PECULIARITIES AND NATURE OF THE ANODIC BEHAVIOR OF NICKEL BEFORE THE BEGINNING OF THE SECOND PASSIVATION

V. M. Novakovskii, G. N. Trusov, and M. F. Fandeeva

UDC 620.193.01

The influence of a number of factors on the shape of the polarization curve of electrolytic nickel in dilute acid in the interval from the stationary potential up to +0.3 V was investigated and analyzed. It was shown that spontaneous anodic activation of nickel at potentials of +(0.25-0.3) V and the loss of this activity at potentials close to the stationary potential are not associated with a displacement of passivating oxygen and activation anions. The cause apparently lies in a change in the crystal chemical characteristics of the surface, which should be a function of its submicrorelief, which varies depending on the dissolution potential.

The anodic behavior of nickel in dilute acid is interesting as a case of a distinct manifestation of a unique competition among the processes leading to facilitation and to hindrance of the anodic reaction $Ni \rightarrow Ni^{2+} + 2e$.

A well-known consequence of such competition is considered to be the broken shape of the potentiostatic polarization curve of the nickel anode, taken slowly [1]. The two passivation potentials, separated by a gap of 0.25-0.30 V; the two passivation branches, the second of which* has a pronounced negative slope $\partial \ln i/\partial\varphi$, while the first more or less approaches the vertical; the two branches with a positive slope, which, in accord with the established, although not entirely fortunate terminology, we shall still call the first and second branches of active dissolution – all these peculiarities of the stationary polarization curve still do not give a complete idea of the external picture of the electrode behavior. A very important peculiarity of this behavior is the ability of actively dissolving nickel to spontaneously increase its apparent activity when the potential is shifted in the positive direction and to decrease it in the case of the opposite change in the potential. These changes in the activity are expressed in a slow spontaneous increase or decrease in the current density, which is still noticeable in the first 15-20 min or more after the corresponding change in the potential.

On certain electrodes, such self-activation can already be observed on the first active branch. Then, in the case of slow recording of the polarization curve, this branch is bound to be very long, while the second active branch is short or even degenerates into a small break. In this case, the first passivation begins at almost the same current density as the second, and the polarization curve as a whole takes on the form of curve A in Fig. 1. On other electrodes, differing in origin or preparation, spontaneous activation cannot be observed on the first branch. The first passivation then occurs at a relatively low current density, and after its completion, a long second active branch appears, on which the spontaneous increase in the current is extremely pronounced in the presence of an unchanged potential. The curve takes on the form B (Fig. 1). In accord with these notations of the curves, we shall also distinguish electrodes in state A and in state B (i.e., capable and incapable of anodic activation on the first active branch, respectively).

The self-activation and self-passivation of nickel on the first active branch (in state A) were investigated and described by Kravtsov et al. [2]. They show that the observed changes in the visible current density at constant potential cannot be explained by a simple change in the true surface area of the electrode, which is clearly insufficient for this. Therefore they introduced a certain activity coefficient x into the preexponential factor of the kinetic equation, which, according to their data, varies in proportion to the

* All the numeration is given, as usual, in the positive direction from the corrosion potential.

L. Ya. Karpov Scientific Research Physicochemical Institute. Translated from Zashchita Metallov, Vol. 5, No. 5, pp. 503-510, September-October, 1969. Original article submitted March 26, 1969.

apparent current density of dissolution of the metal. They did not establish the nature and mechanism of the change in this coefficient.

The activation occurring on the second active branch (on electrodes in state B) was studied by N. Ya. Buné [3], who related it to the presumed displacement of the passivating oxygen by anions (for example, SO_4^{2-}). Later, however, it was discovered [4] that in the transition of nickel from state B to state A, the amount of passivating oxygen present on its surface at the potentials of the end of the first passivation is not reduced, but is increased, although the rate of dissolution of the metal in this case increases sharply. Under such conditions the possibility of explaining the anodic activation of nickel by the action of anions displacing the passivating oxygen seems very doubtful.

A discussion of the possible causes of the change in the activity of nickel will comprise the content of the present work.

