PASSIVATION OF NICKEL IN SOLUTIONS OF SULFURIC ACID

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As was shown previously [1], the passivation of nickel in 1 N sulfuric acid takes places in two stages observed at potentials of +0.110 — +0.230 V (first stage) and above +0.330 V (second stage). In the region of +0.230—+0.330 V there is an increase in the rate of dissolution with potential, characteristic for the active state of the metal (second region of active dissolution).

With the aim of explaining the nature of such a stage-by-stage passivation, in the present work we examined the effect of the pH of the solution on the potential of passivation using a potentiostatic method, and also determined the relationship between the change in potentials and time at polarizations with a constant current and after switching off the anodic polarization.

All the measurements were carried out with spectrographically pure nickel grade "Khil'ger," rolled in the form of thin plates. The instrument and the conditions for the experiment were the same as in the preceeding investigations. The potential was measured by a cathodic voltmeter with a high input resistance and was recorded with the help of an ÉPP-09 potentiometer supplied with a cathodic attachment with a high input resistance. Polarization measurements were carried out in solutions of $H_2SO_4 + K_2SO_4$ with $[SO_4^{--}]$ equal to 1 N, the pH of which changed from 0.3 to 3.85. These measurements, beginning immediately after immersing the electrode in the solution, were carried out with stepped displacement of potential towards the positive side (every 30 mV), staying at each potential for 3 min. In the data given below, the potential is relative to the normal hydrogen electrode.

As can be seen from Fig. 1, an increase in pH is accompanied by a marked decrease in the overpotential of the anodic dissolution of nickel in the active state. The relationship between these values is linear with a gradient $[d\varphi/dpH_i]$ equal to approximately 0.03 V with $i = 1 \cdot 10^{-3}$ A/cm^2. This result, indicating the direct participation of the hydroxyl groups in the anodic process, is in agreement with

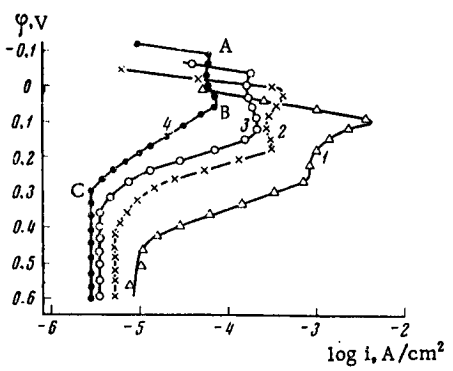

Fig. 1.

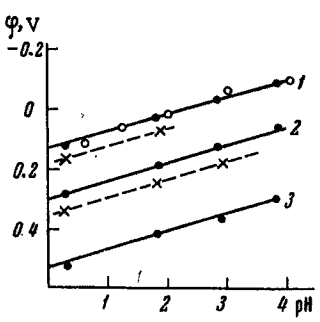

Fig. 2.

Fig. 1. Potentiostatic curves obtained in the following solutions: 1) 1 N H_2SO_4; 2) 0.1 N H_2SO_4 + 0.9 N K_2SO_4; 3) 0.01 N H_2SO_4 + 0.99 N K_2SO_4; 4) 0.001 N H_2SO_4 + 0.999 N K_2SO_4.

Fig. 2. Relationship of the potentials of the first (1) and the second (2) maxima in the potentiostatic curves and the beginning of the region of maximum passivity (3) with pH, ×) data of Arnold and Vetter [4]; ⊙) data of Osterwald and Uhlig [5].

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other investigators [2, 3]. From a comparison of the curves obtained with the stationary curve reported previously [1], it can be seen that, with increase in rate of carrying out the measurements, the length of the second region of active dissolution is decreased. However, even when the electrode is held at each potential for a short time, two maxima can be distinguished on the potentiostatic curves and, correspondingly, two critical potentials which correspond to the first and second stages of passivation (points A and B). An increase in pH results in a displacement of these critical potentials towards more negative values, as in the case of the potential corresponding to the beginning of the region of maximum passivity (point C). The relationship between these potentials and pH (Fig. 2) is characterized by straight lines with a gradient of about 0.06 V, which, for potentials at points A and B, is in good agreement with results of other investigators [4, 5].

The potentials of the points A, B, and C with pH 0, obtained by extrapolation of curves in Fig. 2, are +0.13, +0.30, and +0.53 V, respectively.

A comparison of these values with the thermodynamic potentials for the formation of the well-known oxides of nickel from metal and water (E°_{NiO} = 0.110, $E^{\circ}_{Ni_3O_4}$ = 0.307, $E^{\circ}_{Ni_2O_3}$ = 0.418, and $E^{\circ}_{NiO_2}$ = 0.670 V)* enables us to propose that the first retardation in the anodic process is connected with the formation of NiO, the second with Ni_3O_4, and in the region of maximum passivity, it may be expected that the oxides would be formed with a higher oxygen content. The amount of these oxides right up to the region of maximum passivity obviously does not correspond to complete coverage of the surface. They are probably of an adsorptional character. In addition to oxygen on the surface, ions of $SO_4^{\prime\prime}$ may also be found, and in the second region of the active dissolution, as was noted previously [1], displacement of oxygen adsorbed in the region of more negative potentials by the $SO_4^{\prime\prime}$ ions takes place. The displacement of oxygen by $SO_4^{\prime\prime}$ ions obviously occurs very slowly which also results in the fact that this region, where dissolution occurs with the participation of $SO_4^{\prime\prime}$ ions, becomes sharply expressed only when the measurements are carried out slowly.

