevated temperatures of copper electrorefining (45–55° C) the concentration of Cu^+ in the vicinity of the anode is increased, thus creating a favourable possibility for intensified copper slime formation according to the disproportionation reaction.

The presence of Cl^- ions in the electrolyte decreases the current maximum of the disc polarization curve and shifts the passivation potential in the negative direction, i.e. it accelerates passivation. Simultaneously the concentration of Cu^+ in the vicinity of the anode is decreased.

The addition of PEG to the electrolyte exerts a strong effect upon the ring current, respectively the Cu^+ concentration, similar to that produced by Cl^- ions. The effect of PEG is enhanced in the presence of Cl^- ions in the electrolyte.

The alloying of electrolytic copper with P substantially reduces the ring current, respectively the Cu^+ concentration, at amounts ~ 0.05–0.07% P. Therefore, it may be expected that the use of P-containing anodes efficiently suppresses copper slime formation. Further precise investigations with P-containing industrial anodes under prolonged electrolyses conditions are needed in order to recommend this method for the practice.

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