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1962

SovietRxiv

Abstract

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THE MECHANISM OF ELECTRODEPOSITION OF NICKEL FROM SULFURIC ACID SOLUTIONS

(Presented by Academician V. I. Spitsyn, May 18, 1962)

The experimentally determined value of the overvoltage of metal deposition is a total quantity, including ohmic (η_{ohmic}), concentration (η_{conc}), activation (η_{activ}), crystallization (η_{cryst}), and passivation (η_{passiv}) overvoltage:

$$\eta = \eta_{\text{ohmic}} + \eta_{\text{conc}} + \eta_{\text{activ}} + \eta_{\text{cryst}} + \eta_{\text{passiv}}.$$

The ohmic overvoltage depends on the electrical conductivity of the electrolyte and is proportional to the dimensions of the electrode; therefore, for point electrodes this component of the overvoltage may be neglected. The magnitude of the polarization of a Ni electrode does not depend on the rate at which the polarization curves are recorded, which indicates the absence of appreciable concentration overvoltage at room temperatures. The activation overvoltage is determined by the degree of hydration and the magnitude of the charge of the ions; consequently, for metals of the Fe group and such metals as Cu, Zn, and Pb, this quantity should be of the same order. Thus, the considerably higher overvoltage of Ni deposition compared with the indicated metals cannot be attributed to activation overvoltage. The crystallization overvoltage may be regarded as consisting of three parts (1). The first may be considered as a difficulty associated with the formation of new nuclei. However, in the presence of a large number of active sites on the electrode surface, the formation of new nuclei during the process of metal electrodeposition is unlikely (2). The second part is an ohmic overvoltage caused by distortion of the electric field near growing sites and inversely proportional to the number of growing sites. The third part of the crystallization overvoltage is associated with the accumulation of adsorbed atoms on the electrode surface owing to the slow diffusion of adsorbed atoms to active sites of the crystal. Since the number of crystallographically active sites depends on the melting point of the metal (3) and for nickel should not differ substantially from that of such metals as silver (and in the latter case even the total overvoltage is very small), the crystallization components of the overvoltage may be neglected.

Passivation overvoltage is regarded as a hindrance to the discharge of ions associated with the adsorption of foreign particles on the electrode surface. In this case one of the following mechanisms of passivation is possible:

1. In the case of a continuous film of adsorbed foreign particles, the passivation overvoltage is associated with the work required for metal ions to penetrate through this film.
2. For atoms to enter the crystal lattice, preliminary displacement of foreign particles adsorbed on active sites is necessary.
3. As a result of irreversible adsorption of foreign particles and their incorporation into the crystal lattice, distortion of the crystal lattice occurs, which may also hinder the process of entry of metal atoms into the lattice.

The study of the equilibrium potential of the nickel electrode has shown (^{4}) that passivation phenomena play a decisive role at low temperatures, while at high temperatures (180–250°) the role of the passivating factor ···

of the electrode surface sharply decreases. As a result, it became possible to determine the equilibrium potential and the temperature coefficient of the potential of the nickel electrode and to calculate the reversible potentials of nickel over a wide temperature interval. It is obvious that passivation phenomena, which affect the electrode potential, must also affect the process of electrodeposition of metals of the iron group. In the present work the mechanism of electrodeposition of nickel is studied with allowance for the passivation factor. The experimental procedure was described in the preceding article (4).

Fig. 1. Dependence of the polarization of a nickel electrode on temperature in a 1 N solution of $NiSO_4$ and pH 1.5, $i_k = 20$ mA/cm^2:
1 –relative to equilibrium potentials; **2** –relative to stationary potentials

Usually the overvoltage is determined as the difference between the potential of a polarized electrode and the potential of the same electrode in the absence of current. However, the value of the overvoltage found in this way does not accurately characterize the degree of irreversibility of the electrodeposition process of metals of the iron group, since they are readily passivated and their stationary potential is not an equilibrium one. In Fig. 1 it is seen that the value of the nickel overvoltage relative to the stationary potential (η_{stat}) at low temperatures is considerably higher than the true overvoltage relative to the equilibrium potential (η_{eq}). With increasing temperature, the difference in the values of η_{stat} and η_{eq} decreases, and above 180° these values coincide completely, since the electrode becomes reversible. From Fig. 1 it is seen that the temperature dependence of the overvoltage (curve 1) has two distinctly pronounced regions. Below 150° the overvoltage changes sharply with temperature, while above 150° it is practically independent of temperature. The temperature coefficient of the overvoltage in the interval 20-120° is about 2 mV/deg, and above 150° this value is equal to zero.

