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Abstract

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THE INFLUENCE OF NICKEL ON THE ELECTROCHEMICAL AND CORROSION BEHAVIOR OF STEEL

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The corrosion resistance of metallic structural materials depends mainly on their ability to undergo passivation and to retain the passive state under service conditions. In work (1) it was shown that the most important characteristic of the electrochemical and corrosion behavior of metals under conditions of passivation is the curve expressing the dependence of the steady dissolution rate on the potential over a broad interval of values of the latter. Such a curve, obtained by means of the potentiostatic method, makes it possible to determine the polarization limits of stability of the passive state and the magnitude of corrosion losses of the metal in the region of passivation. It was of interest to apply the potentiostatic method to the study of the influence of the chemical composition of steel on its electrochemical and corrosion behavior under conditions of passivation.

As was shown earlier (1), the phenomenon of passivation and activation of a metal occurs as a result of a change in the state of its surface. In this case the degree of passivation of the metallic surface depends on the potential of the electrode, and at constant potential changes with time, tending toward a stationary value. The change in the state of the electrode surface with time and potential is apparently connected with adsorption on its surface of individual components of the solution, such as, for example, electrolyte anions or OH^- and O^{-2} ions, the adsorption of the latter being able to occur as a result of interaction of surface atoms of the metal with water molecules.

It was natural to suppose that a change in the chemical composition of steel would lead to a change in its adsorption properties and, consequently, to a change in its electrochemical and corrosion properties in the passivation region, which could be observed by comparing potentiostatic curves relating to steels of different composition.

In the present work, with the aid of the potentiostatic method of measuring polarization curves, the influence of nickel on the behavior of steels in the passivation region was investigated.* For this purpose steels of grades Kh22T, Kh22N14T, and Kh20N6S2T were used, the composition of which is given in Table 1.

Fig. 1. Polarization curves of the true dissolution of steels X22T (1), X22N14T (2), and X20N6S2T (3) in 0.1 N H_2SO_4. 4 and 5 are hydrogen overvoltage curves on steels X22T and X22N14T; 6 and 7 are cathodic and anodic curves measured by current on steel X22T in the presence of platinum in a hydrogen atmosphere.

Figure 1: Fig. 1. Polarization curves of the true dissolution of steels X22T (1), X22N14T (2), and X20N6S2T (3) in 0.1 N H_2SO_4. 4 and 5 are hydrogen overvoltage curves on steels X22T and X22N14T; 6 and 7 are cathodic and anodic curves measured by current on steel X22T in the presence of platinum in a hydrogen atmosphere.

Table 1

Steel grade	C	Cr	Ni	Ti	Si	S	P	Mn
Kh22T	0.16	22.50	–	0.55	0.47	0.013	–	–
Kh20N6S2T	0.15	19.42	5.89	0.54	2.12	0.013	0.008	0.83
Kh22N14T	0.14	22.45	14.41	0.72	0.45	0.010	–	–

Chemical composition, %.

* L. N. Belogurova took part in the work.

Measurements were carried out in a 0.1 N solution of H_2SO_4 in a nitrogen atmosphere at 20°. Before the measurements, the mechanically and chemically cleaned electrodes were subjected to preliminary cathodic polarization.

At potentials at which, along with dissolution of the steel, other electrode reactions could occur, such as the evolution of hydrogen or oxygen, the true rate of dissolution of the steel was determined by photocolorimetric analysis of the solution for Fe, Cr, and Ni content after holding the specimen in it for a definite time at constant potential.

Fig. 1. Polarization curves of the true dissolution of steels X22T (*1*), X22N14T (*2*), and X20N6S2T (*3*) in 0.1 N H_2SO_4. *4* and *5*—hydrogen overvoltage curves on steels X22T and X22N14T; *6* and *7*—cathodic and anodic curves measured by current on steel X22T in the presence of platinum in a hydrogen atmosphere.

