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Corrosion behavior of Cu–SiO_2 nanocomposite coatings obtained by electrodeposition in the presence of cetyl trimethyl ammonium bromide

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Abstract Copper silica composite coatings are an attractive alternative to chromium and nickel coatings in order to avoid environmental problems and for application in electrical devices. However, co-deposition of SiO_2 particles with metals occurs to a rather limited extent, generally under 1%, due to the hydrophilicity of SiO_2, which makes the incorporation of particles in a metallic matrix difficult. To overcome this drawback, the influence of cetyl trimethyl ammonium bromide (CTAB) on the deposition and corrosion behavior of Cu–SiO_2 coatings on steel has been studied. It was established that CTAB plays a beneficial role in SiO_2 suspension stabilization, promotes the co-deposition of nanoparticles in the copper matrix and improves the deposit morphology and structure. Consequently, a higher corrosion resistance of Cu–SiO_2 deposits obtained in the presence of CTAB was noticed. The most important effect was observed in the case when CTAB was used in concentration of 10^{-3} M in the electroplating bath.

Introduction

In the field of galvanic deposition, one of the ways to obtain metallic coatings with improved corrosion behavior consists in the incorporation into the metal matrix of inert micro- and nano particles (e.g., TiO_2, SiO_2, Al_2O_3, etc.). The embedded particles confer to the composite layers improved corrosion and wear resistance, increased hardness, improved adhesion of future paint layers and they increase the lifetime of the coatings [1].

However, composite electrodeposition is not without drawbacks. Inert nanoparticles are significantly agglomerated in the plating bath, even at low concentrations, due to the compression of the diffuse double layer surrounding the particles by the high-ionic strength [2]. Moreover, the smaller the particle size, the more difficult the particle incorporation in the deposit [3]. Supplementary difficulties appear when hydrophilic materials are co-deposited with metals. These materials have a smaller tendency to co-deposit than the hydrophobic ones, due to the fact that a rupture of the aqueous film between the particles and the interface must occur, to allow the capturing of particles in the metallic matrix [4].

Introduction of organic additives in an electrodeposition bath loaded with particles in suspension can modify, sometimes in a spectacular way, the suspensions' properties as well as the structure and the morphology of the composite cathodic deposits. On one hand, cationic surfactants increase the stability of the suspension by conferring a positive charge to the inert particles, which results in higher incorporation fraction. On the other hand, the additives increase the incorporation fraction by increasing the particles' hydrophobicity [5]. It was also reported that the addition of a cationic surfactant is able to decrease the agglomeration and leads to a more uniform distribution of the particles in the electrodeposited layer [6].

It has to be mentioned that, surprisingly, there are cases in which an anionic surfactant increases the percent of

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incorporated inert particles in the metallic deposit [5]. An explanation could be the fact that negatively charged particles are attracted by the positively charged electric double layer of the substrate. In the intense electric field at the interface, the double layer of the particles is deformed and the negative ions adsorbed on the particles surface are stripped, allowing the incorporation of the particles in the metallic matrix. Such chain of events suggest he fact that the process of co-electrodeposition is not entirely decided by electrostatic forces.

The use of surfactants for increasing the degree of incorporation of inert particles in a metallic matrix has also some disadvantages. It is possible that, when these additives are not used in adequate concentration, they will also incorporate in the metallic matrix and consequently, will change the mechanical properties of the deposit (e.g., internal tensions, fragility, etc.). This is why the concentration of surfactants in the deposition bath should be very well-controlled [7].

Copper silica composite coatings are an attractive alternative to chromium and nickel coatings in order to avoid environmental problems and for application in electrical devices [8]. However, co-deposition of SiO_2 particles with metals occurs to a rather limited extent, generally under 1% [9] due to the well-known hydrophilicity of SiO_2, which makes the incorporation of particles in a metallic matrix difficult. To overcome this difficulty, combinations of silica with cationic surfactants are in general used due to the clearly expressed interaction between cationic headgroups of surfactant and silanol groups [8, 10, 11]. It was also reported that organic additives such as *N,N* dimethyl dodecylamine [12] have been successfully used to improve the co-electrodeposition of SiO_2 with metals.