METHOD

Just as before [4], we investigated electrolytic nickel, deposited at $D_c = 5$ A/dm^2 from an aqueous electrolyte containing 16% $NiSO_4$ and 4% H_3BO_3 (both cp). Standard treatment of the electrode obtained in this way (selected as a result of numerous tests and ensuring the required reproduceability of the electrode characteristics) consisted of a 1 h exposure at a temperature of 300° and a vacuum of 10^{-2} torr. All the polarization curves cited in the article were taken in 0.1 N H_2SO_4 by gradually increasing the anodic potentiostatic polarization from the potentials close to the stationary corrosion potential. The transition to the following stage was accomplished each time after the current density could be considered constant with an accuracy within 5% in the last 5 min of the preceding stage. The latter value was arbitrarily considered to be stationary. With the exception of one curve (D, Fig. 1), taken in an atmosphere of hydrogen, all the curves were taken in an atmosphere of argon. The potentials were measured and are cited according to a hydrogen electrode in the same solution. The measurement of the double layer capacitance and amount of passivating oxygen present on the electrode was performed with the aid of the method already described [4] according to the charging curves, which were recorded oscillographically during the application of a series of set cathodic potential pulses, with a front of the order of a microsecond and duration and duty factor of up to several tens of milliseconds, to the electrode.

RESULTS AND DISCUSSION

Curves of Type A. If a standard prepared electrode (see above) is kept for 1 h at a potential of +0.3 V before the polarization measurements, and then the polarization curve is taken in the cathodic direction to the hydrogen zero slowly, in stages of 50 mV, each time reaching an arbitrarily stationary current density, then in the case of the opposite stepwise increase in the anodic polarization, the stationary shape of the polarization curve A is stably reproduced (Fig. 1). It almost repeats the curve that was recorded before this in the cathodic direction; moreover, any positive change in the potential within the limits of the first active branch causes not only an instantaneous increase in the current density, but also the already described subsequent slow increase in it for 15-20 min (just as after the cathodic shifts, it gradually decreased before this).

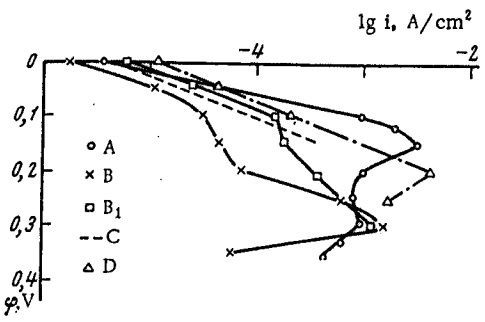

Fig. 1. Potentiostatic curves of anodic dissolution of nickel in 0.1 N H_2SO_4. A) After exposure at a potential of +0.3 V; B) after exposure at the potential of free corrosion; B_1) after annealing in an atmosphere of hydrogen at 900°; C) taken by a pulsed method; D) taken in an atmosphere of hydrogen.

The slope of the stationary curve taken in this way on the first active branch is close to 30 mV. The instantaneous polarization characteristics, taken oscillographically by the application of individual positive pulses from the potentials of the first active branch, have a slope close to 0.10 V (curve C, Fig. 1), which, in general, also is in good agreement with the known data [5].

Curves of Type B. After a prolonged stay at the stationary corrosion potential, the metal passes into state B, and its stationary anodic curve acquires a stepwise shape (curve B, Fig. 1). Spontaneous activation of the electrode begins only after the first passivation branch, at a potential of about +0.29 V, and leads to the appearance of a long second branch of active dissolution.

Approximately the same curve B_1 can also be obtained on an electrode just immersed in the solution, if before this, instead of any electrolytic treatment, it is subjected to annealing in an atmosphere of hydrogen at a temperature of 900°.

In transition from one state to another, it is very important to emphasize that the complete curve of type B cannot be taken in the cathodic direction. If one waits for completion of spontaneous activation, occurring in the potential interval from +0.25 to +0.30. V, then nickel passes into state A, and in the case of a stepwise decrease and reverse increase in the anodic polarization described at the beginning of this section, gives polarization curves of type A. Thus, the second active branch on curves of type B is actually a branch of an irreversible transition of the electrode from state B to state A at these potentials. The high activity of the electrode achieved is preserved in the return to the first active branch and gradually drops only as the stationary potential is further approached.

It is characteristic that if an electrode activated in this way is not kept too long at low anodic polarizations or at the stationary potential of corrosion, then when the anodic polarization is again increased, its activity is spontaneously restored still within the limits of the first active branch, and the polarization curve retains form A. In order words, the processes of anodic activation that are most readily observed on the second active branch can also be realized under definite conditions at potentials of the first branch at which there is not yet any passivating oxygen on the surface of nickel, according to the existing opinions. Consequently, the activation under discussion is not associated with a displacement of oxygen.

In order to consider this question in greater detail, we repeated and supplemented certain pulsed measurements described in our previous work [4].

The results of these measurements can be briefly generalized as follows.

