

THE EFFECT OF ALTERNATING CURRENT ON THE ELECTRODEPOSITION OF NICKEL

A. T. Vagramyan and A. A. Sutyagina

Alternating current is widely used in the study of various kinds of electrochemical processes, and also for effecting or improving a number of technological processes. Thus, alternating current is used in the study of the structure of the electrical double layer [1], for the elucidation of the kinetics of the formation and dissolution of oxide films [2], in the study of the discharge and ionization of hydrogen [3], and also for the anodic dissolution of various metals (Cr, Mn, Pt, etc.) [4].

Studies have been made in a number of papers of the effect of the superposition of an alternating current on the cathodic process in the electrodeposition of metals. Thus, Izgaryshev, Kudryavtsev, and Berkman [5], Kohlschutter and co-workers [6], and others have noted a considerable reduction in the polarization of the cathode in the electrodeposition of nickel. There are also papers showing that the superposition of an alternating current during the electrodeposition of metals greatly affects the structure of the deposit [6,7]. In spite of these investigations on this subject, the causes of the change in structure of electrolytic deposits and of the reduction in the degree of polarization of the electrode remain obscure. In the present investigation, some supplementary data concerning the effect of an alternating current on the electrodeposition of nickel are brought forward.

EXPERIMENTAL

In our study of the effect of alternating current on the structure of electrolytic deposits of nickel we used the following circuit (Fig.1); AC is an accumulator, C a condenser, mA d.c. and a.c. milliammeters, R_1 and R_2 rheostats, Dp a choke, E the source of a.c., A the anode, K the cathode, and B an auxiliary nickel electrode for the superposition of the alternating current. Electrodeposition of nickel was carried out from electrolyte of the following composition:

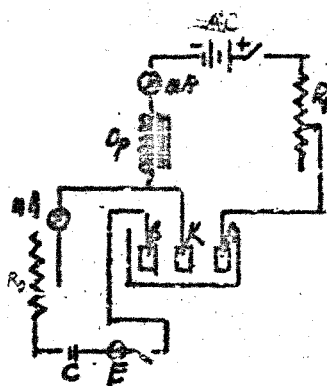


Fig. 1

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	250 g/liter
NaCl	5 g/liter
H_2BO_3	30 g/liter
pH	5.4-6

The temperature of the electrolyte was 20°.

For the electrodeposition of nickel the density of the direct current was varied from 1 to 3 amp/sq.dm, and the density of the superimposed alternating current was varied also from 1 to 3 amp/sq.dm. The structures of the electrolytic deposit of nickel, as exhibited by the electron microscope "replica" method (magnification 7000), are shown in Figs 2,3 and 4*. The frequency of the alternating current was 50 cycles/sec. Fig. 2 shows the structure of a nickel deposit obtained at a direct current density of 2 amp/sq.dm without superimposed a.c. The deposit shown in Fig.3 was formed at a direct current density of 2 amp/sq.dm with superimposed

50 cycles/sec a.c. of the same density. For the deposit shown in Fig.4, the d.c. density was 2 amp/sq.dm and the a.c. density was 3 amp/sq.dm.

As will be seen from the photographs, in the range of a.c. density 1-2 amp/sq.dm there is no appreciable increase in the size of the crystals of the deposit, but at an a.c. density of 3 amp/sq.dm the grain size increases sharply. It is evident that this increase in crystal size is to be observed only when the value of the superposed alternating current exceeds that of the direct current.

Besides studying the structures of electrolytic deposits of nickel, we examined the effect of the super-

* We express our gratitude to A. B. Shekhter and I. I. Tretyakov for the determination of the microstructures of the deposits with the aid of the electron microscope. See Plate, p. 847.

position of an alternating current on the porous character of the deposits. In these investigations electrolytic deposits of nickel were obtained from electrolyte of the same composition of a d.c. density of 2 amp/sq.dm, the a.c. density being varied from 1 to 3 amp/sq.dm. The thickness of the deposit investigated was 18-20 μ . The number of pores was determined by the aid of a reagent of the following composition:

$K_4Fe(CN)_6$ 20 g/liter
NaCl 10 g/liter

The reagent was allowed to act for 2 min. The pores were counted under the microscope at a magnification of 50 [8]. The experimental results are given in Table 1.

TABLE 1

Dependence of the Pore Density* on the Relative Densities of the Direct and Alternating Currents (frequency of a.c., 50 cycles/sec)

D.c. density (amp/sq.dm)	A.c. density (amp/sq.dm)			
	0	1	2	3
Number of pores per sq.cm				
1	20	8	10	16
2	14	8	9	14
3	16	7	11	13

* The pore density results given in Table 1 are average values from 18 experiments.

