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Abstract

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ON THE QUESTION OF THE MECHANISM OF SULFUR INCORPORATION INTO GALVANIC DEPOSITS

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In the literature devoted to elucidating the mechanism of action of surface-active substances on the process of electrocrystallization of metals ([1]), in particular to clarifying the role of special additives in the formation of bright coatings ([2]), ideas have become widespread that relate this action to the physical adsorption of substances introduced into the solution or formed at the cathode. From this point of view, the amount of surface-active substances incorporated into the deposit, with whose action the practically important properties of deposits are associated, must be determined by the adsorptive capacity of these substances, or of the products of their electrochemical transformation, and by the charge of the electrode surface.

Concepts concerning the adsorption of surface-active substances on nickel have been developed in a number of works ([3]). Some authors have attempted to relate the adsorbability of these substances, including sulfur-containing substances, to the structure of their molecules and, in particular, to the presence in them of pairs of free electrons ([4]). At the same time, in the literature, especially in recent years, there have appeared indications that adsorption may be accompanied by irreversible decomposition of molecules ([5]). A number of authors ([6]) explain the incorporation of sulfur into galvanic deposits from organic compounds introduced into the solution by the formation of metal sulfides near the cathode. Thus, the question of the mechanism of the processes leading to the incorporation of impurities into metal deposits remains controversial to this day.

The results of investigations that we obtained in studying the influence of sulfur-containing surface-active substances on the structure and properties of electrolytic deposits of nickel, cobalt, zinc, and copper lead to the conclusion that the amount of impurities incorporated into deposits and the mechanism of their incorporation depend sharply on the nature of the metal.

Our studies of deposits formed in the presence of surface-active substances showed that the amount and form in which impurities, in particular sulfur, are incorporated into deposits depend mainly on the nature of the chemical forces

acting between the surface of the freshly deposited metal and the molecules (or ions) of the surface-active substance located in the immediate vicinity of the cathode. When the amounts of sulfur contained in nickel and zinc deposits are compared, attention is drawn to the fact that these amounts differ sharply for the two metals. Thus, for example, changing the concentration of thiourea in a nickel electrolyte from 0.1 to 0.4 g/liter (pH 2.5, D_k 1.3 A/dm^2) leads to an increase in the sulfur content in the deposit from 0.8 to 5.26%, whereas when the concentration of thiourea in a zinc electrolyte is changed from 0.2 to 4 g/liter (pH 4, D_k 1 A/dm^2), the amount of sulfur in the deposits changes from 0.12 to 0.37%.

Table 1 presents the results of determining the total sulfur content in nickel and zinc deposits obtained, respectively, from electrolytes containing: a) 160 g/liter $NiSO_4 \cdot 7H_2O$, 30 g/liter H_3BO_3, 10 g/liter NaCl and b) 250 g/liter

$ZnSO_4 \cdot 7H_2O$, into which surface-active substances were introduced, such as thiourea, allylthiourea, β-sulfonaphthalic acid, thioacetic acid, etc.

From the data presented in Table 1 it is evident that, in the case of nickel, a sharper dependence is observed, in comparison with zinc, of the quantity of inclusions on the nature of the surface-active component of the solution and on the electrolysis conditions. It was of interest to clarify the causes of these phenomena and to resolve the question of the nature of the sulfur-containing particles included in the deposits, using as examples such metals as nickel and zinc, for which marked differences in the character of crystallization are observed even in the presence of surface-active substances.

Table 1

Amount of sulfur in electrolytic deposits of nickel and zinc, obtained in the presence of surface-active substances

Name of substance	Additive concentration, g/l	Electrolyte pH	Current density, A/dm^2	Total sulfur content, wt. %
In nickel deposits				
Thiourea	0.2	5.5	0.65	2.15
Thiourea	0.2	5.5	1.0	1.24
Allylthiourea	0.2	5.5	1.0	0.75
β-Sulfonaphthalic acid	1.0	3.7	0.6	0.084
Thioacetic acid	0.1	3.6	1.0	0.26
In zinc deposits				
Thiourea	3.0	4.7	0.6	0.27

Name of substance	Additive concentration, g/l	Electrolyte pH	Current density, A/dm^2	Total sulfur content, wt. %
Thiourea	3.0	4.7	1.4	0.19
Allylthiourea	2.0	3.8	1.0	0.049

To this end, in addition to the total amount of sulfur in the nickel and zinc deposits, the carbon content was determined. Analysis of the nickel deposits showed that the carbon content* in them was considerably less than the amount that should have been present in the deposit according to the data on total sulfur content, if it were assumed that the molecules of the surface-active substance were absorbed in unchanged form. Thus, if the quantitative ratio of sulfur to carbon in thiourea molecules is 2.66, then their ratio, found as a result of analysis of nickel deposits, reached 12.6 in some experiments.