The double-layer capacitance found according to the pulsed charging curves is ~30 μF per cm^2 of visible surface in state B before the beginning of the first passivation, while in state A it is ~80 μF, i.e., from a strength three times as high. The apparent current density of dissolution in these states also differs by 1.5-2 orders of magnitude.

No activating effect on the electrodes of both types is exerted by short cathodic potential pulses either at these or at any other points of the first active branch; and no processes, other than a change in the charge of the double layer, are noticeable on the oscillographic charging curves at these pulses.

On the contrary, in any of the two states reaching stationary passivation at any potential of the first passivation branch, the electrode is sharply activated as a result of the application of the cathodic pulse. The anodic current density of the dissolution of nickel, recorded oscillographically on such an electrode after the cessation of the pulse and a reverse charging of the double layer, increases up to a definite limit with increasing amplitude, duration, or number of successively transmitted pulses. In the limit, it proved to be approximately equal to the current density corresponding to a given interval on the first active branch of the corresponding type of stationary polarization curve, with a deduction of the loss of voltage in the electrolyte.

The charging curves recorded oscillographically during these pulses show that the activating effect of the pulses is due to the occurrence on the electrode of a certain Faraday process, and that the limit of activation is reached when the electrochemical capacitance of this process is exhausted. After this, further cathodic potential pulses in rapid sequence produce only the corresponding changes in the charge of the double layer, and the activity of the electrode is not increased any more. Judging by a whole series of characteristics, the indicated Faraday process represents reduction of the passivating oxygen.

On electrodes in state A, the electrochemical capacitance can be easily measured. On the first passivation branch it increases as a linear function of the polarization potential from zero up to a value corresponding (calculated on the basis of true surface) approximately to a monolayer of NiO. In state B the capacitance of the Faraday process begins to become appreciable against a background of the double layer capacitance only toward the end of the first passivation. But here too, calculated on the basis of true surface, it corresponds to no more than 0.1 monolayer of NiO. In other words, at the same potential of the end of the first passivation branch, the total amount of passivating oxygen on the nickel surface in state A (considering roughness) is approximately 1.5 orders of magnitude greater than in state B. The current densities of the dissolution of nickel in these states are related to one another in approximately the same way.

During spontaneous activation at a constant potential on the second active branch, the amount of oxygen on the electrode surface was estimated only extremely approximately. However, it undoubtedly increases with increasing current density of dissolution, and when the electrode reaches state A, it also becomes normal for this state.

Hence: a) under the experimental conditions, the initial state of the electrode – A or B – may be considered unchanged within the limits of the first active and first passivation branch; b) in any of these states, the deposition of oxygen within the first passivation branch is a sufficiently reversible process, which leads to an increase in the constant "a" in the Tafel equation of the overvoltage of the anodic dissolution of nickel; c) the amount of passivating oxygen required for the same change in the constant "a" changes from state B to state A in approximately the same proportion as the apparent current density at the potential of the beginning of the first passivation (or according to Kravtsov's terminology [2], in proportion to the activity coefficient of the electrode reached by the end of the first anodic branch); d) during transition from state B to state A (on the second active branch), the amount of passivating oxygen on the surface increases together with the visible current density, reaching approximately a monolayer of NiO by the end of the branch, characteristic at this potential of state A; the passivating character of this oxygen undoubtedly follows from the fact that when it is removed, the constant "a" in the equation of the overvoltage decreases sharply, and the process of dissolution turns into the first active branch of a curve of type A.

Some Conclusions. The facts cited quite obviously confirm the already-expressed opinion that spontaneous anodic activation is not a consequence of the displacement of passivating oxygen either on the first or on the second active branch. But this is not all.

From these facts it practically unambiguously follows that only those portions of the surface on which the reaction $Ni \rightarrow Ni^{2+} + 2e$ occurs by the end of the first active branch are subject to oxygen passivation on the first passivation branch. In state A this corresponds to practically the entire electrode surface. In state B it corresponds to only a small portion of it. The remainder of the surface of such electrodes, the overwhelming majority, acquires reactivity only in transition to the potentials of the second active branch. Having become reactive, this portion of the surface also is immediately passivated by oxygen.

However, under this condition also the apparent overvoltage of the reaction $Ni \rightarrow Ni^{2+} + 2e$ proved to be far smaller on it than without passivation in the initial stage, which it acquired as a result of annealing or exposure at low anodic potentials.

