ELECTRODEPOSITION:

DISCUSSION

High Current Densities in Electrolytic Refining of Zinc by V. V. Stender et al.

Yu. V. Baimakov. The results of the investigation concerning the preparation of zinc at high current density described by V. V. Stender are extremely important for the zinc industry. More important yet is the work of V. V. Stender concerning the deposition of zinc not on an aluminum, but on a zinc cathode. If one could obtain a 4- to 5-day layer of zinc on a zinc cathode it would open the way to a simple mechanization of the removal of cathode metal and would render the work in zinc electrolysis plants much easier.

N. T. Kudryavtsev. The industrial production of zinc by electrolysis with bipolar electrodes (the report by V. V. Stender) warrants attention. The current density (about 40-50 amp/ dm^2) reached during the production of a narrow ribbon can be increased by using an electrolyte rich in zinc and by agitation of the electrolyte with compressed air.

A New Electrolyte for Lustrous Electrotinning by A. I. Bodnevas and Yu. Yu. Matulis

N. T. Kudryavtsev. It seems to me that a drastic drop in current efficiency at a high concentration of the additional organic element (furfurol), which was observed by A. I. Bodnevas and Yu. Yu. Matulis in lustrous tinning, has no direct connection with the formation and thickening of an adsorptional layer of the organic element on the cathode; the addition of the organic substance to the electrolyte very probably decreases the hydrogen overvoltage sharply.

Binding Strength of Nickel Deposits on No. 2 Steel, Nickel, Chromium, 1Cr18Ni9Ti Steel, and Nickel-Chromium Alloy by M. I. Morkhov and K. N. Kharlamova

O. É. Panchuk. It is well known that the experiments concerning the conditions for obtaining bright deposits from a given bath are very difficult to reproduce, or cannot be reproduced at all, even if all the necessary conditions are maintained. It seems to me that the reason for this lies essentially in the different degrees of preparation of the surface of the sample before electrodeposition, and particularly different degrees of degreasing. This is particularly true in the case of brass, and to some degree for copper, on the surface of which a layer of grease remains even after a degreasing operation. The brightness of the deposit depends on the degree of degreasing. The work done by M. I. Markhov and K. N. Kharlamova is of interest in connection with this. The results of this work make it possible to standardize the preparation of the base metal (in terms of purity) before the deposition. Previously this appeared to be possible only by using ultrasonic methods of degreasing, which give completely reproducible results. One may assume that bright nickel deposits are induced by the formation of colloidal layers of hydroxide in the precathodic layer when organic elements are added to the electrolyte, and by the formation of nickel sulfide when sulfur-containing elements are present in the electrolyte. This concerns baths in which no other colloids are introduced. It is known, for example, that electrodeposition of nickel from baths not containing additional elements, but having sufficiently high pH values, results in bright deposits. The same result is obtained in ordinary baths if some Na_2S is introduced and the electrolyte is strongly agitated. This assertion does not contradict the fact that many elements which induce brightness in nickel plating are substances which are split into ions in the solution and have no tendency to form colloidal solutions.

N. T. Kudryavtsev. The assertion made by M. I. Markhov and K. N. Kharlamova that electrolytic deposits are strongly bound to the base metal only on areas of the cathode free from passivating films is understandable and undoubted.

Contact Deposition of Certain Metals on the Surface of Aluminum Alloys by A. I. Lipin

Yu. V. Baimakov. A. I. Lipin indicates the existence of some kind of embryonic period of elimination of the oxide film from aluminum alloys as the result of ion exchange when they are being coated with zinc, and affirms that during this period zinc is not deposited. I believe that it is deposited, but in separate areas, for example in pores of the layer immediately after their appearance.

Hydrometallurgy of Manganese and Chromium by R. I. Agladze

O. A. Khan. In connection with the very interesting report by R. I. Agladze concerning electrolytic extraction of chromium, I would like to note that in 1949-1950 P. I. Markelov, under the direction of A. A. Bulakh and later V. V. Stender at the Institute of Chemistry of the Academy of Sciences Kaz.SSR, made a considerable contribution to the solution of this problem by electrolysis of chromium-ammonium alums; the conditions necessary for a high yield of chromium were determined. It is not the author's responsibility that these investigations were published only very recently.

Hydrogenation of Steel Cathodes During Electrodeposition of Metals by M. N. Polukarov

Yu. V. Baimakov. M. N. Polukarov notes that zinc protects steel from hydrogenation. However, we have discovered that zinc dissolves hydrogen, and therefore it does not protect steel from hydrogenation. This point can be proved in the following way: Let us take a hollow steel cylinder, with a ground stopper connected to a mercury manometer, and polarize it in the solutions to be investigated. Hydrogen will diffuse through the walls, and the pressure in the cylinder will increase. From this increase of pressure one can calculate the amount of hydrogen which has diffused into the cylinder. In this way one can study the diffusion of hydrogen during the process of coating steel or after it has been coated. It has been found that zinc lets hydrogen pass through. Only copper protects steel from hydrogenation very well, but not during the process of deposition. This subject has a great practical importance, and we must also take into account the very interesting results described by M. F. Smyalovskii.

