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The Effect of Tellurium Presence in Anodic Copper on Kinetics and Mechanism of Anodic Dissolution and Cathodic Deposition of Copper

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The influence of the presence of tellurium, as an impurity in anode copper, on kinetics, and, on the mechanism of anodic dissolution and cathodic deposition of copper in acidic sulfate solution has been investigated. The galvanostatic single-puls method has been used. Results obtained in this study indicate that presence of tellurium in anode copper increase the exchange current density as determined from the Tafel analysis of the electrode reactions. It is attributed to the increase of the crystal lattice parameter determined from XRD analysis of the electrode material.

Keywords: Copper, Anodic dissolution, Cathodic deposition, Lattice parameter

1. INTRODUCTION

Many fundamental studies have been concerned with the mechanism of corrosion [1-6] and deposition of copper [5-21]. Despite these findings, the influence of metal impurities in anode copper on kinetics and mechanism of anodic dissolution and cathodic deposition of copper has been scarcely investigated [22-27]. The study of influence of metal impurities in copper on its kinetics has a two-fold importance theoretical and practical. Namely, besides electrorefining and electrowinning, the processes of anodic dissolution and cathodic deposition of copper are involved in corrosion phenomena, in electropolishing, and in maintaining the supply for electroless processes [1].

For the electrochemical dissolution and deposition of copper:

$$\mathrm{Cu(II)} + 2e^{-} \rightleftarrows \mathrm{Cu} \qquad (1)$$

it has been found by Mattson and Bockris [7] and verified by numerous authors [7-17] that in an acidic sulfate system, the reaction proceeds in two steps:

$$Cu(II) + e^{-} \rightleftarrows Cu(I) \quad \text{(slow)} \tag{2}$$
$$Cu(I) + e^{-} \rightleftarrows Cu \quad \text{(fast)} \tag{3}$$

The assumption of Butler-Volmer kinetics with a symmetry factor $\beta = \alpha_c = 0.5$ for reaction 2 and for the equilibrium of reaction 3 yields:

$$j = j_o / [\exp(\alpha_a F\eta /RT) - \exp(-\alpha_c F\eta /RT)] \tag{4}$$

where j is the net current density, j_o is the exchange current density, α_a and α_c are the anodic and cathodic transfer coefficients – the theoretical values of which are 1.5 and 0.5, respectively.

It has been found by Stankovic [28] that the pseudocapacitance for both anodic and cathodic processes depended upon the current density and time. On the basis of the above findings, the following reaction mechanism has been proposed:

$$Cu(I)_{ad}^{v} + ve^{-} \rightleftarrows Cu \tag{5}$$
$$Cu(I) + (1 - v)e^{-} \rightleftarrows Cu(I)_{ad}^{v} \tag{6}$$
$$Cu(II) + e^{-} \rightleftarrows Cu(I) \tag{7}$$

The aim of this study is to obtain an insight into the effect of tellurium (Te), as a typical example of metal impurity presence into copper electrode, on kinetics and mechanism of anodic dissolution and cathodic deposition of copper. The anodic copper used in electrolytic plants for the production of copper usually contains metal impurities in the range of 0.0002 to 0.1980 wt.% [25].

2. EXPERIMENTAL

The influence of tellurium in anodic copper on the kinetics and mechanism of anodic dissolution and cathodic deposition of copper in an acidic sulfate system was investigated using the single pulse galvanostatic method. The electrochemical cell was a commercial product (AMEL MODEL 494/GC + 494/TJ).

The working Cu-Te electrodes were prepared from specimens obtained by the melting of an appropriate mixture of Cu and Te powder under purified nitrogen at 1780 K. The concentration of Te atoms in copper was chosen to be close to that in the commercial plants for the production of copper, i.e., it was in the range of 0.01 to 14.89 at.% Te.

After melting and solidification, part of the specimens was taken for X-ray diffraction (XRD) and microstructure analysis. For the working electrode, part of the specimens used was in the form of a cube (5 mm edge) embedded in an epoxy resin with the contact of mercury and copper wire exposed to the upward face, so that only the base of a cube was exposed to the solution.

