PHYSICAL CHEMISTRY

N. PANGAROV, V. MIKHAILOVA

1963

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

N. PANGAROV, V. MIKHAILOVA

ON THE TEXTURE OF ELECTRODEPOSITED TIN

(Presented by Academician A. N. Frumkin, 12 VIII 1963)

A number of experimental data obtained in studies of the processes of electrolytic deposition of metals show that, during electrocrystallization, a preferred orientation appears. Finch and co-workers (^1) report data on the (231) orientation in an electron-diffraction study of electrodeposited tin deposits of considerable thickness. Evans (^2), studying the deposition of tin on iron single crystals from pyrophosphate baths, found texture axes [100] and [110].

Kochergin and Nikulin (^3), studying the influence of the composition and temperature of the electrolyte and of the current density on the character of the orientation, established the orientation of tin deposits from sulfuric-acid electrolytes along the texture axes [001] and [221].

In the works cited, the question of the causes of the appearance of one or another type of orientation is not considered, and, moreover, there are certain discrepancies among the experimental data of individual authors. In none of the works mentioned was the orientation of tin investigated over a wide range of current densities and temperatures.

The aim of the present work was to study the influence of overvoltage on the character of the orientation of electrodeposited tin—a characteristic metal with a body-centered tetragonal crystal lattice. Similar studies have been carried out with electrolytic deposits of metals with crystal structures of different types —cobalt (^4), iron (^5), nickel and copper (^6)—and the experimental results obtained are in good agreement with theoretical conclusions. In the present work the experimental data are also explained on the basis of the theory of crystal growth developed in the works of Stranski and Kaishev (^7).

In the work of Pangarov (^7), by means of the method of Kaishev and Bliznakov (^9), the work of formation of two-dimensional nuclei of various crystallographic faces of crystals of the body-centered and face-centered cubic systems was calculated, and it was shown that the magnitude of this work of formation determines the character of the preferred orientation.

The work of formation of two-dimensional nuclei is described by the following expression:

Fig. 1. Dependence between the work of formation of two-dimensional nuclei of faces (100), (110), (101) and supersaturation

Figure 1: Fig. 1. Dependence between the work of formation of two-dimensional nuclei of faces (100), (110), (101) and supersaturation

$$W'_{hkl} = \frac{B_{hkl}}{\frac{1}{mN}(\mu - \mu_0) - A_{hkl}}, \tag{1}$$

where μ is the chemical potential of the equilibrium vapor of a two-dimensional nucleus, μ_0 is the chemical potential of the equilibrium vapor over an infinitely large three-dimensional crystal, m is the number of atoms in the gaseous molecule, N is Avogadro' s number, while A_{hkl} and B_{hkl} are constants determined by the type of two-dimensional nucleus.

In the case of electrolytic deposition of metals, the chemical potential in equation (1) may be replaced by the electrochemical potential

$$\mu^* = \mu + zF\varphi,$$

where φ is the electrode potential, z is the number of electric charges, and F is the Faraday number.

Then equation (1) takes the form:

$$W_{hkl} = \frac{B_{hkl}}{\frac{zF}{N}(\varphi - \varphi_0) - A_{hkl}}, \tag{2}$$

where φ is the electrode potential at the corresponding current density, and φ_0 is the electrode potential under the same conditions without external polarization.

The constants A_{hkl} and B_{hkl} for different faces of crystals of the volume-centered tetragonal lattice of tin, calculated by the method of Kaishev and Bliznakov, are respectively equal to:
$A_{101} = 2\psi_1 + \psi_2 + \psi_3 + 2\psi_4 - \psi_0$;
$A_{110} = 2\psi_1 + \psi_3 + 2\psi_4 - \psi_0$;
$A_{100} = \psi_1 + 4\psi_4 - \psi_0$;
$B_{101} = \psi_4^2$;
$B_{110} = \psi_4^2 + 2\psi_2 \cdot \psi_4$;
$B_{100} = \psi_1 \cdot \psi_2 + \psi_1 \cdot \psi_3 + \frac{3}{2}\psi_2 \cdot \psi_3 + \frac{1}{2}\psi_3^2$, where ψ_1 is the work of breaking one bond between two first neighbors, ψ_2, ψ_3, and ψ_4 are the same works of breaking the corresponding bonds between second, third, and fourth neighbors, and ψ_0 is the work of detaching one atom from the substrate.

Fig. 1. Dependence between the work of formation of two-dimensional nuclei of faces (100), (110), (101) and supersaturation.