Figure 2 gives the dependence of the overvoltage of nickel deposition on current density at different temperatures. At low temperatures the curves have two regions. In the first region the polarization increases sharply with increasing current density, and hydrogen is mainly evolved. In the second region the change in polarization with current density is small and 60–80% of the current is consumed for metal deposition. It should be noted that with increasing temperature the current efficiency of the metal increases and above 150° amounts to 100%. With increasing temperature both the absolute values of the overvoltage and the slope of the polarization curves decrease. If at low temperatures, in the range of current densities corresponding to the simultaneous evolution of hydrogen and metal, the polarization curves have a semilogarithmic character, then at high temperatures this regularity is not observed. Study of polarization by the rapid method showed that at high temperatures the magnitude of polarization of the nickel electrode depends on the rate at which the polarization curves are recorded. With rapid recording the slope of the polarization curves is greater than with slow recording. With very slow recording of the curve, the polarization of the nickel electrode is practically independent of current density. This phenomenon finds its explanation in the study of the structure of electrolytic nickel deposits.

Fig. 2. Dependence of the overvoltage of nickel deposition on current density at different temperatures

It is known that the structure of nickel deposits obtained under ordinary conditions is very uniform and finely crystalline. A study of electrolytic nickel deposits obtained at high temperatures showed that metal deposition occurs not over the entire surface of the electrode, but at separate sites. Such a deposit structure leads to the true current density being much higher than the apparent one calculated for the geometrical surface of the electrode. Thus, the observed overvoltage corresponds to considerably higher current densities than those indicated in Fig. 2. Consequently, the real decrease in overvoltage on going from low temperatures to high ones is considerably greater than the observed decrease. The weak dependence of polarization on current density is explained by the fact that, as the current density increases, the number of growing sites increases, as a result of which the true current density changes practically not at all. Thus, at high temperatures the growing surface of the nickel deposit "adapts" itself to the magnitude of the polarizing current, in a manner analogous to that which occurs for metals that are usually deposited with low overvoltage. When the polarization curve is recorded rapidly, when the surface does not have time to grow, i.e., self-adjustment does not take place, the true current density at the growing areas is higher than during slow recording, and therefore the overvoltage values obtained are also higher.

As has been shown for metals with low overvoltage, in the presence of self-adjustment the magnitude of the true current density at the cathode is determined by the ratio of the rates of passivation and of supply of substance to the growing areas. It may be assumed that at high temperatures the rate of nickel deposition is likewise determined by the rate of supply of substance to the electrode. Indeed, at high temperatures an impoverished diffusion zone is observed near the growing areas of the nickel cathode, since, when the current density in the circuit is increased, new crystals are formed at a considerable distance from the growing areas. An approximate calculation of the magnitude of the concentration overvoltage, made on the basis of the experimentally determined thickness of the diffusion layer, showed that the concentration overvoltage during electrodeposition of nickel at 180° and a current density of 10 ma/cm^2 is about 15 mv.

The sharp change in the structure of electrolytic nickel deposits on going from high temperatures to room temperatures, i.e., the transition from nonuniform coarse-crystalline deposits to continuous and finely crystalline ones, may be regarded as a consequence of an increase in the rate of surface passivation. This change in structure is analogous to that observed upon introducing surface-active substances during electrodeposition of metals in order to obtain uniform coatings. In the case of nickel electrodeposition at low temperatures, the high rate of passivation is the main cause of its high overvoltage. This follows from the fact that, with decreasing temperature, the amount of foreign particles incorporated into the electrolytic nickel deposit increases (^{5}), as does the irreversible part of hydrogen adsorption (^{6}).

The facts presented show that one of the principal factors affecting the rate of nickel deposition is passivation of the surface of the nickel electrode during electrolysis, and that there is no fundamental difference in the mechanism of electrodeposition of metals with high and low overvoltage.

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Received
10 V 1962

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