ELECTROCHEMICAL AND CORROSION BEHAVIOR OF NICKEL IN SOLUTIONS OF SULFURIC AND PERCHLORIC ACIDS

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It was found in [1] that in electrolytes consisting of sulfuric acid containing oxidizing agents, nickel dissolves locally if its potential is maintained within a narrow range between the potential of active dissolution and the potential of the stable passive state. It was important to obtain more complete data on the mechanism of the anodic process within this range of potentials and in particular to determine whether the pitting is due specifically to the oxidizing agents.

METHOD OF INVESTIGATION

Polarization curves of nickel electrodes in solutions of sulfuric and perchloric acids were obtained by the galvanostatic and potentiostatic methods, using the electron potentiostat described in [2]. The curves were obtained under constant conditions and also under accelerated conditions. The electrodes were thin plates which were polished with sand paper, degreased with ethyl alcohol, and rinsed in bidistilled water. Measurements were made at room temperature in a three-electrode cell separated by stopcocks in an atmosphere of purified nitrogen. Nitrogen was also used to mix the solution prepared from bidistillates and acids which were distilled three times. The potentials were measured with respect to a reversible hydrogen electrode in the same solution and then were recalculated with respect to a normal hydrogen potential. We used pure nickel (Hilger), as in [1], and also samples of less pure N-0 nickel (99.99% Ni).

We used successive doubling of the polarizing current to draw the galvanostatic curves in the direct and reverse directions.

EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

In the potentiostatic method the polarization curve for spectrally pure nickel has the shape shown in Fig. 1.

In our experiments the occurrence of the characteristic section CD is facilitated by preliminary cathodic and, particularly, alternating anodic and cathodic polarization of the electrode.* With electrodes kept for some time in the state of maximum passivation, the CD section of the curve could be observed only when measurements were made very slowly. Otherwise, the direct and the reverse branches of the curves made a wide hysteresis loop within this section of the curve (Fig. 2, curves 1 and 2).

In the case of the galvanostatic method of measurements (Fig. 3) the electrode potential reaches the value of +0.130 V and is then rapidly displaced toward more positive values. For electrodes oxidized in air (curve 1) or kept before the measurement in the state of anodic passivation (curve 3) this increase in the potential ceases only when overpassivation sets in (section FG in Fig. 1); with electrodes subjected to long preliminary cathodic polarization or alternating cathodic and anodic polarization between +0.230 and +0.330 V a second Tafel section (LM), corresponding to the second ascending branch of the potentiostatic curve, occurs on the galvanostatic curves (see curves

*Potentiostatic curves with two peaks were obtained also in [3].

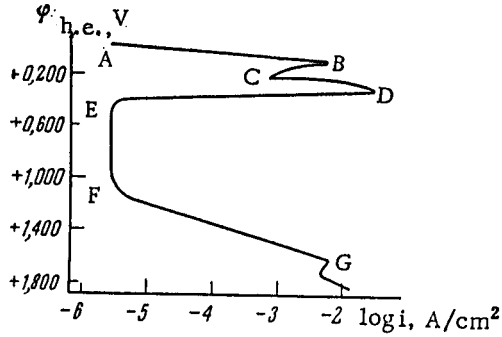

Fig. 1. Steady potentiostatic curves for spectrally pure nickel in 1 N H_2SO_4.

2 and 4 in Fig. 3). In this range of potentials the dissolution is local. When a constant current density is maintained there is spontaneous displacement of the potential toward negative values and an increase of the area of pitting. At the end a steady state is reached (curve 6) and the whole surface becomes bright, although there are traces of local dissolution.

The comparison of the results obtained in this investigation with those obtained earlier [1] showed that the LM section corresponds to the second linear sections of curves characterizing the relationship between the potential and the concentration of such oxidizing agents as chromates and hydrogen peroxide. Dissolution is local along this section, which indicates that the oxidizing agents have no specific effect on the dissolution even in the regions of the occurrence of pitting.

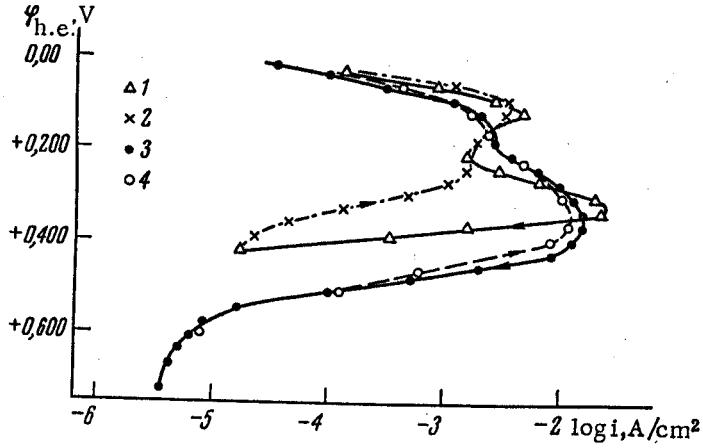

Fig. 2. Potentiostatic curves obtained in 1 N H_2SO_4 with the sample kept at each successive potential (intervals of 30 mV) for 10 min. 1,2) Spectrally pure nickel (decreasing and increasing the potential); 3,4) same with N-O nickel.