As is evident from the data obtained (Fig. 1), the dependence of the steady-state dissolution rate of steel X22T on potential is characterized by a rather complex curve (curve *1*). At potentials more negative than –0.43 V, a systematic increase in the dissolution rate with potential is observed in accordance with the usual Tafel straight line. In the potential interval from –0.430 to –0.270 V, the polarization curve changes its direction several times, while the rate of steady-state dissolution remains within the range $1 \cdot 10^{-4}$–$1 \cdot 10^{-3}$ A/cm^2. A subsequent shift of the potential toward positive values up to –0.160 V is accompanied by a systematic decrease in the dissolution rate to $5 \cdot 10^{-7}$ A/cm^2. In the potential region from −0.160 to −0.010 V, a successive change in the direction of the curve is again observed; however, the magnitude of the dissolution current remains approximately 1000 times smaller than in the potential region preceding the onset of deep passivation.

The minimum dissolution rate of steel X22T is observed in the potential region 0—+0.500 V. In this region the dissolution rate does not depend on potential and amounts to $3.2 \cdot 10^{-7}$ A/cm^2. At potentials more positive than +0.500 V, the dissolution rate again increases with potential and at +0.850 V reaches $1 \cdot 10^{-5}$ A/cm^2, after which passivation again occurs, preceding a new region of active dissolution—the so-called transpassivation region, in which dissolution of the steel is accompanied by the appearance in solution, along with trivalent chromium, also of hexavalent chromium. In this region the dissolution current increases to $1.5 \cdot 10^{-3}$ A/cm^2 at +1.450 V and remains approximately constant* until the potential +1.800 V is reached, beginning from which visible oxygen evolution becomes noticeable.

As is evident from Fig. 1, an analogous dependence of the steady-state dissolution rate on potential is also observed in the case of the other investigated grades of steel. The differences are mainly qualitative in character. The introduction of nickel leads above all to a decrease in the steady-state rate of dissolution dissolution at all potentials lying more negative than +1.200 V. In the passivation region, an increase in the nickel content of the steel corresponds to a systematic decrease in the dissolution rate.

Thus, the transition from steel Kh22T to steels Kh20N6S2T and Kh22N14T leads to a decrease in this rate in the potential region 0.0—+0.50 V from $3.2 \cdot 10^{-7}$ to $1 \cdot 10^{-7}$ and $4.8 \cdot 10^{-8}$ A/cm^2. However, a particularly significant effect is observed in the polarization region preceding the onset of deep passivation. Thus, for example, at a potential of −0.400 V the dissolution rate of steel Kh22N14T is almost 1000 times lower than the dissolution rate of steel Kh22T. This means that the presence of nickel affects not only the electrochemical behavior of steel in the passivation region, but also leads to a noticeable increase in the overvoltage of the anodic reaction in the polarization region in which the active state is stable. The latter is reflected in the magnitude of the anodic current necessary in order to transfer the steel into the passive state. This current is $1 \cdot 10^{-3}$ A/cm^2 for steel Kh22T and $3 \cdot 10^{-6}$ A/cm^2 for Kh22N14T.

It follows from the data in Fig. 1 that the introduction of nickel has almost no effect on the position of the curve characterizing the hydrogen overvoltage. This means that the observed difference in the values of the stationary potentials and rates of spontaneous dissolution of the investigated grades of steels in sulfuric-

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* The nature of the limiting current in the potential region +1.450—1.800 V will be the subject of a separate discussion. It should be noted here that, according to our data obtained in measurements with a rotating steel electrode (up to 1500 rpm), the magnitude of this current for steel X18N9 does not depend on the rotation rate of the electrode.

acid solution is completely due to the difference in the course of the anodic curves.

In the case of steel Kh22T, the rate of hydrogen evolution at the potential of deep passivation (−0.27 V) is lower than the corresponding passivation current. For this reason, the intersection of the hydrogen overvoltage curve with the anodic curve in this case occurs at a potential $\varphi_{\text{st}} = -0.29$ V, i.e., in the polarization region preceding the transition of the alloy into the passive state. Owing to this circumstance, the spontaneous dissolution of this grade of steel in sulfuric acid, proceeding with hydrogen depolarization, occurs at a considerable rate, equivalent to a current density

$$i_0' = 3.5 \cdot 10^{-4}\ \text{A/cm}^2.$$

A different relation between the rates of the cathodic and anodic reactions is observed for steel Kh22N14T. In this case, the rate of hydrogen evolution at the passivation potential considerably exceeds the rate of dissolution of the alloy. For this reason, elimination of cathodic polarization leads to self-passivation of the steel: the stationary potential φ''_{st} is established close to the potential of the reversible hydrogen electrode in the same solution; moreover, such a value of the potential corresponds to the passive state of the metallic surface and to a low dissolution rate, equivalent to a current density

