PHYSICAL CHEMISTRY

V. L. KHEIFETS, E. S. KOZICH, and O. M. DANILOVICH

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. L. KHEIFETS, E. S. KOZICH, and O. M. DANILOVICH

REGULARITIES IN THE INCLUSION OF COPPER, ANTIMONY, LEAD, COBALT, IRON, AND ZINC IN A CATHODIC TIN DEPOSIT

(Presented by Academician A. N. Frumkin on 16 X 1956)

The possibility of codeposition of an impurity with the base metal as a result of discharge is determined by a number of conditions: the position of the standard potential relative to the potential of the base metal, the magnitude of the exchange currents of the impurity and of the base metal, the structure of the impurity-base-metal alloy close to 100% base metal, etc. Depending on which of the conditions is predominant in a given case, the regularities governing the inclusion of an impurity in the cathodic deposit change substantially.

The regularities of several principal cases, using the example of the inclusion of impurities in cathodic deposits of nickel and cobalt, were considered by us earlier ([1,2]).

Tin, unlike nickel and cobalt, has a large exchange current and is only slightly polarized. Thus, for example, in the electrolyte we studied, containing $SnSO_4$ 90 g/l, H_2SO_4 20 g/l, phenolsulfonic acid 50 g/l, and carpenter' s glue 4 g/l, the cathodic potential of tin changes, on going from a current density of 50 A/m^2 to a current density of 200 A/m^2, by only 5-7 mV. This gave grounds to suppose that, in the case under consideration, certain differences should appear from the regularities of impurity inclusion in nickel and cobalt deposits.

The position in the electromotive series and the large exchange current of copper left no doubt that the inclusion of copper in the cathodic tin deposit should proceed at the limiting current. The copper content in the cathodic deposit was determined by the dithizone method. As was to be expected, the dependence of the copper content in the deposit on its content in the solution is expressed by a straight line passing through the origin. In contrast to cases where the deposition of the base metal is strongly polarized, the straight line determining the copper content in the cathodic tin deposit does not lie above the bisector of the coordinate angle, but coincides with it, which is explained by the insignificant polarization of tin discharge. At the same time, the "constant" of the rate of inclusion of copper in the cathodic tin deposit practically coincides with the

Fig. 1

Figure 1: Fig. 1

constant for other metals included in the cathodic deposit—nickel and cobalt—at the limiting current (^{1}).

Copper is the only one of the impurities we studied whose deposition is limited by diffusion. The deposition of all the other impurities is limited, as the investigation showed, by the rate of the discharge stage. These impurities, however, must be divided into two groups. The first should include antimony and lead. The standard potential of antimony is more positive than the potential of tin; however, the appreciable polarizability of the antimony discharge process leads to its deposition being limited by the discharge stage, while it becomes necessary to take into account, though small, the magnitude of the polarization of tin discharge. Lead, both in the magnitude of its standard potential and in polarizability, is very close to tin, and therefore, for lead too, one cannot neglect the magnitude of the polarization

discharge of the base metal. Thus, these two impurities must obey the regularity characteristic of the case in which the rate of deposition of the base metal and of the impurity is limited by the discharge stage. The antimony content in the metal was determined with the aid of radioactive isotopes; lead was determined spectrographically and by the dithizone method.

Figure 1 gives the dependence of the antimony content in the cathode deposit on its content in the solution. It is clear from the figure that this dependence is expressed by a curve of parabolic form, as also follows from theory. Figure 2 gives the dependence of the content of lead (curves 1 and 2) and antimony (curve 3) in the cathode deposit on the current density. It is clear from the figure that the lead content in the deposit at first, up to a current density of $\simeq 200$ a/m^2, increases sharply, and then changes little; the resistance of diffusion begins to have an effect. For antimony there is observed an almost complete independence of its content in the deposit from the current density. As follows from equation (10) of paper (1), for the case under consideration the equation is valid

$$\lg A_i = N + \left(\frac{\alpha_1 Z_1}{\alpha_m Z_m} - 1\right) \lg J, \tag{1}$$

where A_i is the impurity content in the cathode deposit; N is a complex constant; α_1 is the fractional coefficient from the kinetic equation of discharge of the impurity; α_m is the same for the base metal; Z_1 is the valence of the impurity; Z_m is the valence of the base metal; J is the current density at which deposition of the metal proceeds.

Fig. 1. Dependence of the content of the impurity antimony in the cathode deposit of tin on its content in the solution.

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of the content of lead and antimony in the cathode deposit of tin on the current density: 1 –lead at a content in the electrolyte of 16 mg/l; 2 –lead at a content in the electrolyte of 11 mg/l; 3 –antimony at a content in the electrolyte of 1.6 mg/l; 4 –manganese in the cathode deposit of nickel (bilogarithmic coordinates), manganese content in the electrolyte 6.5 mg/l; 5 –curve 1 in logarithmic coordinates; 6 –curve 2 in logarithmic coordinates.