TABLE 2

Dependence of Pore Density on the Frequency of the Alternating Current

D.c. density (amp/ sq.dm)	A.c. density (amp/ sq.dm)	A.c. frequency (cycles/sec)					No. of pores per sq.cm without superposi- tion of a.c.
		20	50	500	4000	12000	
		Number of pores per sq.cm					
1	1	7	8	10	17	18	20
2	1	7	8	11	14	13	14
3	1	9	8	8	14	15	16

As will be seen from these results, when an alternating current of density of 1-2 amp/sq.dm is superimposed, the number of pores diminishes sharply. Besides studying the effect of the density of the alternating current, we investigated the effect of

the frequency of the current on the porous nature of the electrolytic deposits of nickel. Table 2 shows the dependence of the pore density on the frequency of the alternating current. As will be seen from Table 2, a high-frequency alternating current has no effect on the pore density of electrolytic deposits of nickel.

DISCUSSION OF RESULTS

It is evident that, when there is a superimposed alternating current of density greater than that of the direct current, conditions are created at the cathode that lead not only to intensive growth in the nickel crystals formed, but also to their periodic dissolution in association with the changing direction of the alternating current. If it is assumed that the electrolytic deposit on the cathode consists of crystals of variable size (which is indeed so in most cases, see Fig.2), then it may be supposed that when the direction of the current changes there will be preferential dissolution of the fine crystals, owing to their greater excess of surface energy and therefore lower stability when compared with the larger crystals.

The dependence of solubility on surface energy and on crystal dimensions is given by Thomson's equation:

$$RT \ln \frac{p_2}{p_1} = \frac{2\sigma M}{d} \cdot \frac{1}{r_2} - \frac{1}{r_1} \quad (1)$$

where p_2 is the vapor pressure of crystals of radius r_2 , p_1 is the vapor pressure of crystals of radius r_1 ; σ is the surface tension of the crystal, M is the molecular weight, and d is the density of the metal. Denoting the L.H.S. of equation 1 by η , the overvoltage, [9] and assuming r_1 to be sufficiently great, we obtain:

$$\eta = \frac{2\sigma M}{dnF} \cdot \frac{1}{r_2} \quad (2)$$

The determination of the dissolution rates for crystals of various dimensions from this formula is difficult, firstly owing to the absence of exact data on the surface tension of the crystals of solid metal, in particular nickel, and secondly owing to the difficulty of establishing the exact relationship between the overvoltage and the crystal dimensions.

Analogous calculations from equation 2 for the deposition of silver [9] have shown that for a ten-fold change in crystal dimensions ($r^1 = 1.4 \cdot 10^{-5}$ and $r^2 = 1.4 \cdot 10^{-4}$), the overvoltage for silver deposition changes by only 1.7 mV. When it is considered that the order of magnitude of the overvoltage for dissolving nickel crystals scarcely changes in comparison with that of silver with variation in crystal dimensions, it is evident that the overvoltage arising from differences in the crystal dimensions in nickel is very small in comparison with the total overvoltage observed in the electrodeposition of nickel [10]. It may therefore be considered that variations in the rate of dissolution of crystals due to variations in size cannot play an important part in the electrodeposition of nickel, and it is thus impossible to explain the increase in size of nickel crystals when alternating current is superimposed as the result merely of preferential dissolution of small crystals.

Another possible explanation is as follows. When electrodeposition of nickel occurs in the course of electrolysis, there occurs the discharge not only of nickel ions, but also of hydrogen ions, with the result that colloidal particles of hydroxide are formed directly at the surface of the electrode, particularly in neutral or weakly acid solutions [11]. These particles, which separate at the cathode together with the depositing metal, act as passivators, hindering the growth of the nickel crystals. As a result of this inhibition of crystal growth, a finely crystalline nickel deposit is obtained. According to Billiter [12], these particles (passivators) may be detected in the form of black embedded matter at the boundaries of the grains by examination of metallographic preparations of the deposit.

The formation of finely crystalline deposits of nickel resulting from the action of the hydroxide, which is formed at the cathode and becomes embedded in the deposit, has been noted also by other authors [13]. In fact, when the nickel deposit is analyzed, a certain amount of oxygen can be detected, which confirms that the embedding of hydroxide in the deposit has occurred [12-14].

On the basis of the above discussion it may be regarded as probable that the formation of a finely crystalline structure in the electrodeposition of nickel is due to inhibition of crystal growth. The superposition of alternating current in the electrodeposition of nickel must reduce the effect of these passivators, since the electrode is polarized alternately cathodically and anodically — when polarization is anodic, the hydroxide particles not only cannot separate at the electrode owing to their positive charge, but will even move away from the electrode. On the other hand, owing to the anodic polarization of the electrode, the discharge of hydroxyl ions will occur there, leading to acidification of the solution adjacent to the electrode. Increase in the acidity of the layer adjacent to the cathode will result in the destruction of the hydroxide particles that have formed. These two processes will result in a reduction in the concentration of the hydroxide, i.e. of the inhibitor of crystal growth.