In this context, this article reports the obtaining of composite layers with nanometric structure by co-electrodeposition of Cu and SiO_2 nanoparticles on steel, in the absence and in the presence of cetyl trimethyl ammonium bromide (CTAB), a typical cationic surfactant with sixteen long-chain carbons. CTAB is frequently used in the electrodeposition coatings as pigment grinding aid and/or flow control additive [13], but, to the best of the knowledge, its role in the deposition of copper–SiO_2 composites was not yet investigated. The influence of the surfactant on the corrosion behavior of the resulted composite coatings was put on evidence.

Electrochemical measurements (open circuit potential, polarization curves, and electrochemical impedance spectroscopy) were used to evaluate the corrosion resistance of the deposits and the results were corroborated with those obtained by using non-electrochemical methods (scanning electron microscopy, RDX measurements).

Experimental details

Zeta potential measurements

The zeta potential of SiO_2 nanoparticles was tested in the absence and in the presence of CTAB in diluted $CuSO_4$ (2.5×10^{-4} M) solutions by using a ZETA SIZER (Nano-ZS, Malvern, UK).

Electrodeposition

The basic electrolyte solution used for electrodeposition contained 120 g/L $CuSO_4$ and 120 g/L H_2SO_4. For Cu–SiO_2 composite films production, SiO_2 nanoparticles (10 nm diameter, 99.5% purity, Aldrich) were introduced in the plating bath, in concentration of 10 and 20 g/L. The particles were maintained in suspension in the electrolyte by magnetic stirring (200 rpm).

With the purpose of increasing the degree of incorporation of SiO_2 nanoparticles in the copper matrix, cetyl trimethyl amonium bromide (CTAB) 99.9% provided by Merck was introduced in the electroplating bath in various concentrations (10^{-5}–10^{-3} M).

Electrodeposition was carried out at a current of 20 mA, during 20 min, by using a potentiostat/galvanostat (Voltalab PGP201, Radiometer analytical) and a two-compartment electrochemical cell with three electrodes, under magnetic stirring at a speed of 200 rpm, at room temperature. The working electrode was a steel (OL 37) disk with 0.78 cm^2 surface area, the reference electrode was an $Ag/AgCl/KCl_s$ electrode and the counter electrode was a platinum foil. In order to remove oxides and superficial debris, before electrodeposition, the steel electrode was wet polished with emery paper (granulation between 600 and 1200), and with alumina (0.05 μm) suspension, cleaned by ultrasonication and rinsed thoroughly with distilled water.

Corrosion measurements

Potentiodynamic polarization measurements were conducted using an electrochemical analyzer (PARSTAT 2273, USA) connected to a PC for potential control and data acquisition. Corrosion experiments were carried out in 0.2 g/L aerated Na_2SO_4 solution (pH 3), at room temperature. Open-circuit potential (ocp) measurements were performed during 1 h before each experiment. For kinetic parameters determination, polarization curves were recorded in a potential range of $E = E_{corr} \pm 5$ mV and $E = E_{corr} \pm 200$ mV, respectively, with a scan rate of 0.25 mV s^{-1}. Impedance measurements were performed at the open-circuit potential after 1 h of samples immersion in the Na_2SO_4 solution. The impedance spectra were recorded

in the frequency range 10 kHz to 10 mHz at 5 points per hertz decade with an AC voltage amplitude of ±10 mV. The impedance data were then analyzed with software based on a simplex parameter regression.

Morphological and structural analysis

The structural analysis of the coatings were performed by using X-ray diffraction (XRD) method by using a Brucker X-ray diffractometer with a Cu K_α ($\lambda = 0.15406$ nm) at 45 kV and 40 mA. Crystallite size was evaluated by measuring the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. For surface analysis, a LEICA S 440 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray system EDAX NEW XL30 was used.

Results and discussions

Zeta potential of silica nanoparticles

The most important parameter defining surface properties of solid particles in aqueous solutions is the zeta potential value, ζ, which strongly influences the incorporation degree of nanoparticles in a metallic matrix.

As can be seen from Fig. 1, the zeta potential of SiO_2 nanoparticles is negative in the whole studied pH range and it becomes more negative with increasing pH values. It can be presumed that, at high pH values, there are more negative hydroxyl groups on the surface of particles.