At more negative potentials corresponding to the active state, the preliminary treatment of the electrode also has a significant effect on the kinetics of dissolution at the beginning. After the electrode is kept in the passive region it dissolves much easier at the first moment than after oxidation in air; after prolonged cathodic polarization, and particularly after alternating polarization, the rate of dissolution becomes much lower (Fig. 3). This difference disappears, however, with time. According to [4], the slope of the steady curve 5 (Fig. 3) is 0.035 V. The slopes of rapid curves vary from 0.095 to 0.060 V at low current densities to 0.070-0.040 V at high current densities. The steady state was reached after a few hours in the case of weak polarization and after a few minutes after strong polarization. After prolonged cathodic polarization of some electrodes at current densities of the order of 10^{-3} A/cm² the potential jumps toward negative values (point N in Fig. 3) or oscillates; oscillation corresponds to the transition between the prolongation of the first IK branch and the second LM branch of the galvanostatic curve.

Preliminary treatment of the electrode has a similar effect on the position and the shape of polarization curves within the active region also in solutions of perchloric acid (Fig. 4). However, with spectrally pure nickel there is no second linear section on galvanostatic curves in this case and, correspondingly, no second maximum on the potentiostatic curves, i.e., the electrode is passivated in one stage. In this acid, the history of the electrode affects also the value of the critical passivation current. Electrodes oxidized in air or kept for a certain time in the passive region (3) were passivated by a current of $5\text{-}6 \cdot 10^{-3}$ A/cm², while the electrodes which were subjected to preliminary cathodic polarization were passivated by a current of $2.5 \cdot 10^{-4}$ A/cm². In $HClO_4$ no pitting occurred.

During cathodic polarization in solutions of the two acids the hydrogen overvoltage increases. On electrodes oxidized in air this process is very slow (at a current density of $2.5 \cdot 10^{-3}$ A/cm² the potential rises 100 mV in 20 h).

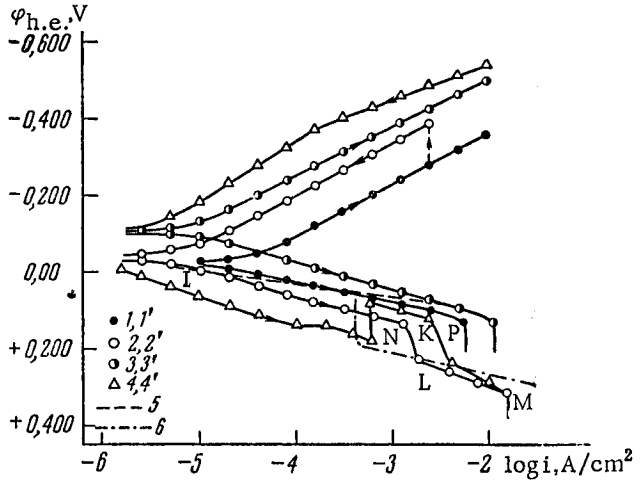

Fig. 3. Rapid anodic and cathodic galvanostatic curves for spectrally pure nickel in 1 N H_2SO_4 immediately after: 1,1')immersion of the freshly cleaned electrode in the solution; 2,2') after cathodic polarization with a current of $2.5 \cdot 10^{-3}$ A/cm^2 for 20 h;3,3') after being kept in the region of maximum passivation; 4,4') after anodic and subsequent cathodic polarization; 5) steady potentiostatic curve; 6) steady galvanostatic curve obtained after prolonged anodic polarization with a current of $8 \cdot 10^{-3}$ A/cm^2.

On electrodes subjected to preliminary anodic polarization the shift is more rapid and greater (up to 150 mV after a few minutes). Subsequent cathodic polarization of these electrodes leads to further increase of the overvoltage by about 50 mV.

The electrochemical and corrosion behavior of N-O nickel is somewhat different from that of the spectrally pure nickel, and the nature of the acid has much less effect. Potentiostatic curves corresponding to N-O nickel in sulfuric (Figs. 2, 3, and 4) and perchloric acids (Figs. 4 and 6) have two peaks separated by regions of low passivation. There is no hysteresis (Fig. 2) with N-O nickel in perchloric or sulfuric acids and no pitting corrosion is visible.