$$i_0'' = 2.8 \cdot 10^{-7}\ \text{A/cm}^2.$$

The establishment of φ''_{st} in the region of the hydrogen zero is connected with the fact that in this case the rate of ionization of hydrogen (when the latter is present in the solution after preliminary cathodic polarization) considerably exceeds the rate of dissolution of the steel. However, this potential is unstable: as the solution becomes saturated with nitrogen and, consequently, as the dissolved hydrogen is removed from the near-electrode layer, it shifts toward positive values, where dissolution of the alloy is compensated by reduction of traces of oxygen present in the nitrogen.

Analogous behavior is also observed in the case of steel Kh20N6S2T, for which the stationary potential $\varphi'''_{\text{st}} = 0$.

Thus, from consideration of the data presented it may be concluded that, in order to transfer steel into the passive state and, consequently, to increase its corrosion resistance in the absence of external polarization, it is necessary to ensure a shift of the stationary potential in the positive direction to values lying more positive than the passivation potential (but not exceeding the potential for the onset of transpassivation). Such a shift can be effected not only by increasing the overvoltage of the anodic

reaction, as occurs in the case considered above, but also by increasing the total rate of the depolarizing cathodic reactions. As our experiments carried out with steel Kh22T showed, the latter can be accomplished either by lowering the hydrogen overvoltage or by introducing into the solution a new oxidizing agent capable of being reduced on the alloy surface in the polarization region under consideration.

In our experiments, the reduction of the hydrogen overvoltage was carried out by depositing a small amount of platinum on the steel surface. As can be seen from Fig. 1, this led to a shift of the hydrogen-overvoltage curve from position 4 to position 6, which caused a shift of the stationary potential $\varphi_{\mathrm{st}}^{\mathrm{Pt}}$ in the positive direction to a value close to the potential of the reversible hydrogen electrode in the same solution, and a considerable decrease in the dissolution rate to a value equivalent to a current density $i_0^{\mathrm{Pt}} = 4.9 \cdot 10^{-6}$ A/cm^2. This value (point A in Fig. 1) is almost exactly equal to the rate of steady dissolution of steel at the corresponding potential, determined by the potentiostatic curve.

Similar results were also obtained when oxygen from air was introduced into the solution. In this case the stationary potential of the steel shifted to the value $\varphi_{\mathrm{st}}^{\mathrm{O}_2} = +0.740$ V, with a simultaneous decrease in the steady dissolution rate to a value equivalent to a current density $i_0^{\mathrm{O}_2} = 2.5 \cdot 10^{-6}$ A/cm^2 (point B, Fig. 1), which is also in agreement with the potentiostatic curve of steel dissolution obtained by an independent method. These results confirm the earlier assumptions that the action of passivators of the type of cathodic additives and of the type of oxidizing agents need not necessarily be associated with their direct participation in the formation of a passivating layer on the metal surface. Obviously, a similar explanation can also be given for the passivating action of other oxidizing agents, such as, for example, Fe^{+3} ions, etc. ($^{2-4}$).

On the basis of the data obtained, it may be assumed that the measurement of potentiostatic polarization curves for different steels can serve as a method for the rational selection of their qualitative and quantitative composition with the aim of obtaining the most corrosion-resistant steels.

In addition, the curves obtained can be used to choose conditions favoring a decrease in the dissolution rate of steel of a given composition both during the passage of current and under stationary conditions. In doing so, it should be borne in mind that the ability of steel to self-passivate is determined by the ratio of the total rates of the cathodic and anodic reactions occurring on it, as well as by the true rate of dissolution of the steel at each given potential. If equality of the total rates of the cathodic and anodic reactions occurs at a potential lying in the passivation region for the given steel, then the steel self-passivates in the absence of an external current. In this case, cathodic polarization of the steel in accordance with its potentiostatic polarization curve may lead not to protection, but to intensification of its corrosion.

The results obtained show that the degree of passivation of the surface of steel of a given composition is a function of the potential and, in the cases described, does not depend on the way in which it is maintained. A shift of the potential by changing the chemical composition of the steel, however, may lead to a substantial change in the degree of its passivation at a given potential.

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