ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 592−595. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.N. Shcherbinina, N.G. Medvedeva, S.S. Popova, E.L. Surmenko, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 4, pp. 599−602.

APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Modification of Copper-Based Matrix Structures with Calcium

O. N. Shcherbinina, N. G. Medvedeva, S. S. Popova, and E. L. Surmenko

Engels Technological Institute, Branch of Saratov State Technical University, Engels, Saratov oblast, Russia

Received June 18, 2008

Abstract—Electrochemical behavior of a copper electrode in solutions of calcium chloride in dimethylformamide was studied in the concentration range 0.027–0.63 M at various electrode potentials. The diffusion-kinetic characteristics of the CaCu alloy formed on the copper surface under the conditions studied were calculated.

DOI: 10.1134/S1070427209040119

Recently, a new field of chemistry, chemistry of intercalated compounds and, in particular, cuprates in the system BiPCaCuO, has been rapidly developing [1, 2]. The interest in these compounds is due to broad prospects for their use as new superconductors, hyperanisotropic materials, and materials for new generations of reversible chemical power sources. Synthesis of superconducting cuprates with exceedingly high transition temperatures (225 K and higher), development of algorithms to be used in a search for compounds with a high temperature of transition into the HTS state, and design of new methods for synthesis of HTS materials are the most important areas of basic research in chemistry and technology of high-temperature superconductors [1–4]. Rather promising as regards controlled synthesis of metallic composites with the HTS stoichiometry, distinguished by homogeneous distribution of components, is the electrochemical method of cathodic incorporation [5]. This method is used to obtain composite structures differing in oxidizing properties from metallic alloys. Studies devoted to this subject are few in number. Thus, development of theoretical foundations of new electrochemical techniques for deposition of complex-composition films possessing the structure and properties of HTS is a topical field of electrochemical technology.

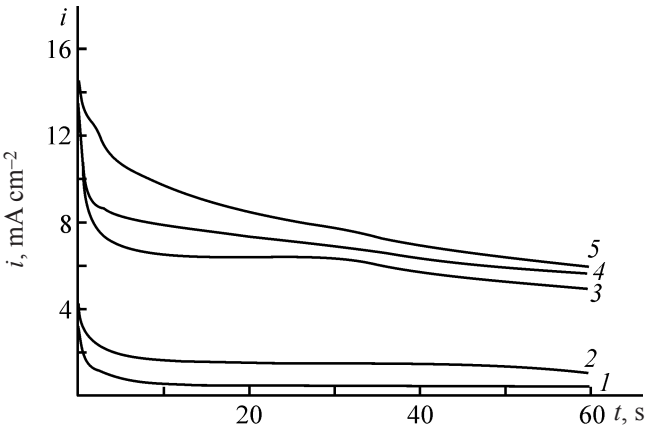

Fig. 1. Potentiostatic curves for cathodic incorporation of calcium into copper from a 0.63 M solution of $CaCl_2$ in DMF at various potentials. (*i*) Current density and (*t*) time; the same for Figs. 3–5. *E* (V): (*1*) –2.2, (*2*) –2.4, (*3*) –2.6, (*4*) –2.8, and (5) –3.0; the same for Figs. 2–4.

Treatment of surface metal layers by the method of electrochemical incorporation at room temperature can change the nature of the metal surface by imparting a number of specific physical properties and provide a high degree of purity of a product [5].

EXPERIMENTAL

The experiment was performed on a setup including a P-5848 potentiostat and a KSP-4 self-recorder or oscilloscope. The cathodic treatment of samples was made in the potentiostatic mode at potentials of –2.2 to –3.0 V in solutions of calcium chloride $CaCl_2$ in dimethylformamide (DMF), with concentrations of 0.027, 0.09, 0.36, and 0.63 M. The polarization time at each prescribed potential was 45 min, and a nonaqueous silver chloride electrode (s.c.e.) served as reference. A high-purity (99.99%) copper plate with a working surface area of 1.5 cm^2 was used as the working electrode.