Comparative Characteristics of Processes of Electrodeposition of Alloys of Molybdenum and Tungsten with Iron-Group Metals by T. V. Frantsevich-Zabludovskaya and A. I. Zayats

A. I. Krasovskii. On the basis of the results of the investigation made by A. T. Vagramyan and Z. A. Solov'eva, in which the variation of the potential was registered with an oscillograph, T. V. Frantsevich-Zabludovskaya has concluded that the Holt catalytic theory, according to which metals of the iron group catalyze the electrolytic deposition of tungsten and molybdenum, does not hold and that our conclusions concerning the codeposition of molybdenum and nickel are incorrect. Holt advanced his catalytic theory on the basis of the investigation by Brenner, who showed that simultaneous deposition of metals of the iron group and tungsten gives deposits having a layered structure. Although one would expect a variation of the deposition potential during the formation of alternate layers of iron and tungsten in the deposit, the investigation of A. T. Vagramyan and Z. A. Solov'eva concerning alternate deposition of layers $1\ \mu$ thick showed no such variation of potential on the oscillogram. This result indicates that the basis on which the catalytic theory has been advanced is incorrect, but it does not negate the possibility of the catalytic effect of the metals of the iron group on simultaneous deposition with tungsten and molybdenum. The term "catalytic effect" does not indicate the physical basis of the effect of the metals of the iron group on the deposition of molybdenum or tungsten. In very general terms it indicates an increase of activation energy with consequent increase of the reaction rate. Thus, we may consider as catalytic the processes in which the co-deposition of a metal induces an increase of the rate of deposition of the other metal which is higher than one would expect from the thermodynamics of a reversible process. In the co-deposition of molybdenum and nickel one observes just this increase in the rate of deposition of molybdenum, an increase which is higher than that which one would expect from the change of its equilibrium potential due to the formation of the alloy.

It must be noted that the coefficients taken for separate reactions do not take into account the mutual effect of the discharging ions in the equation for simultaneous discharge of ions derived by V. L. Kheifets on the basis of the theory of retarded discharge and concentration polarization. For example, the possibility of the formation of an alloy between the co-deposition elements is not taken into account. And yet the composition of the alloy changes with cathode potential, and therefore the values of the coefficients in the equation of retarded discharge must change correspondingly. In many cases the effect of this factor is so great that the rate of deposition of some metals in a pure state (molybdenum, tungsten, aluminum, etc.) from aqueous solutions is very low, and therefore they are easily co-deposited with other metals. Since most metals are mutually soluble to some degree, the presence of one of the metals as an impurity in the other leads to the possibility of the formation of an alloy and, consequently, to the change of the equilibrium potential and of the overvoltage.

Some Problems Concerning the Mechanism of Electrolytic Deposition of Nickel-Molybdenum Alloys by A. I. Krasovskii

Yu. V. Baimakov. The affirmation of A. I. Krasovskii that the Tafel equation is not valid in the simultaneous discharge of ions is apparently based on a misconception; the applicability of the Tafel equation for each type of ions separately during simultaneous discharge has been proven experimentally by many authors.

Cathodic Processes During Deposition of Zinc and Hydrogen on Electrodes of Different Metals by D. P. Zosimovich and N. E. Nechaeva

N. T. Kudryavtsev. D. P. Zosimovich affirms that along the section of the polarization curve corresponding to simultaneous discharge of hydrogen and zinc on nickel the rate of deposition of hydrogen follows the Tafel equation:

$$\varphi = a + b \lg i.$$

This is difficult to understand, since as nickel becomes covered with zinc the surface of the cathode is changed and this change should be accompanied by a change of the constant, a, and thus the Tafel equation drawn in semilogarithmic coordinates should not result in a straight line.

The Part Played by Foreign Anions in the Electrodeposition of Chromium by M. A. Shluger

N. T. Kudryavtsev. According to M. A. Shluger, the potential shows a jump as soon as the current is switched on, which indicates a passive state of the surface. However, this fact is insufficient to affirm that a film caused by the presence of H_2SO_4 is formed on the surface of the cathode. It is well known from the investigation of Muller that during chrome-plating in solutions of six-valent chromium an adsorptional layer is formed on the cathode, which slows down the reduction of chromic acid. It was Muller who first proposed the idea that chromium (6+) is reduced directly to the metallic state.