For comparison of the works of formation of two-dimensional nuclei of different crystallographic faces of the tin lattice, let us consider the cases:

1. At high values of the overvoltage, $n = \varphi - \varphi_0$ in equation (2) the determining quantity is the constant B_{hkl}; then the inequality holds

$$W_{101} < W_{110} < W_{100}. \tag{3}$$

Consequently, on an indifferent cathode substrate, two-dimensional nuclei of the face (101) are formed preferentially, since the rate of formation of two-dimensional nuclei is proportional to $e^{W_{hkl}/kT}$.

2. At low values of the overvoltage, the determining quantity is the constant A_{hkl}:

$$W_{100} < W_{110} < W_{101}. \tag{4}$$

Then the greatest probability of formation of a two-dimensional nucleus exists for the face (100).

These dependences are represented graphically in Fig. 1. As the unit of work, the work of breaking one bond between two first neighbors in the tetragonal lattice of tin is adopted. It is also taken into account that the forces of interaction between atoms in the metal lattice decrease in proportion to the sixth power of the distance. The dashed lines in Fig. 1 denote the supersaturation for each type of two-dimensional nucleus (hkl) at which the denominator of expression (2) becomes zero.

The experimental arrangement and method of work do not in principle differ from those described in ([10]). Tin was deposited on a polycrystalline unoriented platinum wire 0.5 mm in diameter and 10 mm long. The anode was tin, cylindrical. Deposition of tin was carried out with stirring of the electrolyte by an electromagnetic stirrer. The overvoltage was measured by a compensation circuit relative to a saturated calomel electrode. The electrolytic tin deposits were examined by X-ray diffraction, by the Debye–Scherrer method, in a standard camera ($d = 57.4$ mm) with iron and copper K_α-radiation. The thickness of the deposits was about 50 μ.

The obtained experimental data on the preferred orientation of tin deposits under the corresponding electrolysis conditions are given in Tables 1 and 2.

Figure 2 presents some of the most characteristic radiograms.

The experimental results obtained show that at small supersaturations—low overvoltages—deposits of tin with the characteristic texture axis [100] are obtained from the stannate electrolyte, which,

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Fig. 2. X-ray diffraction patterns of electrolytic tin deposits obtained from different electrolytes:
a—no texture (stannate electrolyte), all characteristic diffraction lines of tin are clearly visible;
b—texture axis [100], stannate electrolyte (sample No. 3, Table 1), $D_k = 0.166$ A/cm^2, $t = 85°$;
c—texture axis [110] of a deposit from a sulfuric-acid electrolyte (sample No. 2), obtained at $D_k = 0.025$ A/cm^2, $t = 25°$;
d—texture axis [101], sulfuric-acid electrolyte (sample No. 4), $D_k = 0.058$ A/cm^2, $t = 25°$.

Table 1

Sample Nos.	Current density, A/cm^2	Temp., °C	Overvoltage, mV	Axis and texture characteristic
1	0.042	85	367	[100] perfect
2	0.083	85	398	[100] perfect
3	0.166	85	448	[100] most perfect
4	0.166	75	745	[100] weakly expressed
5	0.166	65	825	Unoriented
6	0.011	65	515	[110] imperfect; [101]

Note. For samples Nos. 1–5 the electrolyte composition was 75 g/l $Na_2SnO_3 \cdot 3H_2O$, 10 g/l NaOH; for sample No. 5: + 2 g/l gelatin.

is in good agreement with theoretical calculations (inequality (4) and Fig. 1), which show that under these conditions the work of formation of two-dimensional nuclei on the [100] face is the smallest.

With increasing current density and, correspondingly, overvoltage, spongy tin deposits are obtained. However, when gelatin is introduced into the stannate electrolyte, dense deposits are obtained at comparatively low current densities but with a high overvoltage of metal deposition. In this case the deposits are oriented parallel to the cathode substrate by the [110] and [101] faces, as should also be expected from the dependence presented in Fig. 1.

Table 2*

Sample Nos.	Current density, A/cm^2	Overvoltage, mV	Axis and texture characteristic
1	0.017	398	[110] perfect
2	0.025	480	[110] most perfect
3	0.050	518	[110] perfect; [101] weakly expressed
4	0.058	572	[101] most expressed
5	0.083	650	[101] weakly expressed
6	0.125	693	Unoriented

Note. Electrolyte composition: 55 g/l $SnSO_4$, 100 g/l H_2SO_4, 20 g/l phenol, 2 g/l gelatin.

* Samples were obtained at 25°C.

In sulfuric-acid solutions the overvoltage of metal deposition is comparatively higher, and the deposits obtained are oriented along the [110] texture axis. At still higher supersaturations the [101] texture axis also appears—as predicted by the theory.

Received
7 VIII 1963

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