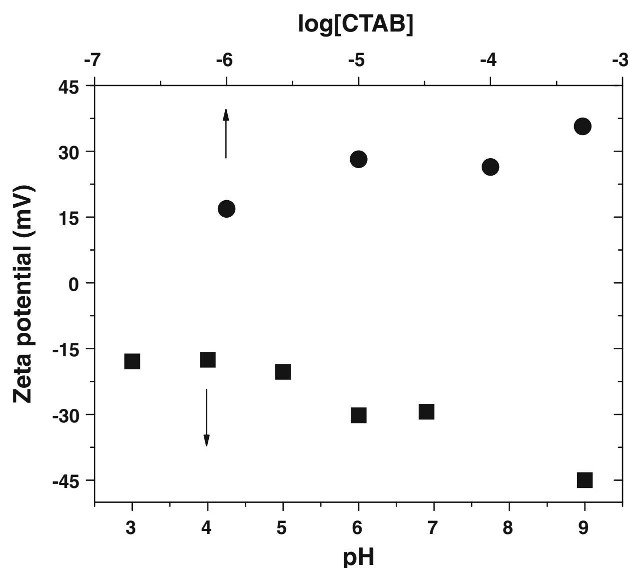

Fig. 1 Zeta potential dependence for the silica nanoparticles in 2.5×10^{-4} M $CuSO_4$ solution on pH and on CTAB concentration (pH 3)

As expected, the introduction of small concentrations of CTAB in the $CuSO_4$ solution changes dramatically the zeta potential of the SiO_2 nanoparticles (see the results for pH 3 in Fig. 1); the zeta potential gets positive values, for the whole investigated concentration range of CTAB ($\zeta = -17.9$ mV in $CuSO_4$ solution without CTAB, at pH 3). These values are close to those determined for CTAB-coated spherical SiO_2 nanoparticles dispersed in aqueous solution ($\zeta = +(37–48)$ mV) reported in the literature [10]).

A reasonable explanation of this behavior is that the cationic surfactant is easily adsorbed onto the silica nanoparticles surface due to the positive charge on the polar part of CTAB molecules. CTAB reacts with the hydroxyl groups on the silica surface, which make the surfactant graft on the surface of silica, and the surface energy of the nanoparticles decrease. On the other hand, the steric effect among the nanoparticles becomes bigger after the organic chain of CTAB grafted on the surface of the silica nanoparticles. As a consequence, the dispersal state of silica nanoparticles is well-improved after the surface modification process, as confirmed by other authors [13].

Morphological and structural analysis

The morphological study of coated samples was undertaken by scanning electron microscopy. In the absence of CTAB, a red-brown Cu–SiO_2 deposit was obtained consisting of irregular crystals. The grain size of the composite coating is smaller at higher concentration of SiO_2 nanoparticles in the plating bath (Fig. 2b) than at lower ones (Fig. 2a). This conclusion is in accordance with literature data, which attribute the grain refining effect of nanoparticles to their ability to provide more nucleation sites and retard crystal growth [14].

In the presence of CTAB, the Cu–SiO_2 deposits become more uniform, compact and finer grained than in its absence, at same SiO_2 concentration in the plating bath (Fig. 2c, d). The crevices, gaps, and micron holes on the surface of the copper coatings are filled. It is most probable that, besides its beneficial interaction with the negatively charged silica nanoparticles, CTAB also modifies the deposit morphology and structure, acting as a leveling agent.

The reduction in the grain size of the composite deposit in the presence of CTAB in the plating solution was confirmed by XRD analysis of the coatings (Table 1). Even if the change in grain size is not spectacular, the decreasing tendency can be related to more uniform incorporation of SiO_2 nanoparticles in the deposit in the presence of surfactant and to the grain refining action of the later.

