EFFECT OF IODIDE IONS ON THE KINETICS OF THE DISSOLUTION OF NICKEL IN ACID ELECTROLYTE SOLUTIONS

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The kinetics of the dissolution of nickel in acid sulfate solutions containing potassium iodide were studied by means of polarization and adsorption measurements.

We studied the retarding action of iodide ions on the anodic dissolution of nickel in solutions of $(1-x)$ N K_2SO_4 + x N H_2SO_4 with various pH values. This action was characterized by a retardation factor T_d equal to the ratio of the dissolution rates (at each specified potential) before and after introducing traces of KI. In the same experiments we measured the adsorption of the iodide ions on the nickel surface radiometrically over a wide range of potentials (by reference to the loss of iodine, indicated by the amount of the radioisotope I^{131} in the solution).

The electrodes, with a visible surface of 25 cm^2, were made from nickel of the NO type, rolled into strip 0.1 mm thick. The methods of initially cleaning the surface of the electrodes and preparing and purifying the solutions were exactly the same as described earlier [1]. Before the measurements the electrodes were usually subjected to cathodic polarization for an hour. In one series of experiments the measurements started immediately after immersing the electrodes in the solution. All the measurements were carried out in an atmosphere of purified nitrogen at room temperature (25°).

RESULTS AND DISCUSSION

The addition of KI retards the anodic dissolution of nickel over a wide range of potentials, including both the region corresponding to an active state of the metal surface and the region of passivation (Figs. 1 and 2). Over the same wide potential range iodide ions are adsorbed on the nickel (Fig. 3). The extent of the observed effects depends greatly on the potential. A displacement of the potential in the positive direction (away from the stationary value) is accompanied first by a rise and then by a fall in both the adsorption Γ and also the retarding factor of the dissolution process. It is also an important point that the position of the maximum on the $\varphi - \Gamma$ and $\varphi - T_d$ curves in each case exactly corresponds to the potential representing the onset of passivation * for nickel in a pure sulfate solution with the same pH. Thus, in the regions respectively corresponding to the active and passive states of the nickel surface, the I^- ions have very different effects on the kinetics of the dissolution process. For this reason the effects typifying each of these regions will be considered individually.

Region Corresponding to the Active State. For a constant pH and sulfate concentration, the retarding factor T_d increases with the concentration of KI; this appears as a displacement of the polarization curve in the direction of positive potentials. However, this kind of displacement only occurs until we reach a certain particular concentration of KI, roughly equal to $1 \cdot 10^{-4}$ N. Further raising the concentration fails to increase the retarding effect any more.

The addition of KI to the sulfate solution also leads to a rise in the slope of the polarization curve, from 33 to 83 mV. This fact should indicate a rise in T_d with increasing potential. The relation between these quantities may be expressed by the equation

$$\varphi = a + \mu \lg T_d, \quad (1)$$

where a and μ are constants.

* We are considering the potential corresponding to the first current-density maximum.

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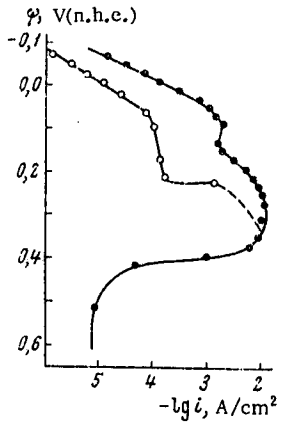

Fig. 1. Anodic polarization curves obtained for nickel in solutions: ●) 1.0 N H_2SO_4; ○) 1.0 N H_2SO_4 + $5 \cdot 10^{-6}$ N KI.

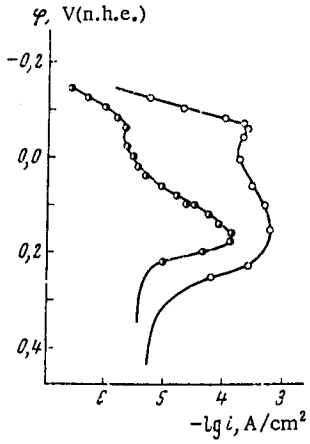

Fig. 2. Anodic polarization curves obtained for nickel in solutions: ○) 0.01 N H_2SO_4 + 0.99 N K_2SO_4; ◑) the same + $5 \cdot 10^{-6}$ N KI.