Effect of Boric Acid on Cathodic Polarization of Nickel in Sulfate Solutions by D. M. Chizhikov and L. P. Pliginskaya

N. T. Kudryavtsev. D. M. Chizhikov and L. V. Pliginskaya have not made it very clear why cathodic polarization of nickel in sulfuric acid solutions increases by 100-200 mv when the solution is acidified to a pH of 1-2, when one would expect a reverse result. One can assume that at a low pH a large part of the current is used for the evolution of hydrogen, and in reality the polarization curve corresponds to this process.

Electrolytic Coatings Applied with the Use of Ammonia and Ammonium Hydroxide Electrolytes by S. Ya. Popov

N. V. Gudin. In connection with the report by S. Ya. Popov, it appears to me important to investigate the mechanism of the anodic process during the deposition of bright nickel deposits from complex ammonia salts.

The instability of the electrolyte and the decrease of the quality of the nickel deposit are due essentially to the deviation of the anodic process from optima conditions. It is possible that the anodic process plays a lesser role in the cases described by S. Ya. Popov.

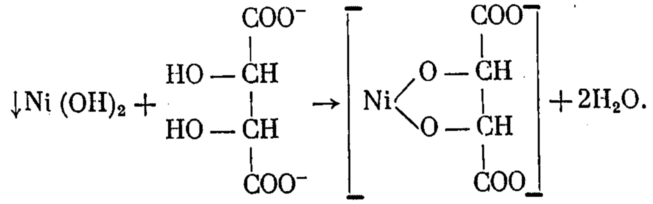
Local passivation of nickel anodes in ammonia complex electrolyte.

The dissolution of nickel at the anode in an electrolyte containing ammonia leads to the formation of ammonia complex ions. The investigation showed that the formation of the complex ion precedes the appearance on the anode of a layer of products of the different degrees of oxidation of nickel. The oxidation of nickel is due to the discharge of hydroxyl ions, a fact confirmed by the study of the anodic polarization of nickel in the electrolyte under consideration.

Due to the possibility of the formation of compounds of nickel of different valences, the oxide film may be formed essentially out of products of lower degrees of oxidation (nickel protoxide and its hydrate) or higher degrees of oxidation (oxide, peroxide, and their hydrated forms). Normal dissolution of nickel anodes occurs at current densities which are not higher than 0.5-0.6 amp/dm^2 if the total concentration of ammonia does not exceed 3.7 M. In this case it is essentially the lower degree of oxidation of nickel which is formed. This observation is in complete accord with the properties of nickel peroxide and hydrate of nickel peroxide: relatively higher solubility with respect to the corresponding compounds of trivalent nickel, and also a great tendency to form complexes with ammonia.

A passive state of the anode occurs in areas to which the supply of fresh electrolyte is rendered difficult. The figure shows that films (dark streaks) are formed in those places of the nickel anode which are screened by the products of anodic dissolution of the most active areas of the anode, and this makes the diffusion of ammonia from the solution to the electrode difficult. When the anode current density is high, the formation of the passive film can occur over the entire surface of the anode, which can prevent the increase of the concentration of ammonia up to 4.2-4.3 M. In this case the passivation of the anode starts at a current density higher than 2 amp/dm^2.

The addition of chloride, which increases the solubility of nickel anodes in acid electrolyte, is much less effective in ammonia solutions. The introduction of tartaric acid (50-60 g/liter) has a much greater effect on the solubility of the anode. When the total concentration of ammonia does not exceed 3.7-3.8 M the passivation of the anode does not begin even at current densities of 1.8-2 amp/dm^2. The role of these additional elements consists in the formation of the soluble complex nickel salt, according to the following reaction:



When the anode current density is high, the concentration of H^+ ions in the preanodic layer increases due to the increase of the number of OH^- ions discharging per unit time; the H^+ ions attach themselves immediately to the ammonia, which leads to the decrease of concentration of ammonia in the preanodic layer of the electrolyte, and renders the formation of the nickel complex $[Ni(NH_3)_6]^{2+}$ very difficult. As the result, a nickel compound of a higher degree of oxidation is formed and the anode is passivated.

Thus the necessity of increasing the concentration of ammonia in order to prevent the passivation of the anode is a reaction which one would expect. It is quite possible that an analogous mechanism of dissolution of anodes occurs in the case of silver, zinc, and cadmium in ammonia electrolytes.

The quality of the nickel layer deposited from the complex ammonia electrolyte decreases sharply when the nickel anodes are passivated. This is probably due not so much to the change of the concentration of nickel ions in the solution as to the cataphoretic transfer of dispersional particles to the cathode and their inclusion in the precipitate. The dispersional particles are formed by peptization of the anodic layer.

The results described here have found practical applications. In Kazan we have successfully used a nickel-plating bath composed of a complex ammonia salt for the production of mirror finish nickel deposits. These deposits adhere strongly to the base metal and have lower porosity and higher corrosion resistance compared with ordinary nickel deposits. It was possible to stabilize the electrolyte. The quality of the nickel deposits did not decrease after utilization of the electrolyte up to 500 amp · hr/liter and higher.