The SiO_2 presence in the nanocomposite coatings was put on evidence by EDX analysis. In spite of the fact that

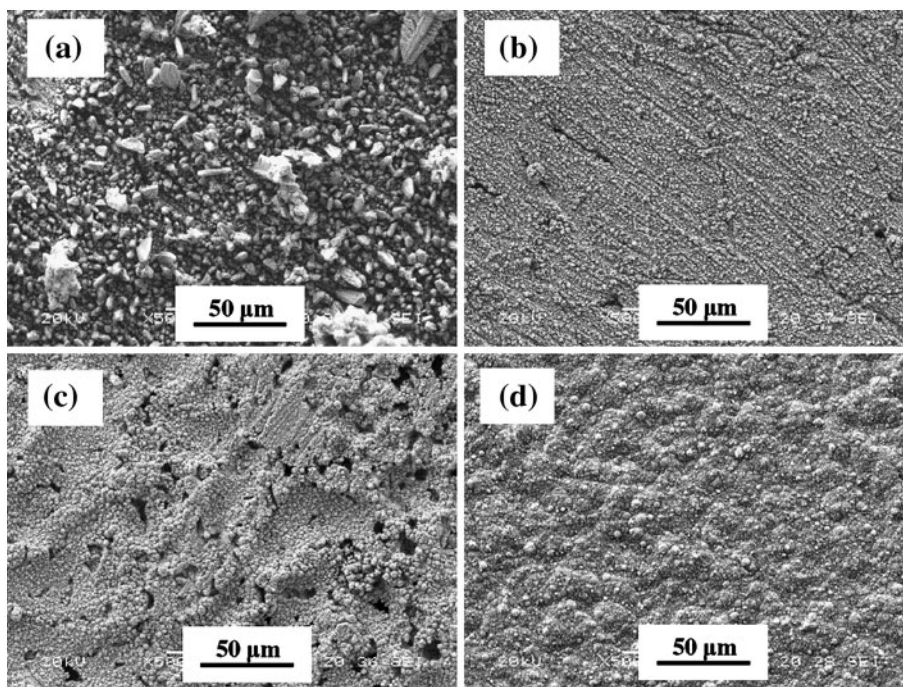

Fig. 2 SEM images of Cu–SiO_2 coatings obtained with different SiO_2 and CTAB concentrations in the plating baths: **a** 10 g/L SiO_2, **b** 20 g/L SiO_2, **c** 10 g/L SiO_2, and 10^{-3} M CTAB, **d** 20 g/L SiO_2, and 10^{-3} M CTAB

Table 1 Microstructural parameters for Cu-20 g/L SiO_2 and Cu-20 g/L SiO_2 + 10^{-3} M CTAB samples

Sample	Parameter a (Å)	Volume V (Å^3)	Effective crystallite size D_{eff} (Å)	Average strain value $\langle \varepsilon^2 \rangle_m^{1/2} \times 10^{-2}$
Cu-20 g/L SiO_2	3.6172	47.328	885	0.087
Cu-20 g/L SiO_2 +10^{-3} M CTAB	3.6122	47.132	734	0.103

hydrophilic silica incorporation in copper deposits at acid pHs, was reported as less probable even in the presence of certain surfactants (such as CTAHS) [8], the EDX spectra clearly revealed the presence of Si, indicating the presence of SiO_2 nanoparticles in the copper matrix (Fig. 3). The Si content in the deposit is relatively weak (0.37 weight% Si corresponding to 0.79 weight% SiO_2 in the absence of CTAB), but a slight increase can be noticed in the deposits prepared in the presence of CTAB (0.43 weight % Si corresponding to 0.92 weight% SiO_2). However, it should be emphasized that the incorporation degree of SiO_2 nanoparticles remains low.

Corrosion measurements

Open-circuit potential (ocp)

In order to evaluate the effect of CTAB on the corrosion behavior of the coatings, the evolution of ocp for Cu and Cu–SiO_2 deposits obtained in the presence and in the absence of CTAB was investigated (Fig. 4).

From Fig. 4 it can be observed that, when SiO_2 nanoparticles were used in the electroplating bath, the ocp of the resulting deposits was more positive than in the case of pure copper, suggesting an ennoblement of the deposit. The