Considering the rise in the adsorption of I^- with potential observed in this region (Fig. 3), it would be natural to suppose that the observed rise in T_d was entirely due to the increase in the degree of coverage of the surface with these ions. However, this supposition is not supported by the results of Fig. 4, in which the horizontal axis indicates the potential and the vertical indicates the ratio of the degree of retardation to the adsorption for each specified potential. We see that this ratio, which would remain constant if the supposition in question were valid, in actual fact rises regularly with potential, reaching a maximum at the passivation potential.

In order to understand the mechanism responsible for this effect of the iodide ions, it is particularly important to consider that, in the presence of these ions, the relation between the velocity of the process and the pH value changes substantially. For a constant sulfate concentration, the effect of pH on this velocity in pure sulfate solutions only appears at pH > 2,* while in solutions containing $5 \cdot 10^{-6}$ N KI it appears at pH > 3.2. Any increase in pH above the values indicated increases the velocity of the reaction, the relationship between these quantities being expressed (in semilogarithmic coordinates) by a straight line, the slope of which depends substantially on both the method of previously treating the surface of the metal and also the presence of KI in the solution (Fig. 5). For pure sulfate solutions and electrodes not subjected to preliminary cathodic polarization, this slope is approximately 1.65.† Preliminary cathodic polarization of the electrode reduces the slope to 1.36. In the presence of $5 \cdot 10^{-6}$ N KI in the solution the slope falls to 0.70.

It follows from these data that, under the conditions envisaged (pH > 2), the inhibiting action (T_d) of the iodide ions on the anodic dissolution of nickel increases with increasing pH of the solution. Considering that a rise in pH is accompanied by an appreciable reduction in the adsorption of the iodide ions on the nickel (Fig. 3), we may conclude that for higher pH a smaller quantity of adsorbed iodide ions has a stronger inhibiting action.

A transition from solutions with pH > 2 to solutions with pH < 2 is accompanied by a sharp fall (over ten times) in the maximum degree of retardation, referred to the same degree of coverage of the surface

* This result agrees excellently with the data of V. I. Kravtsov and Yang-P'ien-Chao [2]. Working with heat-treated electrolytic nickel and sulfate solutions of the same (1.0 N) concentration, these authors showed that the dependence of the rate of dissolution on pH only started from pH 2.3.

† This result agrees closely with the recently-published data of Heusler [3], according to which, in acid solutions of perchlorates, the order of the reaction (nickel dissolution) equals 1.75 with respect to the OH^- ions. At the same time, according to the results of Kravtsov and Yang-P'ien-Chao and also Sato and Okamoto [4] obtained in sulfate solutions, this quantity is close to unity.

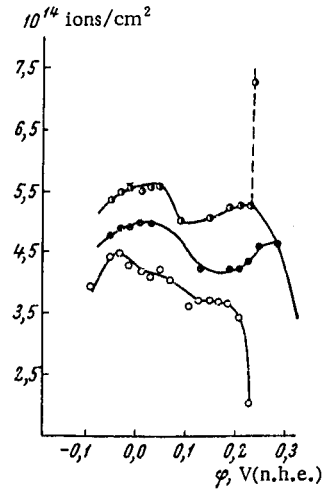

Fig. 3. Adsorption of iodide ions as a function of potential in solutions with different pH: ◑) 0.4; ●) 2.1; ○) 2.2.

with adsorbed iodide ions (Fig. 4). This difference in the effectiveness of the inhibiting action of the iodide ions in solutions with pH > 2 and pH < 2 is evidently associated with the different mechanisms responsible for the dissolution of nickel in acid and weakly acidic sulfate solutions respectively. The observed dependence of the rate of dissolution on pH naturally leads to the conclusion that, in weakly acidic solutions (pH > 2) the process involves the direct participation of OH^- ions. However, since the volume concentration of OH^- ions in the pH range under consideration is low, we must assume that a dissociative adsorption of H_2O molecules may take place on the surface of the nickel [5]. This kind of adsorption is due to the chemical affinity between the surface atoms of the metal and the oxygen of the water. However, this is not equivalent to a discharge of OH^- ions, as some authors appear to think [4, 6-8]. We may suppose that only a certain proportion (σ) of the charge of each adsorbed ion is transferred to the metal, while the remainder ($1-\sigma$) is retained on the surface complex so formed and hence in the compact part of the double layer.