The high overvoltage value for the electrodeposition of nickel is to be explained by the difficulty, due to the inhibiting effect of adsorbed nickel hydroxide on the electrode surface, of discharging nickel ions [10]. The lowering of the overvoltage by the superposition of alternating current is to be explained by the partial removal of the nickel hydroxide.

On the basis of this discussion it is evident that, as the factors causing passivation of the crystals are removed, conditions are created that encourage the growth of individual crystals, and the factors preventing coalescence of crystals are removed also. Curtailment of the growth of a group of growing crystals appears to be one of the causes of the formation of pores between them [8].

Reduction in the number of pores when alternating current is superimposed is to be explained by a reduction in the adsorption of the passivators (nickel hydroxide) that inhibit the growth and coalescence of the growing crystals and prevent the formation of more compact deposits. The absence of any effect due to the alternating current on the number of pores in electrolytic deposits of nickel when the frequency is increased may be explained by the fact that at high frequencies the composition of the solution in the cathodic layer does not alter — acidification and the removal of hydroxide particles from the cathode layer do not occur owing to the high frequency with which the direction of the current changes [15].

SUMMARY

1. The effect of alternating current on the electrodeposition of nickel has been studied. It has been shown that, when alternating current of greater than a certain density is superimposed, the deposit is of a coarsely crystalline structure.

2. It has been shown that, when alternating current is superimposed, the number of pores in electro-

lytic deposits of nickel is reduced. With increase in the frequency of the alternating current, its effect gradually disappears.

3. A hypothesis is given in the paper concerning the possible mechanism of the action of alternating current on the structure of the deposit and also on the overvoltage for the discharge of nickel ions.

Received December 28, 1951

Institute of Physical Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

- [1] V. I. Melik-Gaykazyan and P. L. Dolin, New Methods for the Physico-chemical Investigation of Surface Phenomena. Trans. Inst. Phys. Chem., No. 1. Acad. Sci. USSR Press, 1950; M. A. Proskurnin and M. A. Vorsina, Proc. Acad. Sci. USSR 24, 915 (1939); M. A. Proskurnin and A. N. Frumkin, Trans. Far. Soc. 31, 110 (1935).
- [2] B. V. Ershler, Trans. Second Conference on Corrosion of Metals. Acad. Sci. USSR Press. Part II, 1943.
- [3] P. L. Dolin and B. V. Ershler, J. Phys. Chem., 14, 886 (1940).
- [4] F. Halla, Z. Elektrochem. 35, 842, 1929; A. Brochet and J. Petit, Z. Elektrochem. 10, 909 (1904).
- [5] N. A. Izgaryshev and S. S. Berkman, Z. Elektrochem. 31, 10 (1925); N. A. Izgaryshev and N. T. Kudryavtsev, Z. Elektrochem. 38, 131 (1932).
- [6] V. Kohlschutter and Schodl, Helv. chim. Acta 5, 490, 593 (1922).
- [7] G. T. Bakhvalov, Trans. Second All-Union Conference on Theor. and Applied Electrochem. Acad. Sci. USSR Press, Kiev, 1949.
- [8] A. A. Sutyagina and A. T. Vagramyan, J. Appl. Chem., 24, 945 (1951).*
- [9] A. T. Vagramyan, Electrodeposition of Metals. Acad. Sci. USSR, 1950.
- [10] A. T. Vagramyan and Z. A. Solovyeva, Proc. Acad. Sci. USSR, 77, 629 (1951).
- [11] G. S. Vozdvizhensky, J. Appl. Chem., 20, 813 (1947); M. N. Polukarov, J. Gen. Chem., 19, 1583 (1949)**; V. V. Kuznetsov, J. Phys. Chem., 24, 574 (1950).
- [12] Zh. Billiter, Fundamentals of Galvanotechnics. United Sci.-Tech. Press, 1937.
- [13] K. M. Gorbunova, T. V. Ivanovskaya, and N. A. Shishakov, J. Phys. Chem., 25, 381 (1951).
- [14] D. J. Macnaughtan and A. W. Hotherhall, Trans. Far. Soc. 24, 497 (1928); 387 (1928); D. J. Macnaughtan and R. A. F. Hammond, Trans. Far. Soc. 26, 481 (1930); 27, 633 (1931); A. K. Gardam and D. J. Macnaughtan, Trans. Far. Soc. 29, 753 (1933).
- [15] N. I. Stepanov, Bull. Acad. Sci. USSR, 8, 1395 (1914); M. Lettanc and K. Schick, Z. phys. Chem. 46, 213 (1903); Z. Elektrochem. 16, 25 (1910).

* See Consultants Bureau translation, p. 1025

** See Consultants Bureau translation, p. 2-1.