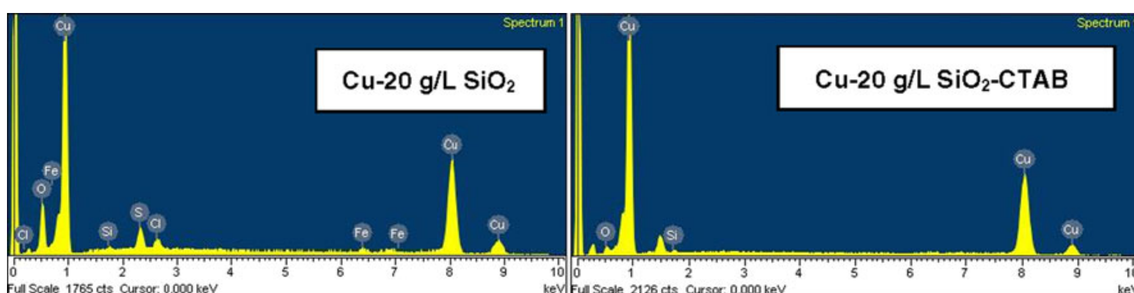

Fig. 3 EDX spectra of Cu–SiO_2 composite deposits

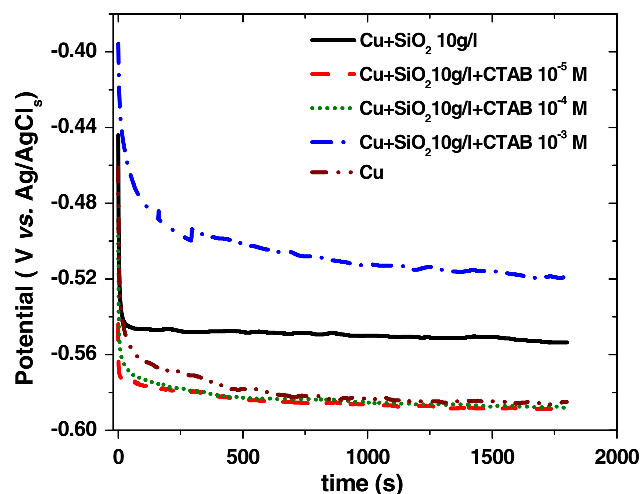

Fig. 4 Evolution of ocp of Cu and Cu–SiO_2 deposits obtained in the absence and in the presence of different concentrations of CTAB. Electrolyte, Na_2SO_4 0.2 g/L, pH 3

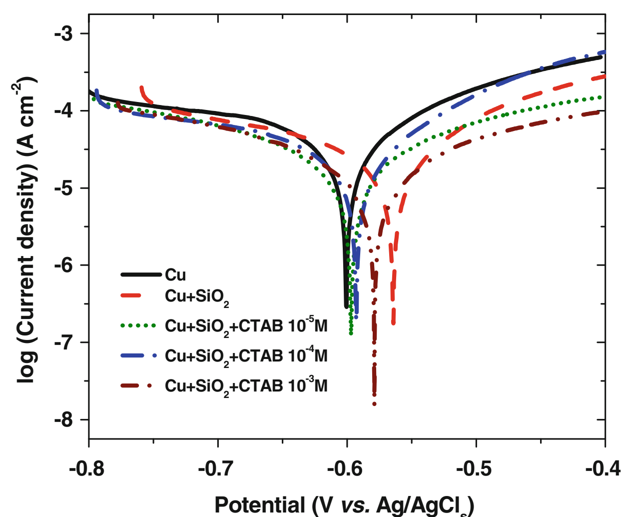

Fig. 5 Polarization curves of Cu and Cu–SiO_2 deposits in the absence and in the presence of CTAB

ocp becomes even more positive with the addition in the electroplating bath of 10^{-3} M CTAB. This outcome can be explained by the fact that the presence of cationic surfactant induces an increase of the positive charge of the particles and hence, of their incorporation degree.

Nevertheless, it has to be mentioned that by using CTAB in the concentration of 10^{-5} and 10^{-4} M no important changes take place as compared to the case without additives, this suggesting that the additive has to be in a right concentration to improve the incorporation of the SiO_2 particles and hence, the corrosion properties of the coatings.

Polarization curves

Polarization measurements were carried out in a potential range of ±200 mV versus ocp to aid a mechanistic understanding of the influences of SiO_2 and CTAB on copper electrodeposition (Fig. 5).

The values of E_{corr} and the corrosion current density (i_{corr}) were evaluated from non-linear regression calculation near zero overall current, taking into account that, according to Stern–Geary theory [15], in the close vicinity of the open-circuit corrosion potential, the current density, i could be expressed by the following equation:

$$i = i_{corr}\{\exp[b_a(E - E_{corr})] - \exp[b_c(E - E_{corr})]\} \quad (1)$$

where b_a and b_c are the anodic and cathodic activation coefficients, respectively. The results are presented in Table 2.