The analysis of the results obtained shows, first of all, that the observed nonsteady effects, their irreversibility, the jumps of potentials, and the oscillation of the potentials are the result of the presence of adsorption processes which have a significant effect on the kinetics of electrode reactions. In particular, the increase of the dissolution rate after the electrode is kept in the region of maximum passivation (curves 3 in Figs. 2 and 3) is due, as was shown for many other metals [5-8], to the activating effect of oxygen within the region of active dissolution. However, the activating effect of oxygen is manifest only within a rather narrow range of potentials. In the BC region close to the equilibrium potential of the formation of NiO, oxygen already has a passivating effect, which sharply decelerates the anodic process within the region of maximum passivity.

It is difficult to imagine that the increase of the dissolution rate with increasing potential within the region between active dissolution and the maximum passive state (section CD) is due to some new manifestation of the activating effect of oxygen. The strong dependence of the behavior of nickel over the CD section on the composition of the solution, the purity of the metal, and its preliminary electrochemical treatment leads us to assume that the activation of the anodic process within this range of potentials is the result of adsorption of anions which prevent the addition of passivating oxygen or the expulsion of it from the surface. The results obtained in [9] can be interpreted in the same way. According to these results, the capacitance of the nickel electrode in a sulfuric acid solution increases within the potential range corresponding to the CD section. The possibility of the elimination of oxygen from the surface by the anions is determined by the adsorbability of anions and the properties of passivating oxides. We may assume that in the case of N-O nickel the oxide formed is a less effective passivator because of the impurities present and in this case oxygen can be expelled from the surface by adsorption of SO_4^{--} and ClO_4^- ions. In the case of spectrally pure nickel, the ClO_4^- ions cannot prevent the addition of passivating oxygen or, even less, the expulsion of it from the surface.* According to these assumptions, curve 6 in Fig. 3 corresponds to complete expulsion of oxygen by the SO_4^{--} ions. It is intereresting that this curve is the prolongation of curve 4, which is characterized by the highest overvoltage of the anodic process within the region of active dissolution. Therefore, we may assume that the surface state of the electrode is the same in both cases, i.e., curve 4 in Fig. 3 characterizes the dissolution in the presence of adsorbed anions in sulfuric and in perchloric acids. The effect of cathodic polarization and the alternating and cathodic polarization which are responsible for the CD section in Fig. 2 and curve 4 in Fig. 3 is apparently due to the elimination of the oxide film formed in air, which prevents the adsorption processes [10-13].

*It is also possible that the observed singularities of the two types of nickel investigated are due to structural differences resulting from the difference in the techniques used to prepare them.

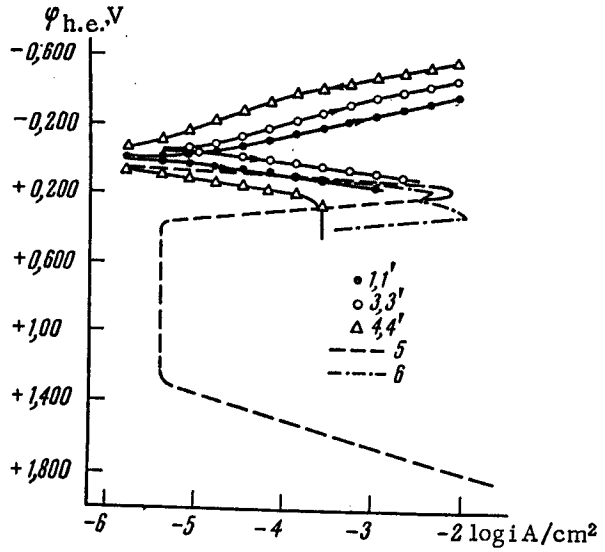

Fig. 4. Rapid anodic and cathodic galvanostatic curves obtained in 1 N H_2SO_4 with spectrally pure nickel immediately after: 1,1') the immersion of freshly cleaned electrode in the solution; 3,3') after being kept in the region of maximum passivation; 4,4') after anodic and subsequent cathodic polarization. The steady potentiostatic curves were obtained with spectrally pure nickel (5) and with N-O nickel (6).

The results obtained allow us to assume also that in the presence of adsorbed SO_4^{--} and ClO_4^- ions (curves 3' and 4' in Figs. 3 and 4) the overvoltage of hydrogen evolution increases, as was observed for iron [14-16] and cobalt [17] in the case of halogen ions.

In our experiments pitting occurred only on spectrally pure nickel (result which agrees with that in [18]) in that region of potentials where the adsorption of SO_4^{--} and passivating oxygen are possible. It follows, then, that the dissolution is local only when there are simultaneously areas of the surface coated with anions and oxygen, which are effective decelerators of the anodic process.

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