Thus, the stage-by-stage passivation of nickel can be observed, thanks to the adsorption of $SO_4^{\prime\prime}$ ions which retards the complete passivation of the electrode displacing it to a more positive potential.

The charge curves were recorded in 1 N sulfuric acid on freshly prepared electrodes and on electrodes subjected to preliminary cathodic and anodic polarization. In the first case, the polarization by a current of constant density began immediately after immersing the electrode in the solution. In the second case it began after cathodic polarization for times of from several minutes to 20 h. In the third case, the measurements began after stopping the preliminary anodic polarization and establishing the stationary potential (– 0.05 to – 0.15 V).

As was noted earlier [9], $(\varphi\text{-}t)_i$ curves (Fig. 3) are characterized by the presence of two sharply expressed steps in the potentials (AB the first; CD the second), the position and length of which depend markedly on the prehistory of the electrode and the value of the polarizing current. An increase in the time of cathodic polarization –in particular, alternate cathodic and anodic polarization –is accompanied by a decrease (curve 2) and afterwards by a complete disappearance (curve 4) of the first step with, at the same time, an increase in the second. During this, the first step is displaced in the direction of more positive, and the second, more negative, potentials. The opposite effect is caused by preliminarily holding the electrode in the passive state. As can be seen from the figure (curve 3), such a treatment results in the disappearance of the second step with simultaneous displacement of the first in the direction of more negative potentials. On the curves taken immediately after immersion of freshly cleaned electrodes in the solution, both the steps are present although they are less clear.

Figure 4 gives the mean potentials of the linear parts of the $(\varphi\text{-}t)_i$ curves in the regions of the steps (in relation to the logarithm of the corresponding values of i) and the rapidly recorded polarization curves. As can be seen, the points corresponding to the first step fall on the curve III (points 3-6) or a continuation of the first part of curve II (points 1, 2) characterizing the relationship of the anodic process in the presence of adsorbed oxygen. The second step corresponds to the lower part of the polarization curve II, appearing as a result of adsorption of $SO_4^{\prime\prime}$ ions.

*The following values for free energy were used during the calculations [6]: NiO 51300, Ni_3O_4 170150, Ni_2O_3 112270, NiO_2 51420, H_2O 56690 cal.

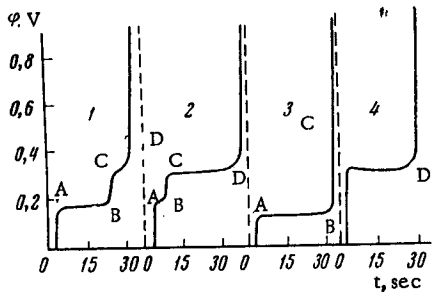

Fig. 3. Charge curves obtained in 1 N H_2SO_4: 1) freshly cleaned electrode cathodically polarized for 45 min; $i_A = 1.12 \cdot 10^{-2}$ A/cm^2; 2) after passivation, polarization for 30 min, $i_A = 1.2 \cdot 10^{-2}$ A/cm^2; 3) held at +0.500 V for 2.5 h and afterwards the current was switched off and, after displacement of the potential to – 0.087 V, the anodic polarization was again switched on, $i_A = 1.06 \cdot 10^{-2}$ A/cm^2; 4) after four passivations, cathodically polarized for 20 h, $i_A = 1.2 \cdot 10^{-2}$ A/cm^2.

According to the shape of the polarization curves, during an increase in polarizing current, there occurs a displacement of the steps in the direction of positive potentials (points 3-6).

Data on the extent of the steps have fairly poor reproducibility. Thus, the quantity of electricity necessary for carrying out complete passivation of the electrode at $i \approx 1 \cdot 10^{-2}$ A/cm^2 was from 0.05 to 2.8 C/cm^2.

The charge curves in the studied system can therefore be used neither for determining the quantity nor for explaining the nature of the oxides which form, because in the regions of the steps, the electricity is consumed mainly in the process of dissolution. The appearance of two steps may be interpreted as the result of the presence on the surface of the nickel of two types of regions unequal in relation to adsorption on them of oxygen and SO_4'' ions and dissolving correspondingly by different mechanisms. The preliminary cathodic and, particularly, the alternate cathodic and anodic polarization obviously favors the appearance of the regions where the preferential adsorption of SO_4'' ions takes place, resulting in an increase in the overpotential for the evolution of hydrogen (curve IV, point 2'' on Fig. 4), while preliminary holding of the electrode in the passive region results in the disappearance of these regions.