In all cases, the correlation factor R^2 varies between 0.9989 and 0.9998 indicating a good fitting result. The E_{corr} values were determined with an error margin lower than 1 mV.

From the analysis of the kinetic parameters corresponding to the corrosion process, some conclusions can be drawn. Thus, a decrease of the corrosion current for the composite deposits Cu–SiO_2 can be observed, suggesting that the presence of nanoparticles has a beneficial effect in slowing down the corrosion, probably by lowering of the electrode surface area in contact with the electrolyte and by a more fine-grained, compact structure of the coating.

The corrosion is hindered even more when CTAB was added in the plating bath. This may be happening because the surfactant increases the incorporation degree of SiO_2 by modifying the superficial charge of nanoparticles (the negative initial charge turns into a positive one) through formation of bi- or multilayers on the silica surface [10]. As a result, the incorporation of nanoparticles at the cathode is favored. The optimum concentration of CTAB to be used in this process was found 10^{-3} M.

Table 2 Corrosion parameters of Cu and Cu–SiO_2 deposits obtained in the absence and in the presence of different concentrations of CTAB

Electrode	E_{corr} (V vs. Ag/AgCl$_s$)	i_{corr} (μA cm^{-2})	b_a (V^{-1})	$-b_c$ (V^{-1})
Cu	−0.588	75 ± 2.40	11.5 ± 0.18	2.14 ± 0.18
Cu–SiO_2 10 g/L	−0.563	40 ± 0.09	9.07 ± 0.07	5.70 ± 0.09
Cu–$SiO_2$10 g/L + CTAB 10^{-5} M	−0.597	30 ± 2.29	11.39 ± 0.41	9.85 ± 0.41
Cu–$SiO_2$10 g/L + CTAB 10^{-4} M	−0.592	40 ± 0.03	14.27 ± 0.17	4.49 ± 0.16
Cu–$SiO_2$10 g/L + CTAB 10^{-3} M	−0.578	20 ± 0.06	12.69 ± 0.31	11.43 ± 0.32

Table 3 Polarization resistance values of steel electrodes coated with Cu and Cu–SiO_2, in the absence and in the presence of CTAB in the plating bath

Electrode	R_p (Ω cm^2)	R^2
Cu	500	0.9995
Cu–SiO_2 10 g/L	1000	0.9996
Cu–SiO_2 10 g/L + CTAB 10^{-5} M	1341	0.9988
Cu–SiO_2 10 g/L + CTAB 10^{-4} M	628	0.9996
Cu–SiO_2 10 g/L + CTAB 10^{-3} M	1769	0.9994

Same conclusions can be drawn from the estimated polarization resistance values (R_p), another important parameter of the corrosion process that has been calculated from the slopes of the polarization curves recorded in a small potential interval (±5 mV vs. ocp) (Table 3).

It can be seen that the highest value for R_p is noticed in the case of the coatings prepared from the bath containing 10 g/L SiO_2 and 10^{-3} M CTAB, confirming the beneficial effect of this additive in electrolytic deposition of metal-nanoparticles composites [16]. As already mentioned, this effect could be attributed, on one hand, to the modification of the hydrophilicity of the nanoparticles and on the other hand, to the positive charge that these particles get after CTAB is added into the bath, both leading to a better incorporation of SiO_2 in the coating.

Electrochemical impedance spectroscopy

The impedance spectra recorded at ocp during the corrosion process of the coatings obtained in the absence and in the presence of SiO_2 nanoparticles and/or of CTAB in the copper plating solution (Fig. 6) exhibit a capacitive behavior.