Prior to each experiment, the electrode was polished with a 400 grade emery paper and washed with bi-distilled water. The counter electrode was spiral-shaped Pt wire of 0.5 mm diameter and 20 cm length. A spectroscopically pure copper wire, 4 cm in length, has been used for equilibrating solution [29], with respect to the reaction:

$$\mathrm{Cu(II)} + \mathrm{Cu} \rightleftarrows 2\mathrm{Cu(I)} \quad (8)$$

The reference electrode was a saturated calomel electrode (SCE) and all the potentials are referred to SCE. Solutions were made from copper sulfate (p.a. Merck), sulfuric acid (supra-pure Merck), and bi-distilled water. The concentrations of copper sulfate and sulfuric acid were 0.7 and 1.5 M, respectively. The solutions were de-aerated by bubbling nitrogen of high purity for 1 h. The stirring was carried out by employing a magnetic stirrer.

During measurements, stirring was stopped while nitrogen was slowly bubbled through the solution. The single-pulse method was carried out using a potentiostat/galvanostat (AMEL model 551) programmed with function generator (AMEL model 565). The pulses were made long enough for the activation over-voltage to reach a constant value (from 5 ms for the highest current density to 500 ms for the lowest). A series of transients was recorded covering the current density range 0.06-90 mA/cm^2. All the anodic transients were taken firstly; followed then by cathodic polarization, starting from low to high current densities. The overvoltage-time transients were recorded by a personal preamplifier computer system. Between the electrode system and analog-to-digital converter (RTI-800, Analog Devices), an instrumentation preamplifier AMP-01 (from PMI) with input resistance ≥109 Ω was used. Temperature was maintained at 298±0.1 K.

3. RESULTS AND DISCUSSION

Quasi-steady-state overvoltage values at different current densities were found from plateaus of the galvanostatic transients and Tafel plots were determined. The regression analysis to obtain Tafel slopes and exchange current densities was done using the principle of least squares and the corresponding application program. This has been done for both the anodic and cathodic direction of the process and for each of the investigated electrodes with a different content of Te atoms. Tafel plots were made with the potential expressed versus SCE and corrected current densities, Y, obtained from the relation:

$$Y = j / [1 - \exp(-2F\eta/RT)] = (j_o)_{a,c} \exp[\pm\alpha_{a,c}F\eta/(RT)] \quad (9)$$

where j is the net current density, $\alpha_{a,c}$ is the anodic, i.e., cathodic transfer coefficient, and (j_o) is the exchange current density for the anodic, i.e., cathodic reaction, respectively.

Since it is very well-known how difficult it is to obtain the reproductive and reliable data for the exchange current densities and other kinetic parameters, that are used as diagnostic criteria in the study of the mechanism and kinetics of the electrode processes, it is necessary to test the apparatus of the experimental procedure in relation to the reproducibility and reliability of the obtained data. This was of special importance in this study, in which the mechanism and kinetics of the copper electrode with the addition of foreign atoms were investigated.

Therefore, two test experiments were performed under similar conditions as described in earlier studies [17, 22, 28, 29], the results of which were used as a reference point for comparison with the results of test experiments obtained in this study. In the first of two test experiments, the Cu electrode was prepared as described in the experimental procedure, i.e., by melting copper powder in purified nitrogen. In the second test, a copper deposit was freshly grown on the electrode for 30 min at the current density of 15 mA/cm^2 from the solution employed in the experiment. The obtained results for the disssolution and electrodeposition of Cu are collected in Table 1 together with the reference data, and apart from being very reproducible, they are in a satisfactory agreement with the reference ones as well.

Table 1. Comparison of kinetic parameters for dissolution and electrodeposition of Cu in 0.7M Cu(II) + 1.5M H_2SO_4 solution, T=298 K

Experimental parameters	Exchange current density, [mA cm^{-2}]		Tafel slopes, [mV]		Transfer coefficient		Summary transfer coefficient
Type of electrode	$(j_o)_a$	$(j_o)_c$	b_a	b_c	α_a	α_c	$\alpha_a + \alpha_c$
Refs. [17, 22, 28, 29]	5.00	9.00	43	115	1.37	0.52	1.89
Electrodeposit of Cu	2.20	3.70	44	118	1.35	0.50	1.85
Obtained by melting of Cu powder	0.72	1.30	44	118	1.35	0.50	1.85

The data presented in Table 1 refer to the medium values. Cathodic Tafel slopes were 118 mV and anodic slopes 44 mV (115 and 43 mV in references [17, 22, 28, 29]). The corresponding transfer coefficients were $\alpha_c = 0.5$ and $\alpha_a = 1.35$. The sum of α_c and α_a was 1.85 and that was close to the theoretical value of 2.

