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Abstract

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ANODIC PASSIVATION OF CHROMIUM IN ACID SOLUTIONS

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In a previous paper (⁀1) we considered data on the electrochemical behavior of chromium and nickel in a K_2SO_4 solution, obtained by the potentiostatic method of polarization measurements. It was shown that the curve obtained by this method, expressing the dependence of the steady dissolution rate on potential, makes it possible to determine the polarization limits of the passivation region, as well as the magnitude of corrosion losses in this region and, consequently, is a most important corrosion characteristic of the metal.

In the present work, the electrochemical behavior of pure chromium during its anodic passivation in sulfuric acid solutions of various concentrations (1.0; 0.10; $0.01N$) was investigated by means of the potentiostatic method. The steady dissolution rate was determined not only from the final value of the anodic current by which the electrode was polarized in order to maintain a constant prescribed value of the potential, but also by analysis of the solution for chromium ions. In the range of potentials lying more negative than the potential of the reversible hydrogen electrode in the same solution, in which the transition of chromium into solution occurred mainly at the expense of self-dissolution, the analytical method of determining the dissolution rate was the only one. The diphenylcarbazide method of analysis used in the work made it possible to determine colorimetrically the content of Cr^{+3} and Cr^{+6} in solutions at concentrations down to $2 \cdot 10^{-8}$ g/cm^3. The content of Cr^{+2} was determined iodometrically; the sensitivity of this method was two orders of magnitude lower than that of the diphenylcarbazide method. All measurements were carried out in an atmosphere of purified nitrogen. The methods of preparation and preliminary purification of electrodes and solutions were the same as those described in the communication (⁀1). Each experiment was conducted at a constant temperature, maintained to within $\pm 0.1^{\circ}C$. The experiments were carried out with electrodes preliminarily activated by cathodic polarization. After switching off the cathodic current, the rate of self-dissolution and the value of the stationary potential of active chromium in the investigated solution were determined. In the anodic region, after a constant current density had been attained at the prescribed value of the potential, the electrode was polarized for a definite time in a fresh portion of

Fig. 1. Dependence of the logarithm of the steady dissolution rate on potential in H_2SO_4 solutions of various concentrations: a –1N H_2SO_4, b – 0.1N H_2SO_4, c –0.01N H_2SO_4

Figure 1: Fig. 1. Dependence of the logarithm of the steady dissolution rate on potential in H_2SO_4 solutions of various concentrations: a –1N H_2SO_4, b –0.1N H_2SO_4, c –0.01N H_2SO_4

solution, which was then analyzed for the content of dissolution products.

Dependence of the steady dissolution rate on potential*. For a 1.0N solution of H_2SO_4, this dependence is expressed by the curve $ABCDE$ (Fig. 1). In its general form the curve under consideration is similar to the corresponding curves obtained previously for nickel in a K_2SO_4 solution (⁀1) and for stainless steel of the 18-8 type in an H_2SO_4 solution (⁀2). At potentials lying more negative than −0.350 V,

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* All potential values are given relative to the potential of the normal hydrogen electrode.

an increase in the potential is accompanied by an increase in the dissolution rate in accordance with the usual Tafel straight line with a slope of 0.07.

In the potential interval from −0.350 V to 0.00 V (segment BC), a decrease in the steady dissolution rate with potential is observed, although the dependence between these quantities in this case also corresponds to a Tafel straight line, but with a slope of the opposite sign. Analysis of the solution for dissolution products in this polarization region revealed both Cr^{+2} ions and Cr^{+3} ions in ratios close to equilibrium.

Fig. 1. Dependence of the logarithm of the steady dissolution rate on potential in H_2SO_4 solutions of various concentrations: a –1N H_2SO_4, b –0.1N H_2SO_4, c –0.01N H_2SO_4

Over a considerable interval of potentials lying positive to 0.0 and negative to +1.10 V (segment CD), the steady dissolution rate retains a constant value equivalent to a current density of $5 \cdot 10^{-8}$ A/cm^2. A similar absence of a dependence of the dissolution rate on potential was observed by B. V. Ershler ([3]) for a platinum electrode in HCl solutions and by Bonhoeffer and co-workers ([4]) for an iron electrode in H_2SO_4 solutions.