Table 1. Calcium content of the copper electrode

Depth, μm	Content, wt %, in indicated sample	
	no. 1	no. 2
145	11.1	11.3
185	9.4	10.2
210	8.3	8.3
230	7.8	8.2

Prior to experiments, the electrode surface was subjected to a mechanical treatment. The experiments were carried out at a temperature of 20°C.

It was found that the time dependences of the current density, i–t, in cathodic polarization of the copper electrode in a solution of $CaCl_2$ in DMF at potentials of –2.2 to –3.0 V (relative to nonaqueous s.c.e.) have a form characteristic of the process of cathodic incorporation to give a solid solution of calcium in copper (Fig. 1). The fact that, in the course of time, the current density at the electrode tends to zero indicates that a diffusion front of calcium ions is formed and moves into the copper electrode [5, 6]. The potentials of an unpolarized copper electrode in solutions of $CaCl_2$ in DMF are given below:

Solution concentration, M	0.027	0.09	0.36	0.63
Zero-current potential $E_{z/c}$, V	–0.38	–0.47	–0.52	–0.41

The shift of the zero-current potential of the copper electrode into the negative region after the cathodic polarization (Fig. 2) indicates that calcium is incorporated into copper via the reaction

$$x\mathrm{Ca}^{2+} + 2xe = x\square\mathrm{Cu} \leftrightarrows \mathrm{Ca}_x\mathrm{Cu} \quad (1)$$

The highest negative value of the steady-state zero-current potential (–0.93 V) and a uniform, homogeneous surface of the Ca(Cu) electrode are obtained, as shown by visual inspection with an MPD-1 microscope, at a polarization potential of –2.6 V.

The presence of calcium atoms in copper was confirmed by a laser microspectral analysis [7] on an OMMZ.450.501-M installation (Spektr 2000) at depths of 145, 185, 210, and 230 μm for three spectral lines: 3181.28, 2997.31, and 3179.53 Å (Table 1). A calcium gluconate sample served as reference. The data acquisition system included a recording unit, electronic interface with laser and spectrograph control systems, and IBM-compatible personal computer.

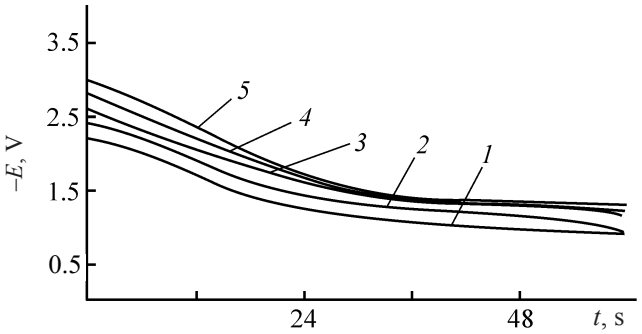

Fig. 2. Effect of the potential of cathodic incorporation of calcium on the run of zero-current E–t curves for a CaCu electrode in a 0.63 M solution of $CaCl_2$ in DMF.

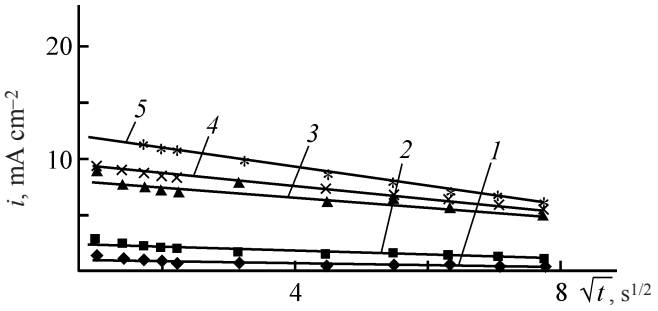

Fig. 3. i–$\sqrt{t}$ dependence for the copper electrode at different potentials of cathodic incorporation of calcium from a 0.63 M solution of $CaCl_2$ in DMF.