The exchange current density obtained at the electrode prepared by melting of copper powder in nitrogen atmosphere was lower than that prepared by electrochemical deposition of copper from solution used in these experiments. This may be seen from the data presented in Table 1.

The exchange current densities obtained from the Tafel lines for the Cu-Te electrodes with different concentrations of Te atoms, prepared by melting, were found to increase with an increasing concentration of Te atoms, as can be seen in Fig. 1 and Table 2. The rise of the exchange current density with increasing Te content (Fig. 2) implies a catalytic effect of Te in the investigated process.

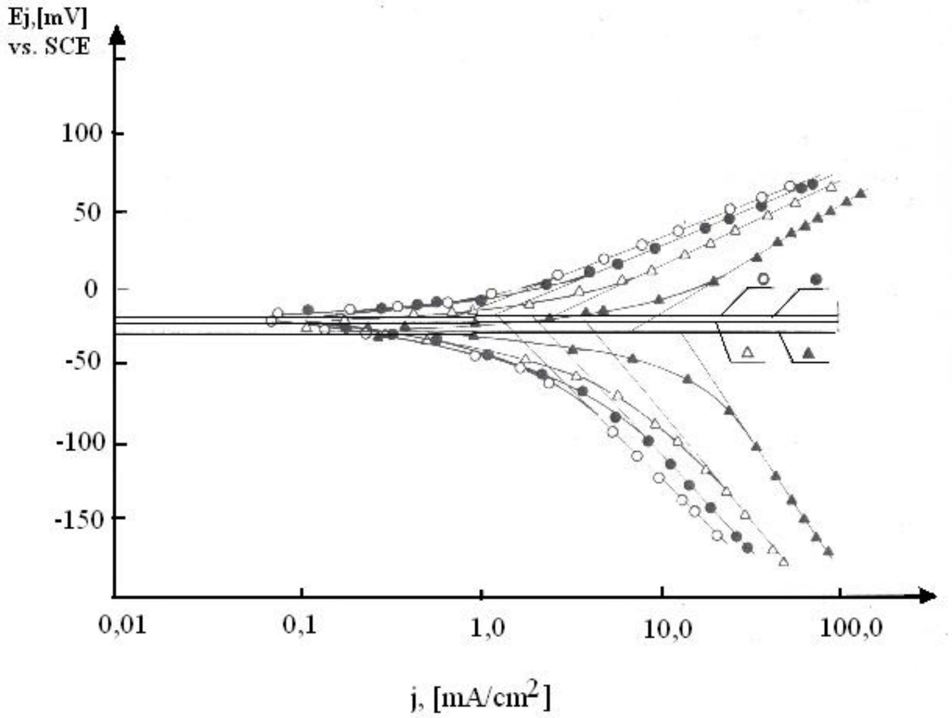


Figure 1. The anodic and cathodic Tafel plots for different concentrations of Te (at %) in Cu electrode: o-: 0.0149, -●-: 0.149, -Δ-: 1.63, and -▲-:14.890

Table 2. Kinetic parameters for dissolution and electrodeposition of Cu-Te in 0.7M Cu(II) + 1.5M H_2SO_4 solution, T=298 K

Te content	Exchange current density, [mA cm^{-2}]		Tafel slopes, [mV]		Transfer coefficient		Summary transfer coefficient
at.%	$(j_o)_a$	$(j_o)_c$	b_a	b_c	α_a	α_c	$\alpha_a + \alpha_c$
0	0.72	1.30	44.0	118.0	1.35	0.5	1.85
0.0149	0.72	1.30	44.0	118.0	1.35	0.50	1.85
0.149	1.20	1.98	47.2	128.7	1.25	0.46	1.71
1.363	2.20	3.80	55.0	143.1	1.07	0.41	1.48
14.890	6.90	12.80	69.4	178.2	0.85	0.33	1.18