As noted earlier ([1]), rapid displacement of the potential toward positive values in this region is also accompanied by an increase in the dissolution rate, analogous to that which occurs on the active surface, and only as a result of further, rather prolonged polarization of the electrode at the new value of the potential does this rate reach the minimum steady value corresponding to the curve under consideration.

As the analytical results showed, the dissolution of chromium in this polarization region occurs mainly in the form of trivalent ions.

Positive of 1.10 V (segment *DE*) the phenomenon of transpassivation of chromium sets in. As can be seen from Fig. 1, a further increase in the potential is accompanied by an increase in the dissolution rate in accordance with a Tafel straight line with a slope of 0.04 V. Table 1 gives the results of analysis of the solution for the content of chromium ions after holding the electrode in it at a potential of 1.252 V, lying in the polarization region under consideration. Also given there are the calculated values of the potential corresponding to the oxidation-reduction equilibrium for the found ratio of concentrations of tri- and hexavalent ions. As can be seen from Table 1, the calculated values of the potential practically coincide with the experimental ones. This result indicates either that dissolution of chromium in the transpassive region proceeds with the simultaneous formation of Cr^{3+} and $Cr_2O_7^{2-}$ ions in a ratio satisfying equilibrium, or, more probably, that equilibrium between these ions is rapidly established.

Table 1

Concentration of Cr ions, g-equiv./L · 10^4	Concentration of Cr ions, g-equiv./L · 10^4	Potential, V relative to n. h. e.	Potential, V relative to n. h. e.	Potential, V relative to n. h. e.
$[Cr_2O_7^{2-}]$	$[Cr^{3+}]$	exp.	calc.	$\Delta\varphi$
7.54	1.01	1.252	1.255	+0.003
8.64	0.986	1.252	1.256	+0.004
9.50	1.08	1.252	1.255	+0.003

Effect of solution pH. Data characterizing the rates of self-dissolution and the stationary potentials of active chromium in solutions

H_2SO_4 of various concentrations are shown as separate points in Fig. 1. They fall well on the same linear segment (*AB*), which may be regarded as a continuation of the polarization curve obtained in 1.0 *N* H_2SO_4 on the active surface of chromium. This indicates that the dependence of the dissolution rate of active chromium on the potential in sulfuric-acid solutions of different concentration is expressed by one and the same kinetic curve. In this respect the behavior of chromium is similar to that of nickel, studied in the work of Ya. M. Kolotyrkin and A. N. Frumkin ([5]).

A change in the pH of the solution has a noticeable effect on the electrochemical behavior of chromium in the passivation region. As can be seen from Fig. 1, a decrease in the acid concentration is accompanied by a shift of the upper boundary of the passivation region toward negative potential values. According to the data we obtained, the dependence of the potential corresponding to the onset of passivation on the acid concentration satisfies the equation:

Fig. 2

Figure 2: Fig. 2

$$\varphi_n = -0.350 + 0.050 \lg C$$

A decrease in the acid concentration also leads to a shift of the portion of the polarization curve lying in the transpassivation region toward negative potential values. As can be seen from Fig. 2, the dependence of the potential corresponding to one and the same rate of chromium dissolution in this polarization region on the concentration of H_2SO_4 is expressed by a straight line with a slope $\left(\frac{\partial \varphi}{\partial \mathrm{pH}}\right)_i$ close to 0.063. The data obtained in $0.1N$ NaOH satisfy the same dependence.

Fig. 2. Dependence of the potential on the pH of the solution in the transpassivation region at a constant value of the anodic polarizing current $(i = 1 \cdot 10^{-4}$ a/cm$^2)$

Taking into account the dependence of the chromium dissolution rate in the transpassivation region on the potential and pH of the solution, it can be shown that the rate-limiting stage of the reaction by which chromium dissolution occurs in the polarization region under consideration proceeds with the participation of two OH^- ions and three electrons. This conclusion agrees with the results recently obtained in the work of Heumann and Rosener ([6]).