We can scarcely assume that in the process of activation (on the second active branch), strictly parallel to the gradual coverage of the surface by a monolayer of passivating oxygen (or oxide), activating ions, far exceeding its passivating effect, are also adsorbed on it to the same or a greater degree. Having ascribed such an action to the anions, by the way, it would be extremely difficult to understand why they are reversibly desorbed and absorbed on electrodes in state A at the potentials of the first active branch, while on electrodes in state B the potential required for their deposition is 0.15 V more positive (although oxygen begins to be deposited on this electrode at the same potential).

Supplementary Data. Unsatisfied with these indirect evidences, we experimentally compared the behavior of nickel in 0.1 N H_2SO_4 and in a solution of H_3PO_4 possessing the same pH value. This replacement of the electrolyte did not produce any significant changes either in curves of type A or in curves of type B, although sulfate and phosphate anions are considered to be quite nonequivalent in their activating abilities [6].

A new and somewhat unexpected fact was the inhibition of processes of dissolution of nickel by molecular hydrogen. In a hydrogen atmosphere, the Tafel slope of the stationary polarization curve of a standard prepared electrode in state A (curve D, Fig. 1), roughly speaking, is twice as high as in argon. In this case, any point of curve D can be obtained not only by the usual change in the electrode potential in a stationary hydrogen atmosphere, but also by replacement of an argon atmosphere by hydrogen at the corresponding potential. These transitions from curve A to curve D and back begin immediately after replacement of the gas passed through the electrolyte.

Still another experimental fact which, among other things, can be used as important evidence against the hypothesis of activation of nickel by anions was detected in a verification of the influence of cathodic polarization on the subsequent behavior of electrodes that prior to this had been in state A.

If we assume that activation is associated with an adsorption of anions, then the loss of ability to be activated after exposure at potentials close to the stationary should be considered a consequence of their irreversible desorption. Evidently, they should have been even more intensively desorbed in the case of cathodic polarization. And up to this time, actually, the opinion had prevailed [1, 3] that after cathodic polarization nickel becomes even more inert. However, if a negative potential of the order of −0.5 V is delivered to a standard prepared electrode immediately after an hour's exposure of it at a potential of +0.3 V, then after 12 h of continuous cathodic polarization it also gives a stationary anodic curve of type A after the usual recording from the corrosion potential. The only difference in its behavior is the lower rate of reaching of a stationary state.

Thus, the reactivity of a nickel surface, which it acquired at a potential of +0.3 V, is entirely lost in several hours at the stationary corrosion potential and low anodic potential, but seems to be conserved in the case of a high cathodic polarization.

Submicroscopic Factors in the Activity of an Electrode

Returning to the usual illustration model of a hypothetical perfect crystal with a simple cubic lattice, used for the electrochemistry of metals (Fig. 2), let us attempt to estimate in a rough approximation the influence that can be exerted on the anodic process by the existing submicrotopography of the metallic surface.

It may be considered a generally accepted truth that in the case of sublimation or dissolution of crystals, the atoms that are on projections of the atomic steps "b" most readily leave their normal position in the lattice points (regardless of whether they immediately go off into the surrounding medium or whether they remain on the surface for some time in the form of ad-atoms or ad-ions). A peculiarity of such a projection is the fact that after the removal of the atom situated on it, it seems to "reproduce itself" – its function is taken up by the closest following atom in the chain, and the conditions of further dissolution are unchanged until the projection disappears after reaching the end of the face.

A new projection on the remaining step is most readily generated at its end emerging at the intersection with the neighboring face. In order to remove an atom in the model under consideration not from a projection, but from the edge of a step (including that formed by the emergence of a single dislocation), it is necessary to break one more bond, the energy of which, strictly speaking, is of the order of an electron volt. Therefore, even considering the fact that such "k" atoms on the surface of a more or less completed crystal are many orders of magnitude more plentiful than the atoms "on projections," their independent participation in the product of anodic dissolution can become appreciable only when the potential is significantly increased. This is utilized, in particular, for the production of perfect single-crystalline phases by "equilibrium etching," in which the projections and steps present on a face are successively removed from it during very low anodic polarization, while practically no new steps are generated on the edges of the crystal (see, for example, [7]).

It is clear that the increased reactivity of atoms "on a projection" should be manifested not only in processes of evaporation and dissolution, but also in any other chemical and electrochemical reactions with the components of the external medium.

In particular, precisely such sites should usually be the first centers of deposition of oxygen and any other passivating and inhibiting particles.

Without going into further details and refinements, on the basis of the aforementioned we can sketch the following preliminary scheme of the behavior of nickel in the electrolyte.