According to the results of an analysis of diffusion parameters (Table 2) found by plotting i–$\sqrt{t}$ (Fig. 3) and i–$1/\sqrt{t}$ (Fig. 4) dependences, their values tend to increase with the cathodic treatment potential. Extrapolation of the i–$\sqrt{t}$ dependences to the i axis makes it possible to find the current density at the instant when the polarization is switched on, $i(0)$, which characterizes the rate of the event of electrochemical incorporation itself [8]:

$$x\mathrm{Ca}^{2+} + 2xe = \mathrm{Cu} \leftrightarrows \mathrm{Ca}_x\mathrm{Cu} \quad (2)$$

and to estimate the amount of introduced calcium atoms in copper, $\Gamma_{Ca(Cu)}$, in terms of the log i–t dependence by the equation

$$\Gamma_{Ca(Cu)} = i(0)/nF(\Delta\log i/\Delta t) \quad (3)$$

This enabled calculation of the diffusion coefficient of calcium atoms in the Ca_xCu alloy, $D_{Ca(Cu)}$, from the product $c_{Ca}\sqrt{D}_{Ca}$ (Table 2).

It is known [9] that, as the electrolyte concentration increases, the fraction of ion–ion interactions grows and the solution structure may be transformed. This reflects on the state of the interface between the electrolyte

Table 2. Diffusion-kinetic characteristics of the copper electrode at various cathodic treatment potentials Ec in a 0.63 M solution of $CaCl_2$ in DMF

E_c, V	k_{in},[a] mA cm^{-2} s$^{-1/2}$	$c_{Ca}\sqrt{D_{Ca}} \times 10^8$, mol cm^{-2} s$^{-1/2}$	$i(0)$, mA cm^{-2}	$\Gamma_{Ca(Cu)}$, mol cm^{-2}	$D_{Ca(Cu)} \times 10^{15}$, cm^2 s^{-1}
–2.2	0.81	0.7	2.0	2.21	0.121
–2.4	1.49	1.37	3.0	4.44	0.484
–2.6	3.05	2.8	8.5	12.6	1.936
–2.8	2.18	2.0	10.2	48.05	1.024
–3.0	6.68	6.13	13.5	33.31	9.409

[a] k_{in}, incorporation constant.

Table 3. Diffusion-kinetic characteristics of the copper electrode at a cathodic treatment potential of –3.0 V in a 0.63 M solution of $CaCl_2$ in DMF

$CaC1_2$, M	k_{in},[a] mA cm^{-2} s$^{-1/2}$	$c_{Ca}\ D_{Ca} \times 10^8$, mol cm^{-2} s$^{-1/2}$	$i(0)$, mA cm^{-2}	$\Gamma_{Ca(Cu)}$, mol cm^{-2}	$D_{Ca(Cu)} \times 10^{15}$, cm^2 s^{-1}
0.027	8	7.35	2.6	5.18	7.29
0.09	5.6	5.14	3.2	7.54	0.32
0.36	12.9	11.8	5.0	21.6	0.11

solution and the electrode and, consequently, on the behavior of calcium ions being incorporated. According to the run of the *i–t* curve, the maximum current density $i(0)$ increases with the solution concentration (Fig. 5). Results of an analysis of the *i,t* curves plotted in the $i–\sqrt{t}$ and $i–1/\sqrt{t}$ coordinates are listed in Tables 2 and 3. The dependence of $c_{Ca}\sqrt{D}_{Ca}$ on the solution concentration is ambiguous. The maximum value of $c_{Ca}\sqrt{D}_{Ca}$ (11.8×10^{-8} mol cm^{-2} s$^{-1/2}$) was obtained for $CaCl_2$ solutions with a concentration of 0.36 M.

The products of the concentration c_{Ca} of calcium ions being incorporated by their diffusion coefficient raised to power 1/2 were calculated, for the cathodic potentials and $CaCl_2$ solution concentrations under study, by the equation [8]

$$k_{in} = \Delta i/\Delta(1/t) = nF/\sqrt{\pi}c_{Ca}\sqrt{D}_{Ca}. \quad (4)$$

from the slope coefficient of the dependences $i–\sqrt{t}$ (Fig. 4). The values obtained are listed in Tables 2 and 3.