It is clear from the equation that if $\alpha_1 Z_1 > \alpha_m Z_m$, the impurity content in the cathode deposit will increase. An example of such a case may be the inclusion of manganese in nickel and of lead in tin. If $\alpha_1 Z_1 = \alpha_m Z_m$, the impurity content should not depend on the current density, as is observed in the case of inclusion of antimony in tin. Curves 1 (ascending section) and 2 of Fig. 2, in logarithmic coordinates, are transformed into straight lines 5 and 6 with a tangent of the angle of inclination ($\simeq 1.7$) equal to the tangent of the angle of inclination in the case of inclusion of manganese in nickel (straight line 4).

Iron and cobalt are metals considerably more electronegative than tin and, in addition, possess a small exchange current. Zinc, although it possesses a large exchange current, stands in the series of potentials more negative than tin by 0.62 V and forms with tin neither a solid solution nor chemical compounds. Naturally, on the one hand, the rate of discharge of these me-

metals should be determined by the rate of the discharge stage, while, on the other hand, the polarization of deposition of the base metal, owing to its small value, cannot have any appreciable effect on their inclusion in the deposit. Assuming that the base metal is deposited without polarization, and that the rate of deposition of impurities is limited by the discharge stage, it is not difficult to obtain equation (2)

$$A_i = \frac{100 M C_i}{J C_m^{\alpha_1 z_1 / Z_m}}, \tag{2}$$

where C_i is the concentration of the impurity in the electrolyte; C_m is the concentration of the base metal in the electrolyte; M is a composite constant including the value of the standard exchange current of the impurity, the values of the standard potentials, etc.; the remaining notation is as before. Using the case of inclusion of cobalt in a tin deposit as an example, we checked the dependence of A_i on the current density J for this group of impurities. The experimental results are shown in Fig. 3. It is evident from the figure that equation (2) is fully justified for this dependence as well.

Fig. 3. 1 –dependence of the cobalt content on current density (cobalt content in the electrolyte 50 mg/l), 2 –the same in logarithmic coordinates

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

An increased tin content in the electrolyte led, as follows also from theory, to a noticeable decrease in the content in the cathode deposit of impurities whose rate of deposition is determined by the discharge stage. From equation (2) it follows that between C_i and A_i in this case, just as in the deposition of impurities at the limiting current, there should be a linear dependence. At the same time, different values of M for different impurities should lead, in contrast to impurities depositing at the limiting current, to different slopes of the curves.

Figure 4 gives data for iron, cobalt, and zinc illustrating these propositions. The contents of Fe, Co, and Zn in the cathode tin deposit were determined by the method of radioactive isotopes.

Fig. 4. Dependence of the content in the cathode deposit of impurities of iron, cobalt, and zinc on their content in the electrolyte. The dotted straight line is the bisector of the coordinate angle

It is of interest to compare the rates of inclusion in the deposit of various impurities. Such a comparison is presented in Table 1. The deposition rates are characterized by the ratio of the impurity content in the deposit to its content in solution, i.e., by the so-called separation coefficient (3). In the cases of Mn in Ni and Sb and Pb in Sn, the initial, practically straight-line portion of the curve was taken.

It is evident from the table that in the case when the rate of deposition of the base metal is determined by discharge, and the rate of deposition of the impurity by diffusion, the individual properties of the impurity and of the base metal cease to play a role, and the composition of the deposit is considerably richer in impurity than the solution. In the case of small polarization of deposition of the base metal and deposition of the impurity at the limiting current, the composition of the deposit turns out to be the same as the com-

Table 1

Base metal	Impurity	Stage determining impurity deposition	Stage determining deposition of the base metal	Content in deposit / Content in solution
Ni	Cu, Zn, Pb, Cd, Co	Diffusion	Discharge	2.5

Base metal	Impurity	Stage determining impurity deposition	Stage determining deposition of the base metal	Content in deposit / Content in solution
Co	Cu, Zn, Pb	Diffusion	Discharge	3.0
Sn	Cu	Diffusion	Polarization may be neglected	160
Ni	Mn	Discharge	Discharge	0.07
Sn	Pb	Discharge	Polarization must be taken into account	0.5
Sn	Sb	Discharge	Same	0.033
Sn	Fe	Discharge	Polarization may be neglected	0.0012
Sn	Co	Discharge	Same	0.0005
Sn	Zn	Discharge	Same	0.0002

the composition of the solution. And, finally, in the case when deposition of the impurity is determined by the discharge stage, the composition of the deposit proves to be considerably purer than the composition of the solution, and the rate of inclusion of the impurity proves to depend on the individual properties of both the impurity and the base metal.

Scientific-Research and Design Institute
of the Nickel, Cobalt, and Tin Industry
Leningrad

Received
10 VIII 1956

CITED LITERATURE

[1] V. L. Kheifets, A. L. Rotinyan, DAN, **82**, No. 3, 423 (1952). [2] A. L. Rotinyan, V. L. Kheifets, *Tsvetnye metally*, No. 2, 24 (1954). [3] G. A. Tsyganov, A. I. Chernilovskaya, Dokl. AN Uzbek SSR, No. 9, 32 (1952); No. 6, 37 (1954).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.