Fig. 3 shows that the increase in the anodic and cathodic exchange current densities with the increase in the concentration of Te atoms, can be expressed by the quotients, i.e., electro-chemical orders:

$$(n_o)_a = [\log (j_o)a/\log C_{Te}]_{E,T} = 0.32 \quad (10a)$$

$$(n_o)_c = [\log (j_o)c/\log C_{Te}]_{E,T} = 0.32 \quad (10b)$$

respectively, where C_{Te} is the atomic concentration of Te atoms.

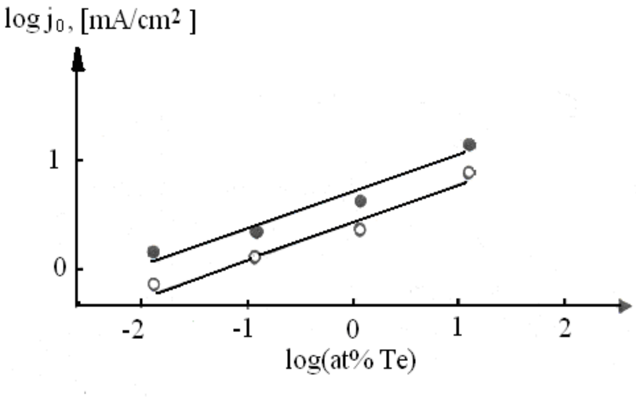


Figure 2. The dependences of log j_o on log (at. % Te);- o- j_{oa}, -●- j_{oc}

However, in order to analyze the effect of tellurium on the mechanism of processes occurring on copper, the data in regard to the partial electrochemical orders are required. Fig. 3 shows the dependence of the anodic current density on the concentration of Te atoms at any constant value of potential in the anodic region between 10 and 70 mV. Similarly, Fig. 4 indicates the existence of a linear relationship between the cathodic current density and the concentration of Te atoms at any constant value of potential in the cathodic region of 80-170 mV. Therefore, these dependences may be expressed on the basis of partial electrochemical orders. Experimentally determined values of these orders are: n_a = 0.24 - 0.46 and n_c = 0.25 - 0.38. This reveals a partial participation of tellurium in the reaction mechanism on copper in an investigated system. The influence of Te is more pronounced in the case of anodic dissolution than in the case of cathodic deposition of copper.