CONCLUSIONS

(1) The surface of copper can be, in principle, modified with calcium from an aprotic organic solution of the corresponding salt by the method of cathodic incorporation.

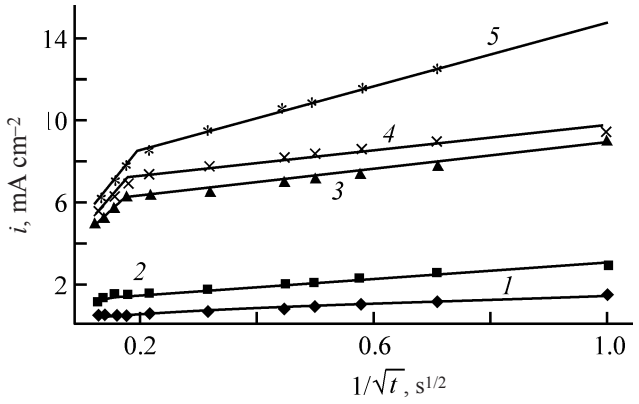

Fig. 4. $i–1/\sqrt{t}$ dependence for the copper electrode at different potentials of cathodic incorporation of calcium from a 0.63 M solution of $CaCl_2$ in DMF.

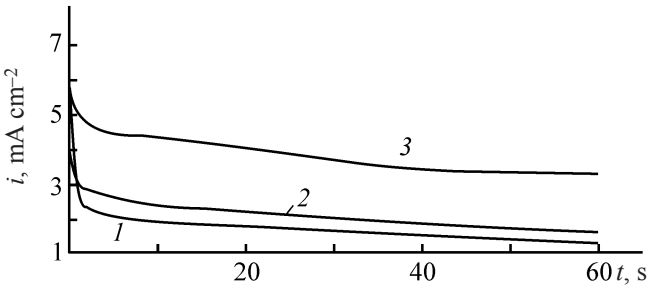

Fig. 5. Potentiostatic curves for cathodic incorporation of calcium into copper from at a potential of –3.0 V from various-concentration solutions of $CaCl_2$ in DMF. Solution concentration (M): (*1*) 0.027, (*2*) 0.09, and (*3*) 0.36.

(2) Under the conditions studied, the calcium distribution across the thickness of a copper sample steadily decreases from 11% at a depth of 145 μm to 8% at 230 μm.

(3) Under the polarization conditions specified, a solid solution of calcium in copper is formed.

REFERENCES

1. Graboi, I.E. and Putlyaev, V.I., *Zh. Vses. Khim. O–va im. D.I. Mendeleeva*, 1989, vol. 34, no. 4, pp. 473–480.
2. Petrii, O.A. and Tsirlina, G.A., *Ross. Khim. Zh. (Zh. im. D.I.Mendeleeva)*, 1993, vol. 37, no. 1, pp. 116–126.
3. Mal'tsev, V.A., Sokolov, Yu.S., and Kulikovskii, A.V., *Fiz. Met. Metalloved*., 1994, no. 7, pp. 140–145.
4. Semenov, V.B., Faifer, S.I., and Bolyshova, A.M., *Elektron. Tekhn.*, 1989, Ser. 6, no. 3(240), pp. 12–22.
5. Kabanov, B.N., Kiseleva, I.G., and Astakhov, I.I., *Elektrokhimiya*, 1972, no. 7, pp. 955–971.
6. Abyaneh, M.Y., *Electrochim. Acta*, 1991, vol. 36, no. 34, pp. 727–732.
7. Kriger, A.E., Surmenko, E.L., Surmenko, L.A., and Tuchin, V.V., *Proc. SPIE, Bellingham*, SPIE, 1999, vol. 4001, pp. 299–303.
8. Popova, S.S., *Metody issledovaniya kinetiki elektrokhimicheskikh protsessov: Uchebnoe posobie* (Methods for Study of the Kinetics of Electrochemical Processes: Textbook), Saratov: Saratov Politekhn. Inst., 1991.
9. Izmailov, N.A., *Elektrokhimiya rastvorov* (Electrochemistry of Solutions), Kharkov: Kharkov Gos. Univ., 1959.