The results of the investigations carried out indicate that, in the case of nickel and cobalt, what occurs is, in the main, not physical adsorption of molecules of the surface-active substance in unchanged form, but chemical sorption with rupture of certain bonds in its molecules. This assumption was checked in two ways. Analysis for the sulfur content in nickel deposits bound in the form of sulfide was carried out by the method of determining the quantity of hydrogen sulfide liberated during dissolution of the deposits in dilute hydrochloric acid.

To confirm that the H_2S liberated under the action of HCl is a product of decomposition of sulfides included in the deposits, and does not arise as a result of the catalytic action of nickel (in the presence of hydrogen liberated during dissolution) on the process of decomposition of the additives

* Carbon in nickel and zinc deposits was determined by V. S. Sedova by the method of combustion of the deposit powder in a stream of oxygen. We take this opportunity to express our gratitude to her for the assistance rendered in the work.

(in particular thiourea), special experiments were carried out on the separation of sulfides from the metal by anodic dissolution. The latter was performed in neutral solutions of sodium chloride and nickel chloride salts. To avoid the appearance, in the sulfide powder, of sludge of metallic nickel, the deposits subjected to anodic dissolution were held on a magnet. The black sulfide powder remaining after dissolution was subjected to chemical and X-ray analyses.

Chemical analysis of the powders obtained showed that the ratio between the amount of sulfur and nickel in them varies depending on the total sulfur content in the nickel deposits. The ratio of sulfur to nickel in the sulfides obtained did not correspond to the stoichiometric ratio of these elements in known sulfides; for sulfides separated from deposits with a high sulfur content, the ratio of the amount of sulfur to nickel reached 2.5. The formation of sulfur-rich sulfides has been noted in the literature previously as well (7). As our investigation showed,

a considerable part of the sulfur in the sulfides separated from the deposits is weakly bound to nickel; during heating of the powders at a temperature of about 130° it is removed. The weakness of the sulfur bond is also indicated by the results of experiments involving heating of electrolytic nickel at a temperature of 400–500°. In the powder remaining after anodic dissolution of the heated deposit, the sulfur–nickel ratio has a value of about 0.45. The change in this ratio in the sulfide powders as a result of heating the deposit is apparently due to interaction of metallic nickel with unstable nickel sulfides occurring in the solid state, and not to sulfur burning out, since the total sulfur content in the nickel deposits after heating changes little.

Comparing the data obtained by these two methods on the amount of sulfur present in the form of sulfides with the total amount of sulfur in the deposits, one may conclude that the greater part of the incorporated sulfur (over 90%) is present in the form of sulfides. The remaining part of the sulfur was detected in the solution after anodic dissolution of the deposit or in the solution after chemical dissolution of the metal; the appearance of sulfur in these solutions should apparently be explained by the passage into solution of thiourea molecules present in the deposits in their original form. This is also indicated by the results of carbon analysis in the deposits.

Consideration of the results relating to zinc shows that the mechanism by which sulfur-containing surface-active substances are incorporated into zinc deposits differs from that described above. Zinc deposits contain a very small amount of sulfide sulfur. The greater part of the sulfur is not chemically bound to zinc. On the basis of the data obtained on the quantitative content of carbon and unbound sulfur, it should be assumed that the greater part of the sulfur is incorporated into zinc through adsorption of the additive molecules in unchanged form. This confirms the correctness of the previously expressed (8) proposition concerning the action of 2,6-2,7-disulfonaphthalene acid on the electrocrystallization of zinc.

It is known from the literature that nickel prepared by a special method and saturated with hydrogen, the so-called Raney nickel, has the ability to split off sulfur quantitatively from both organic and inorganic compounds (9). It may be assumed that freshly deposited electrolytic nickel containing hydrogen possesses the properties of Raney nickel and, analogously to the latter, interacts with sulfur-containing additives. It is apparently by this property of nickel that the high sulfur content in the deposits, as compared with zinc, should be explained.

The results of the investigations carried out indicate differences in the pathways by which sulfur from surface-active substances introduced into the electrolyte is incorporated into metallic deposits and, consequently, it is hardly correct to assume that the influence of surface-active substances on the process of electrocrystallization and, in particular, their role in the formation of the structure of depos-

can provide an explanation for different metals and different surface-active substances from a unified point of view.

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