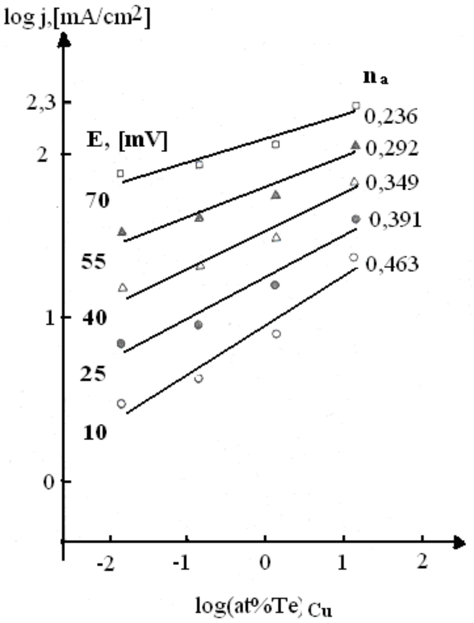


Figure 3. Partial anodic electrochemical orders at various potentials

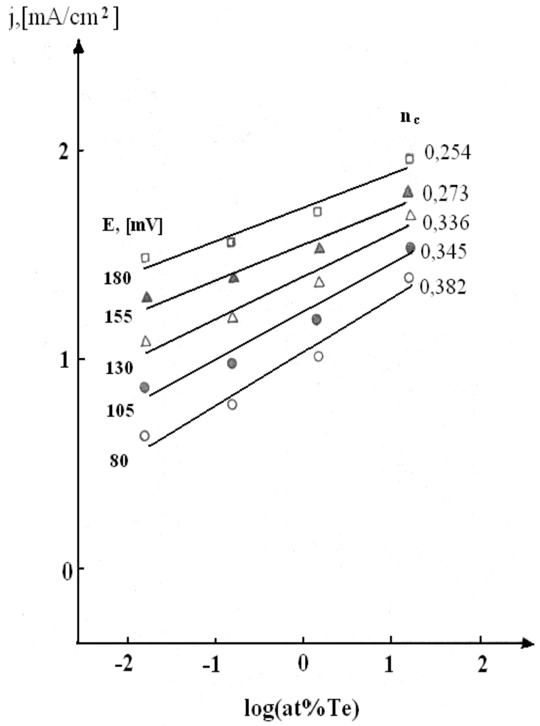


Figure 4. Partial cathodic electrochemical orders at various potentials

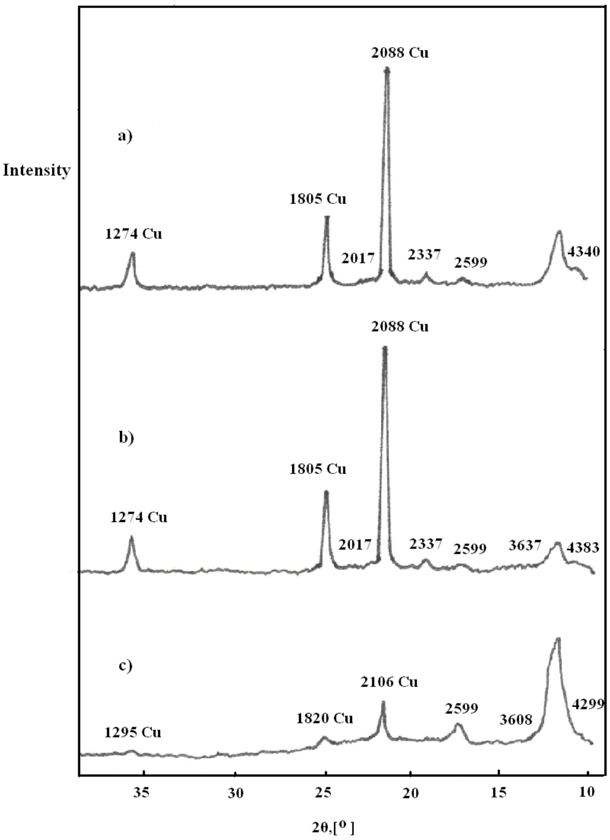
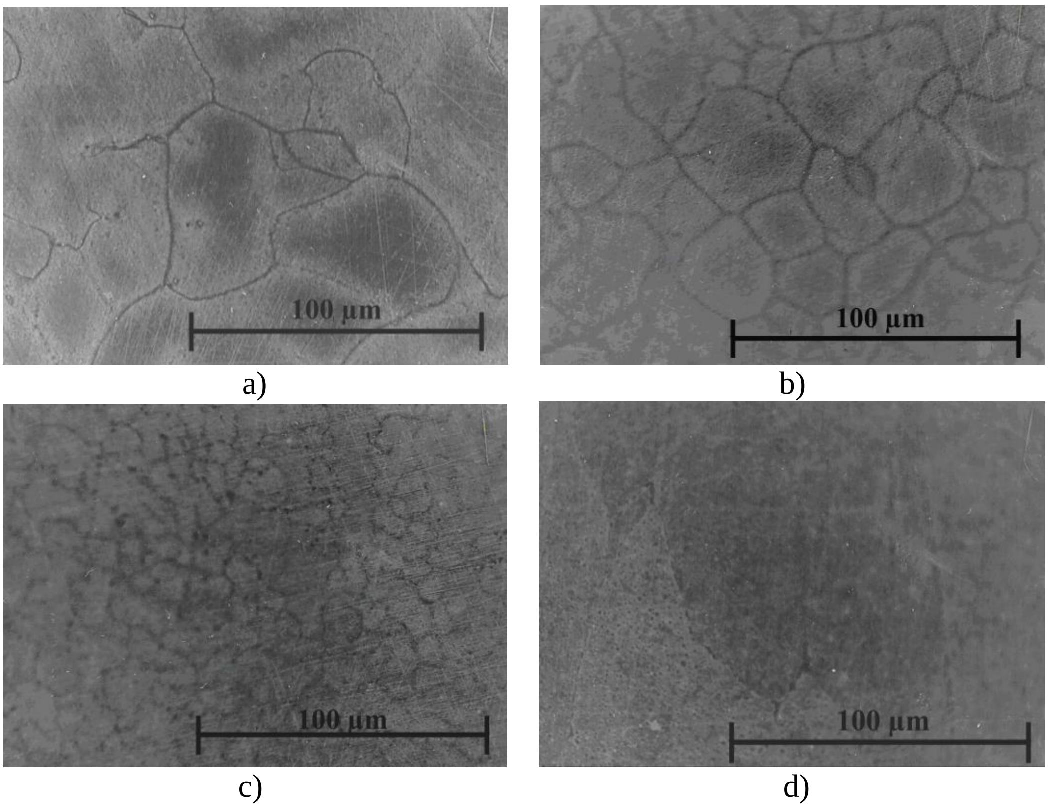