At the corrosion potential and in the case of low anodic polarization, the generation of new steps on the surface of the crystal is relatively improbable. Dissolution from the existing projections, however, is still rather rapid. Gradually more and more perfect faces with a minimum number of projections, steps, and vertices remain on the surface. Moreover, in this potential region there is a substantial probability of occupation of the available projections by adsorbed hydrogen atoms, which can be electrochemically deposited on these sites even at potentials appreciably more positive than the hydrogen zero and performing, to a definite degree, the role of a fourth neighbor, increase the summary energy of the bond of the metallic atom "on the projection." All this makes the surface of nickel rather inactive.

One of the causes of the visible activation of the surface when the potential is shifted in the positive direction may be a decrease in the probability of blocking of the projections by hydrogen deposited and

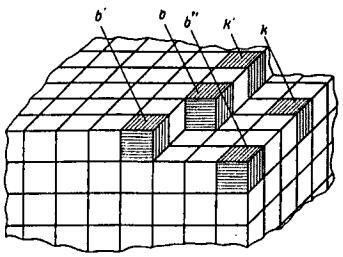

Fig. 2. Scheme of arrangement of atoms on edges and protrusions of atomic steps on the surface of a crystal with a simple cubic lattice.

removed from them on account of electrochemical exchange with the solution. In this case, however, the rate of anodic removal of adsorbed hydrogen, all the way up to the beginning of the first passivation, remains low in comparison with the rate of its nonelectrochemical deposition from a solution saturated with elementary hydrogen (curve D, Fig. 1).

At the potential of the electrochemical formation of NiO on projections passivating oxygen begins to be deposited, which can require more positive potentials, if the projections are occupied by nonelectrically adsorbed hydrogen.

The most powerful processes of activation of the surface begin after the reaching of positive potentials at which massive generation of new steps and projections not only at the vertices, but also on other edges of the crystals, becomes possible. However, in this case the probability of anodic blocking of the projections that arise by oxygen is already very great. The combination of these rapid anodic processes leads to the fact that ultimately no appreciable portions of perfect faces with low indices remain on the electrode surface. Everyone is converted to a randomized accumulation of microscopic and submicroscopic nuclei of faces with relatively high indices, up to the limit of the "saturated" projections and steps.

In the case of instantaneous transition to the region of high negative potentials, all this surface (the microgeometrical area of which has not increased so much) is under the joint influence of cathodic protection and the blocking action of adsorbed hydrogen, which has displaced oxygen on the projections. Therefore the high activity of the surface can be "conserved" for an extremely long period.

Many hours of exposure at the corrosion potential eliminates this activity entirely. At the usual rates of recording of the polarization curve, the time of stay at low anodic potentials proves to be insufficient for all the nonequilibrium faces rich in steps on which new steps could be generated comparatively easily to have disappeared from the surface exposed at +0.3 V. Therefore in the reverse recording of the curve in the anodic direction, we still observe an appreciable activation on such electrodes, even on the first branch of active dissolution.

CONCLUSIONS

1. The spontaneous activation of nickel, observed when its anodic polarization in dilute sulfuric acid is increased (to a potential of about +0.3 V), cannot be explained either by displacement of the passivating oxygen or by adosrption of the anions.

2. This activation is based on anodic initiation of submicroscopic steps and projections, which serve as labile reaction centers of interaction of the metal with the surrounding medium (dissolution, passivation, etc.). The loss of activity of the electrode at potentials not far from equilibrium (in particular, at the corrosion potential) is associated with their extensive "equilibrium etching."

3. Since the apparent rate of dissolution of the metal can be changed by an order of magnitude as a result of a change in the number of such reaction sites, the theoretical and experimental study of the conditions and peculiarities of their appearance, disappearance, and functioning should be considered a necessary condition for the further development of the theory of corrosion and passivity of metals.

LITERATURE CITED

1. N. Ya. Buné, Zashchita Metall., 1 (1965).
2. Kravtsov and Chang Chih-ping, Zh. Fiz. Khimii, 34 (1965).
3. N. Ya. Buné, Zashchita Metall., 3 (1967).
4. G. M. Trusov, E. P. Gochalieva, and V. M. Novakovskii, Electrokhimiya, 4 (1968).
5. Kronenberg, Banter, Geager, and Hovorka, J. Electrochem. Soc., 110 (1963).
6. J. R. Evans, Corrosion and Oxidation of Metals [Russian translation], Mashgiz (1962), p. 129.
7. N. A. Pangarov, Zashchita Metall., 5, 467 (1969).