Considering the foregoing arguments and (to a first approximation) assuming the independence of σ of the potential, the mechanism of the process may be represented thus:

$$Ni + uH_2O \rightleftarrows Ni(OH)_u^{-(1-\sigma)u} + uH^+ + u\sigma e \quad (2)$$

$$Ni(OH)_u^{-(1-\sigma)u} \rightleftarrows Ni(OH)_u^{[1-(1-\sigma)u]} + e \quad (3)$$

$$Ni(OH)_u^{[1-(1-\sigma)u]} \rightarrow Ni(OH)_u^{+(V-u)} + (V - \sigma u - 1)e \quad (4)$$

$$Ni(OH)_u^{+(V-u)} + uH^+ \rightleftarrows Ni^{+V} + uH_2O. \quad (5)$$

In accordance with the laws of electrochemical kinetics we must write the following for the velocity of the limiting stage (4)

$$i = K_1[Ni(OH)_u^{[1-(1-\sigma)u]}] \exp\left[\frac{(V - \sigma u - 1)F\beta}{RT}\varphi\right]. \quad (6)$$

It follows from the equilibria (2) and (3) that

$$[Ni(OH)_u^{[1-(1-\sigma)u]}] = K_2[H^+]^{-u} \exp\left(\frac{(\sigma u + 1)F}{RT}\varphi\right). \quad (7)$$

Substituting (7) in (6) we obtain:

$$i = K_3[H^+]^{-u} \exp\left\{\frac{[\sigma u(1-\beta) + \beta(V-1) + 1]F}{RT}\varphi\right\}^{*} \quad (8)$$

Qualitatively this equation correctly represents the observed dependence of the rate of dissolution on pH. However, the equation fails to explain certain leading aspects of the kinetics, in particular the fractional order of the reaction with respect to H^+ ions. A satisfactory explanation of this feature may very well be secured on allowing for the inhomogeneity of the surface of the dissolving solid metal.

It follows from Eq. (8) that the slope (b_a) of the straight line indicated is a function not only of the transfer coefficient β and the temperature but also of the values of u and σ. Only in the limiting case, i.e., when $\sigma \to 0$, will this effect of u and σ be absent and will the slope b_a have a maximum value.

* The σ in Eqs. (2) to (8) may be calculated from the relation: $\frac{2.303 \cdot RT}{F[\sigma u(1-\beta) + \beta(V-1) + 1]} = b_a$. In our case b_a = 33 mV, V=2.00, and u=1.36. Thus we obtain $58/(1.5 + 0.68\sigma) = 33$. Hence $\sigma \simeq 0.383$.

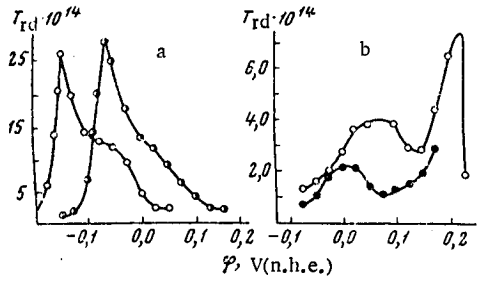

Fig. 4. Degree of retardation, reduced to the same degree of coverage (T_{rd}), for solutions of 1 N H_2SO_4 + $5 \cdot 10^{-6}$ N KI with different pH: a) ◑) pH 3; ○) pH 4; b) ◠) pH 0.4; ●) pH 2.

Physically the quantity σ should characterize the strength of the adsorption bond in the transitional complex. Judging from available published data, mainly obtained when studying the adsorption of anions on metals, this strength depends greatly on time [9, 10]. As a rule, a long time is required for the strength of the adsorption bond to reach a steady value. Hence the value of σ and consequently the slope of the straight line in question should depend substantially on the rate of taking the polarization measurements. Evidently a change from rapid to slow measurements should be accompanied by a sharp rise in σ, and this should appear as a reduction in the slope of the straight line.

According to many published results and also the results of our own measurements, this conclusion agrees closely with experimental observations, both for nickel and for other metals. This kind of change in b_a clearly cannot be explained by an increase in the true surface of the metal as the period of measurement increases (attempts have been made to do this) [2, 11].