The analysis of the impedance diagrams was carried out by adopting of a 2RC equivalent circuit and applying the non-linear regression calculation with a simplex method [17]. The significance of the notations are: R_e electrolyte resistance; R_t charge transfer resistance; C_d double layer capacitance at the copper | electrolyte interface; R_F faradic resistance of the corrosion products accumulated at the interface; C_F Faradic capacitance due to an oxidation–

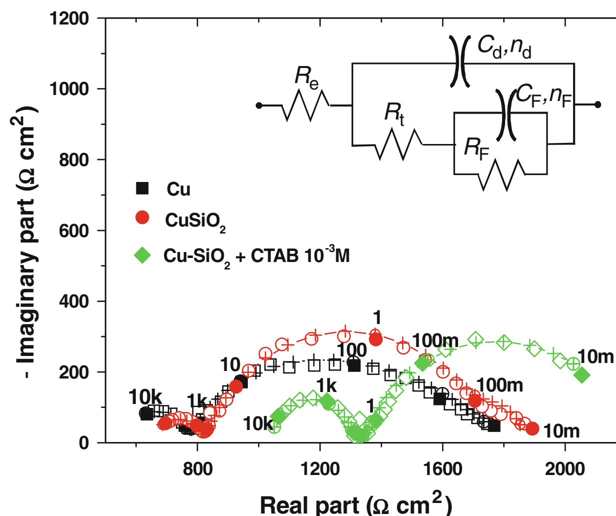

Fig. 6 Nyquist impedance diagrams for corrosion of copper and copper composite deposits (10 SiO_2 g/L) recorded at ocp in a 0.2 g/L aerated Na_2SO_4 solution (pH 3), at room temperature in the absence and in the presence of 10^{-3} M CTAB in the plating bath. (+)-simulated diagrams. The *inset* presents the (2RC) equivalent electrical circuit used

reduction process taking place at the electrode surface, possibly involving the corrosion products; n_d, and n_F coefficients represent the depressed characteristic of the two capacitive loops in the Nyquist diagrams. The calculated parameters of the corrosion process are shown in Table 4.

It can be observed that the variation of the polarization resistance calculated from impedance data is moderate. Although, the highest charge transfer and polarization resistances were observed in the case of Cu–SiO_2 obtained in the presence of 10^{-3} M CTAB and 10 g/L SiO_2 in the plating bath. At same CTAB concentration, higher concentrations of SiO_2 do not improve the corrosion behavior of the deposits, probably because the nanoparticles are more difficult to keep in suspension and tend to agglomerate in the bath, leading to a less uniform incorporation.

The observed discrepancies between the R_p values obtained from polarization curves and impedance measurements are probably due to the fact that the surface

Table 4 Corrosion parameters of the corrosion process of samples immersed in a 0.2 g/L aerated Na_2SO_4 solution (pH 3)

Deposit	SiO_2 (g/L)	R_e (Ω cm^2)	R_t (Ω cm^2)	C_d (μF cm^{-2})	R_F (Ω cm^2)	C_F (mF cm^{-2})	R_p^a (Ω cm^2)
Cu	–	578.14	146.63	0.10	993.41	0.10	1140.04
Cu–SiO_2	10	659.36	152.08	0.20	1014.80	1.14	1166.88
	20	317.29	152.35	8.23	965.90	1.86	1118.25
Cu–SiO_2 + CTAB 10^{-3} M	10	1026.8	301.24	0.26	947.09	4.98	1248.33
	20	267.77	190.70	50.8	937.7	5.77	1128.4

[a] $R_p = R_t + R_F$

changes occurring during potentiodynamic polarization and impedance measurements are not similar [18]. Moreover, the measuring accuracy might be affected by the complexity of the investigated processes and by the fact that the theoretical model developed on the basis of impedance measurements does not include all the properties of the tested system [19].

Conclusions

When SiO_2 nanoparticles are added in the plating bath, a decrease tendency of the corrosion current for the resulting composite Cu–SiO_2 deposits could be observed. The corrosion process is slowed down due to particles incorporation in the metal matrix that reduces the active surface of the coating in contact with the corrosive environment and hence, the corrosion rate.

CTAB can diminish the thermodynamical surface energy of silica nanoparticles by adsorption and hinder their agglomeration, leading to more uniform, finer grained cathodic Cu–SiO_2 deposits with higher SiO_2 incorporation fraction. The most important effect was observed when CTAB was used in 10^{-3} M concentration in the electroplating bath. It is very plausible that, besides its beneficial action on particles surface energy and charge, CTAB also modifies the surface of the metallic electrode, influencing additionally the co-deposition of particles and the deposit morphology and structure.

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