Figure 5. XRD patterns of Cu-Te alloys: a) 0.15 at.% Te; b) 1.36 at.% Te; c) 14.89 at.% Te

The increase in the anodic and cathodic exchange current densities with the increase in the concentration of Te atoms may be attributed to the increase in the lattice parameter. The values of crystal lattice parameter obtained on the basis of X-ray analysis for analyzed Cu-Te alloys (Fig. 5) were in the range from 0.3616 to 0.3649. It is quite obvious that the increase in the exchange current densities follows well the increase in the lattice parameter of the crystal structure. It seems that the presence of tellurium (in the range of 0.01 to 14.89 at.%) in the crystal structure of copper facilitates in the increasing of inter-atomic distances.

Given these results, it may be assumed that the accelerating effect of Te atoms on the kinetics of the electrodissolution/deposition of copper is due to the decrease of inter-atomic forces in the crystal structure of copper in the presence of Te atoms.

The Cu-Te phase diagram reveals that copper and tellurium completely dissolve when they are in a liquid state, while during the solidification process they form chemical compounds [26]. Chemical or metallic compounds are characterized by a certain composition, that is a ratio among various components. In this system, at the concentration of 34 at.% and temperature of 857 ^{o}C, the Cu_2Te appears as a compound. Thus, in the range of investigated compositions of alloys at the temperature of 25 ^{o}C, one can expect the formation of two-phase alloys with a structure which well depict a primarily solidified grains of copper and a finely dispersed phase Cu_2Te deposited along the grain boundaries as well as grains of copper.



a) b)

c) d)

Figure 6. Microstructures of Cu – Te alloys: a) 0.01 at.% Te; b) 0.15 at.% Te; c) 1.36 at.% Te; d) 14.89 at.% Te

The microstructures of samples with the contents of tellurium in the range of 0.01 at.% and 1.36 at.% indicate that the Cu_2Te phase was created over boundaries of copper grains (Fig. 6a-c), while it was finely dispersed within the copper grains in the sample with the highest amount of Te (14.89 at.%), as shown in Fig. 6d.

Presence of tellurium in copper leads to a fine dispersed microstructure of Cu-Te alloys. The lattice parameter increases with increasing tellurium concentration. The increase in the exchange current densities obtained for Cu-Te alloys may be attributed to the increase of the lattice parameter and a fine dispersed microstructure.

4. CONCLUSION

The exchange current densities obtained from the Tafel lines for the Cu-Te electrodes with different concentrations of Te atoms, prepared by melting, were found to increase with increasing concentration of Te atoms.

The noticed increase in the anodic and cathodic exchange current densities can be attributed to the increase of the lattice parameter and a fine dispersed microstructure.

The values of partial electrochemical orders (n_a = 0.24 - 0.46 and n_c = 0.25 - 0.38) reveal a partial participation of tellurium in the reaction mechanism on copper in an investigated system. The influence of tellurium is more pronounced in the case of cathodic deposition of copper.

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