ISSN 1070-4272, Russian Journal of Applied Chemistry, 2006, Vol. 79, No. 7, pp. 1200–1201. © Pleiades Publishing, Inc., 2006. Original Russian Text © Yu.P. Perelygin, S.Yu. Kireev, A.Yu. Kireev, 2006, published in Zhurnal Prikladnoi Khimii, 2006, Vol. 79, No. 7, pp. 1210–1211.

BRIEF COMMUNICATIONS

Electrodeposition of Bismuth from Acid Lactate Electrolyte

Yu. P. Perelygin, S. Yu. Kireev, and A. Yu. Kireev

Penza State University, Penza, Russia

Received February 2, 2006

Abstract-Electrodeposition of bismuth from acid lactate electrolyte was studied.

DOI: 10.1134/S1070427206070317

Bismuth and its alloys are widely used in industry as antifriction and corrosion-resisting coatings, as electrical contacts to semiconductors, including rectifying and ohmic contacts formed by them on silicon and germanium, and as coatings for soldering [1].

Presently, perchlorate, fluoroborate, phenolsulfonic, fluosilicate, sulfate, EDTA, pyrophosphate, and other electrolytes are used for the electrodeposition of bismuth and bismuth-containing alloys [1].

Though ensuring deposition of high-quality coatings at high cathodic current efficiency and possessing a high throwing power, the above electrolytes contain, apart from bismuth ions, toxic anions, which makes them more environmentally hazardous.

Much attention is given today to replacement of toxic anions in electroplating solutions by less toxic anions [2]. Lactic acid is abundant in nature and is an intermediate product of metabolism in biological tissues. The acid is readily biodegradable and, therefore, environmentally safe. In this respect, the development of a lactate bismuth-plating electrolyte is of certain theoretical and practical significance.

The effect of the electrolysis mode and electrolyte composition was studied at 20°C and a cathodic current density of 0.3 A dm⁻² in the solution containing 80% lactic acid [GOST (State Standard) 490–79] 100 ml l⁻¹, bismuth nitrate (in terms of metal) 10 g l⁻¹, sodium sulfate 20 g l⁻¹, and 65% nitric acid (GOST 4461–77) 50 ml l⁻¹.

With an increase in the concentration of bismuth ions in the electrolyte from 10 to 20 g 1^{-1} , the cathodic current efficiency decreases from 97.5 to 91.7%, with the coating quality improved. Raising the bismuth concentration further results in a drastic deterioration of the coating quality and a decrease in the cathodic current efficiency.



Fig. 1. Cathodic current efficiency (CE) by bismuth vs. (1) concentration of lactic acid c in the electrolyte, (2) cathodic current density i_c and (3) solution temperature.

As the concentration of lactic acid in the electrolyte is increased from 25 to 150 ml l^{-1} , the cathodic current efficiency by bismuth increases from 90.4 to 98.7%. In this case, light gray, good-quality coatings are deposited. Raising the concentration of lactic acid to 200 ml l^{-1} leads to a decrease in the cathodic current efficiency by bismuth to 55.1%, with the coating quality deteriorated (Fig. 1, curve *1*).

The further study was carried out in the electrolyte containing lactic acid 150 ml l^{-1} , bismuth nitrate (in terms of metal) 10 g l^{-1} , sodium sulfate 20 g l^{-1} , and 65% nitric acid (GOST 4461–77) 50 ml l^{-1} .

Increasing the cathodic current density within 0.3-0.75 A dm⁻² leads to deterioration of the coating quality and a sharp decrease in the cathodic current efficiency by bismuth from 97 to 4.87%, which is due to intensification of hydrogen evolution (Fig. 1, curve 2).

With an increase in temperature from 12 to 24°C, the cathodic current efficiency by bismuth increases



Fig. 2. Cathodic potentiodynamic curves taken in the course of bismuth deposition at different concentrations of bismuth ions in the solution. (*E*) Potential and (i_c) current density. Bi³⁺ concentration, g l⁻¹: (1) 2.5, (2) 5, and (3) 10. Insert: log i_c vs. log [Bi³⁺] dependence at a cathode potential of -260 mV.

from 93 to 97%. At higher temperatures, the cathodic current efficiency by bismuth decreases to 88%, which may be accounted for by acceleration of chemical dissolution of the coating or by intensification of hydrogen evolution (Fig. 1, curve 3).

Stirring of the solution results in drastic deterioration of the coating quality and a decrease in the cathodic current efficiency by bismuth.

The potentiodynamic curves taken at a potential sweep rate of 4 mV s⁻¹ (Fig. 2) show that, with decreasing bismuth concentration, the polarization curves shift toward more negative potentials. For example, at the cathodic current density of 0.3 A dm⁻² the cathode potentials (relative to SHE) in the solution containing 10, 5, and 2.5 g l⁻¹ bismuth ions are 262, 274, and 278 mV, respectively (Fig. 2).

The log-log dependence of the cathodic current density on the bismuth concentration in the electrolyte is linear (Fig. 2, insert at the top). The slope of this straight line is 1.3, which shows that the discharge of bismuth ions occurs in steps [3].

The study of the processes occurring at the anode showed that, as the anodic current density increases from 0.1 to 0.5 A dm⁻², the anodic current efficiency by bismuth (in terms of Bi^{3+}) decreases from 141 to 102%. This high value of the current efficiency is

likely due to the fact that the electrochemical dissolution is accompanied by the chemical dissolution of the anodes.

CONCLUSIONS

A process for the electrodeposition of high-quality bismuth coatings was developed, and a less toxic electrolyte containing 80% lactic acid (GOST 490–79) 150 ml l⁻¹, bismuth nitrate (in terms of metal) 10 g l⁻¹, sodium sulfate 20 g l⁻¹, and 65% nitric acid (GOST 4461–77) 50 ml l⁻¹ was suggested. At a cathodic current density of 0.3 A dm⁻² and 20–25°C, the cathodic current efficiency is 95–98%. The deposition rate of the bismuth coatings at these electrolysis conditions is 7.6 μ m h⁻¹.

REFERENCES

- Azhogin, F.F., Belen'kii, M.A., Gal', I.E., et al., *Gal'-vanotekhnika: Spravochnik* (Electroplating: Reference Book), Moscow: Metallurgiya, 1987.
- 2. Vinogradov, S.S., *Ekologicheski bezopasnye gal'vanicheskie proizvodstva* (Environmentally Safe Electroplating Plants), Moscow: Globus, 2002.
- 3. Vetter, K.J., *Elektrochemische Kinetik*, Berlin: Springer, 1961.