The mechanism under consideration [(2) to (8)] is clearly not the only one possible. It may nevertheless be asserted that in 1.0 N sulfate solutions with pH > 2 the dissolution of nickel is effected predominantly by way of chemical-adsorption interaction with water molecules. The action of the iodide ions is evidently associated with the displacement of reactive $Ni(OH)_u^{-(1-\sigma)u}$ particles from the surface. In the potential range considered we can hardly expect dissolution of the nickel involving the participation of I^- ions, in view of the increase in T_d with rising [KI].

The position changes on passing to acid solutions (pH < 2). The absence of any pH effect in this case indicates that the rate of dissolution by the mechanism under consideration becomes lower than that attributable to other mechanisms. As shown earlier [1], the rate of dissolution of nickel in acid solutions depends greatly on the sulfate concentration. We may suppose that in this case the dissolution of the nickel is affected mainly by way of chemical-adsorption interaction with the SO_4^{2-} ions. The experimentally observed fall in the inhibiting action of iodide ions on passing to acid solutions is evidently associated with the fact that, on adsorption at low pH, these compete less effectively with the SO_4^{2-} than with the OH^- ions.

Passivation Region. The appearance of a sharp maximum (Fig. 4) on the $T_d - \varphi$ curves is apparently a result of the fact that, on reaching a certain potential, the oxygen in the water starts taking part in retarding the dissolution process, in addition to the iodide ions. The deposition of passivating oxygen is accompanied by a certain slight desorption of iodide ions, as indicated by the weak maximum on the $\Gamma - \varphi$ curves (Fig. 3), coinciding in potential with the maximum on the $T_d - \varphi$ curves. It is a characteristic feature that these potentials practically coincide with the passivation potential determined from the polarization curve in a pure sulfate solution with the same pH. This means that the presence of iodide ions in the solution has no effect on the potential corresponding to the onset of nickel passivation by the oxygen in the water. It is important to note, however, that in weakly-acidic solutions (pH > 2) the retarding effect of the iodide ions weakens on further raising the potential, and the rate of nickel dissolution approaches still closer to the values characteristic of pure sulfate solutions. This fall in T_d is not associated with the desorption of the iodide ions. As indicated by Fig. 3, the adsorption of these ions remains practically constant over quite a wide range of potentials, lying to the positive side of the potential representing the onset of passivation. It follows from this that, as the potential increases and the Ni–O bond becomes stronger, the retarding effect passes all the more to the oxygen. Appreciable (almost complete) desorption of the iodide ions is only found in this case on approaching the region of stable passivation. It is a characteristic feature that this desorption is not accompanied by a rise in the rate of dissolution.

A different picture arises in acid solutions. As indicated by Fig. 4b, in this case there is a reduction in the retarding action of the iodide ions over a very narrow potential range as the potential moves in the positive direction from $\varphi_{\text{onset pass.}}$; on the positive side of this, T_d again starts rising and then falls sharply. This rise is evidently associated with the fact that the presence of iodine in the passivating layer prevents the penetration of SO_4^{2-} ions (which accelerate dissolution in acid sulfate solutions) into this layer.

TABLE 1

KI concentration (N)	mV (n.h.e.)
$5 \cdot 10^{-6}$	+212,5
$1 \cdot 10^{-5}$	+265
$1 \cdot 10^{-4}$	+345
$1 \cdot 10^{-3}$	+397

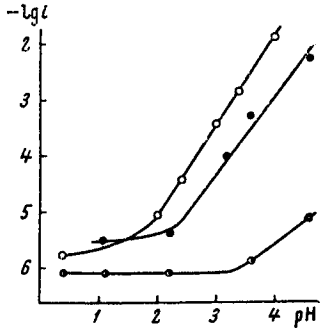

Fig. 5. Rate of dissolution of nickel as a function of pH for $\varphi = -0.025$ V in sulfate solutions with $[SO_4^{2-}] = 1$ N: ○) without cathodic polarization; ●) with previous cathodic polarization; ◑) in the presence of $5 \cdot 10^{-6}$ N KI.

On the other hand, the ensuing sharp fall in the retarding effect of the iodide ions, coinciding in potential with the beginning of the nonpolarizability region, is associated with a sharp rise in the rate of dissolution of the nickel.

We see by comparing the curves in Figs. 1, 3, and 4 that the onset of nonpolarizability and the sharp fall in the retarding action of the I^- ions is accompanied by a considerable increase in the adsorption of these ions (Fig. 3, broken line). However, this effect is only observed if the adsorption curve is measured slowly; on taking the curve rapidly a sharp reduction in the retarding effect is accompanied by an equally sharp desorption of the iodide ions (continuous line in the same figure). From this we may conclude that the increase in the adsorption observed on slow measurement is due to the sorption of the iodide ions by nickel dissolution products.