In order to answer the problem of the nature of the processes leading to complete passivation of nickel in 1 N H_2SO_4, curves of the fall in potential were recorded after preliminary holding the electrode in the regions of maximum passivity and also of oxygen evolution (at potentials > + 1.8 V). These measurements, in agreement with the results of other investigators [7, 8] showed that the shape of the curves depended considerably on the time of holding the electrode in the indicated regions of potentials. Steps on the curves (Fig. 5) were observed

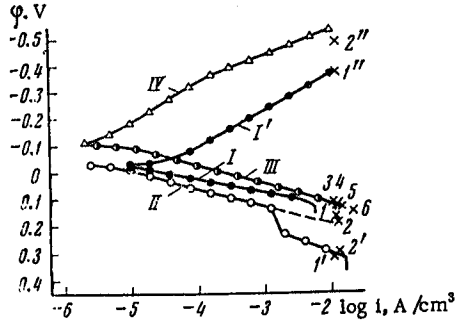

Fig. 4.

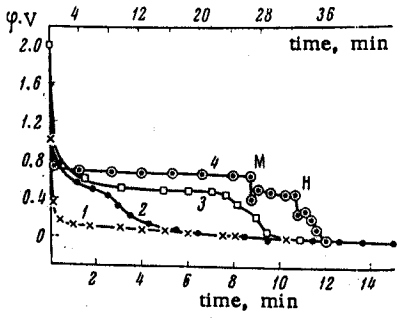

Fig. 5.

Fig. 4. Anodic and cathodic polarization curves recorded immediately after immersion of a freshly prepared electrode in the solution (I, I'), cathodic polarization for 20 h (II), staying in the passive region (III), alternate anodic and cathodic polarization (IV). Points 1-6 and 1', 2' are the average potentials respectively of the first and second steps in relation to current density during recording of φ-t curves. Points 1, 1', 2, 2', 3 were taken from the corresponding experiments of Fig. 3. Points 1'', 2'' characterize the rate of evolution of hydrogen before the φ-t curves were recorded which correspond to points 1, 2.

Fig. 5. Change in potential with time in 1 N H_2SO_4 after switching off the polarizing current which was held at a constant potential for a definite time: 1, 2) + 1.000 V, 4 h; 3) + 1.990 V, 30 min (time given on lower axis); 4) + 1.990 V, 4 h (time given on the upper axis).

only after prolonged holding, although even in this case the curves had insufficiently good reproducibility. The average potential of the step which was most often observed was from +0.38 to +0.51 V. The displacement of the steps in the direction of positive potentials, as a rule, was accompanied by an increase in their length. After prolonged holding of the electrode in the region of oxygen evolution, the steps appeared also in the region of more positive potentials. Thus, the potential of the middle of the first step of curve 3 was +0.67 V. In this experiment, rapid decreases were observed with subsequent increase in potential (points M and H).

The presence on the curves of sharply expressed steps indicate the formation in the passive region of comparatively thick oxide layers. A comparison of the results obtained with thermodynamic calculations showed that, in the region of maximum passivity, the formation of Ni_2O_3 would be expected and in the region of oxygen evolution the formation of NiO_2. However, the content of oxygen in the oxides, as was proposed also by the authors of [7], may obviously differ from the stoichiometric composition, during which, with increase in time of anodic polarization, there occurs an enriching of the oxides with oxygen.

The data obtained enabled us also to conclude that SO_4'' ions may have a substantial action of the oxide film in the region of maximum passivity. Thus, the curves 1 and 2 given in Fig. 5 were recorded after holding the electrode for the same time at the same potential (1.0 V). However, in the first case the decrease went very rapidly and in the second case there was a sharply expressed step. In these experiments, the curves characterizing the change in polarizing current with time when held at a given potential were also different. In experiment 2, the rate of dissolution of the passive nickel was extremely low all the time but in experiment 1, after the original decrease, the current began to increase indicating activation of the surface. The activation is obviously connected with the action of SO_4'' ions which are capable of removing the oxygen even in the region of high potentials. This results in destruction of the oxide films and, correspondingly, in an increase in the rate of fall of potential. Since the adsorption of anions is determined not only by the purity and the structure of the metal but also by several chance factors, depending, in particular, on the preliminary treatment of the electrode (the presence of scratches and cracks), then the poor reproducibility of the curves noted also by other investigators [4, 7] becomes understandable.

On the basis of the investigations carried out it can be concluded that the original passivity of nickel is connected with adsorption of oxygen [9-11] and with the formation of oxides of an adsorption character [12, 13], but in the process of anodic polarization there occurs an increase both in the quantity of oxides and in the content of oxygen in them. The oxides may also contain an excess quantity of oxygen compared with the stoichiometric composition. The effective passivating action, as was considered also by authors of [8, 14], is also obviously possessed by oxides with a high content of oxygen, and the formation of NiO in sulfuric acid results in only insignificant retardation of the anodic process.

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