Effect of temperature. In Fig. 3 the results obtained in a $0.1N$ H_2SO_4 solution at three different temperatures—25, 50, and 75° C—are compared. An increase in temperature leads, above all, to a noticeable increase in the chromium dissolution rate in the passivation region.

On the basis of these results we determined the activation energy of the process in that polarization region in which the rate of steady-state dissolution does not depend on the potential. The value thus obtained proved to be close to 5000 cal.

In the preceding communication we concluded that anodic passivation of chromium is not associated with the formation of a phase film on its surface, but is a consequence of kinetic inhibition of the anodic reaction, caused by a change in the state of the metallic surface with time and potential, occurring as a result of adsorption-chemical interaction of the surface with the oxygen of water. This conclusion agrees with the results of the polarization observations obtained in the present work. In Fig. 4, along with the stationary polarization curve, data corresponding to the initial values of current densities at the corresponding potentials are plotted. As can be seen from this figure, when the point corresponding to the final steady current density at each given value of

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

the potential (open circles) is connected with the point corresponding to the initial

current density at the subsequent more positive potential (dark points) yield straight lines with a slope close in magnitude to the slope of the upper linear segment of the curve (see Fig. 1), which characterizes the dependence of the dissolution rate of active chromium on potential. Thus, if transient phenomena are eliminated or reduced to a minimum, the polarizability of chromium and, consequently, the dependence of the dissolution rate on potential in the passivation region remain the same as in the active state, which, in our opinion, is not consistent with the concept of the existence on the surface of the passive metal of a phase oxide film, the presence of which should have led to increased polarizability of the electrode.

Fig. 3

Fig. 4

Fig. 3. Dependence of the logarithm of the steady dissolution rate on potential in a solution of $0.1N$ H_2SO_4 at various temperatures: a–25°, –50°, –75° C
Fig. 4. Dependence of the logarithm of the chromium dissolution rate on potential and time in a solution of $0.1N$ H_2SO_4 at $t = 50^\circ$

In accordance with the concepts developed, the observed dependence of the position of the upper boundary of the passivation region on the pH of the solution finds a comparatively simple explanation. If it is assumed that the adsorbing particles are OH^- ions, then it can easily be shown that the degree to which they cover the surface and, consequently, the degree of its passivation must depend not only on the potential, but also on the pH of the solution. It is also obvious that the higher the concentration of OH^- ions, the more negative must be the potential at which they begin to penetrate into the surface layer and, consequently, at which passivating adsorption can begin. On the basis of the adsorption mechanism of passivation, the observed dependence of the steady dissolution rate on potential also finds a simple explanation, if one takes into account, as was done earlier ([1,2]), that the state of the metallic surface, which determines the overvoltage of the anodic reaction, changes with potential according to an exponential law.

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CITED LITERATURE

1. Ya. M. Kolotyrkin, V. M. Knyazheva, ZhFKh, **30**, 1990 (1956).

2. N. Ya. Bune, Ya. M. Kolotyrkin, DAN, **111**, 1050 (1956).

3. V. V. Escher, Tr. 2nd Conf. on Corrosion of Metals, 2, Publ. House of the Academy of Sciences of the USSR, 1943, p. 52.

4. K. F. Bonhoeffer, Zs. Elektrochem., **59**, 594 (1955); U. F. Frank, K. Weil, Zs. Elektrochem., **56**, 814 (1952); K. U. Weil, K. F. Bonhoeffer, Zs. Phys., Chem., **4**, 175 (1955).

5. Ya. M. Kolotyrkin, A. N. Frumkin, DAN, **33**, 446 (1941).

6. Ih. Heumann, W. Rösener, Zs. Elektrochem., **59**, 722 (1955).

Note: Figure translations are in progress. See original paper for figures.