Judging from the results of our own investigations and the data of other research workers [12, 13], the appearance of a region of nonpolarizability, characterized by a sharp rise in the dissolution rate on reaching a certain potential (φ_0), is one of the most important features characterizing the action of iodide ions on the anodic behavior of iron-group metals. Our experiments show that the value of φ_0 depends both on the concentration of iodine and on the concentration of sulfate. As indicated by Table 1, for constant pH and sulfate concentration (0.4 and 1.0 N respectively), a rise in the KI content is accompanied by a systematic displacement of φ_0 in the positive direction. The relation between these two quantities may be represented as follows:

$$\varphi_0 = 0.1 \lg ([KI] - K) \quad \text{for} \quad K = 4.7 \cdot 10^{-6}$$

A rise in the sulfate concentration for constant pH and KI content has the opposite effect, i.e., it displaces φ_0 in the negative direction. Visual observations also showed that, at a potential of φ_0, the dissolution of the nickel was accompanied by pitting corrosion.

The existance of a connection between the sharp rise in the rate of dissolution and the desorption of iodide ions gives grounds for supposing that this kind of desorption is an intrinsic and necessary condition for the activation of the surface. However, this condition is not sufficient, since desorption may also be related to the passivation of the surface, as indicated by the data presented.

We may thus conclude that the desorption of iodide ions only leads to the freeing and depassivation of individual, microscopic parts of the metal surface, and that the subsequent fate of these regions depends on the acidity of the solution. In weakly acidic solutions these parts are again passivated quite rapidly by the oxygen of the water; this leads to less sharply expressed activation. In acid solutions, however, where this kind of passivation takes place more slowly, pitting is able to develop on the more active parts. The observed dependence of φ_0 on the concentration of the sulfate suggests that the SO_4^{2-} ions take a direct part in the generation, development, and steady-state functioning of the pitting corrosion.

CONCLUSIONS

On the basis of polarization measurements we have studied the kinetics of the anodic dissolution of nickel in sulfate solutions with various acidities and various KI contents. At the same time we have determined the adsorption of iodide ions under the same conditions, using the T^{131} isotope.

The results obtained may be explained on the basis of the chemical-adsorption interaction of the components of the solution, and also the possibility that these may transfer some of their charge to the electrode metal. In this connection, the inhibiting action of the iodide ions may be explained by the face that these dislodge the activating ions, while the development of a region of nonpolarizability on the electrode may be explained as being due to the effects of pitting, in the generation and development of which the sulfate ions play a direct part.

LITERATURE CITED

1. G. G. Lopovok, Ya. M. Kolotyrkin, and L. A. Medvedeva, Zashchita Metal., 2, No.5 (1966).
2. V. N. Kravtsov and Yang-P'ien-Chao, Vestn. Leningr. Gos. Univ., No.10 (2), 107 (1962).
3. K. E. Heusler and Kaiser, Electrochim. Acta, 13, 59 (1968).
4. N. Sato and Y. Okamoto, J. Electrochem. Soc., 111, 897 (1964).
5. K. A. Christiansen, Acta Chem. Scand., 15, 1 (1961).
6. K. E. Heusler, Z. Elektrochem., 62, 582 (1958).
7. J. O'M. Bockris, D. Drazic, and A. R. Despic, Electrochim. Acta, 4, 325 (1961).
8. K. E. Heusler, Z. Elektrochem., Ber. Bunsenges. Phys. Chem., 66, 177 (1962).
9. Ya. M. Kolotyrkin and L. A. Medvedeva, Dokl. Akad. Nauk SSSR, 140, 168 (1961).
10. N. A. Balashova and V. S. Kazarinov, Élektrokhimiya, 1, 512 (1965).
11. M. L. Kronenberg, J. Banter, E. Geager, and A. Hovorka, J. Electrochem. Soc., 110, 1007 (1963).
12. Z. A. Iofa and Pei-Pao-Ming, Zh. Fiz. Khim., 37, 230 (1963); Z. A. Iofa and E. N. Mikhailova, Elektrokhimiya, 1, 107 (1961).
13. K. E. Heusler and G. H. Gartledge, J. Electrochem. Soc., 108, 732 (1961).