BRIEF COMMUNICATIONS

EFFECT OF BICHROMATE AND MOLYBDATE IONS ON THE PASSIVATION POTENTIAL OF CHROMIUM

V. A. Goryachkin and G. M. Florianovich

UDC 620.193.01

It was shown earlier [1] that passivation of metal with the introduction of an oxidizing agent into the electrolyte may be related not only to its depolarizing action, but also with the direct participation of the agent in the formation of passivating layers. Using the example of the passivation of chromium in solutions containing hydrogen peroxide, it was shown that such an effect may be expressed in a shift of the passivation potential of the metal in the negative direction in the presence of the oxidant. It may be proposed that just such a shift in passivation potential due to the interaction of the metal with the oxidant may be connected with the phenomenon, which we noted earlier [2], of strong inhibition of the solution of chromium in sulfuric acid in the region of active solution potentials with the presence of a sufficient amount of nitrate and bichromate, as well as with the phenomenon of facilitated passivation of iron in solutions containing molybdate [3].

In order to substantiate the above hypothesis, we studied the effect of sodium molybdate and sodium bichromate on the passivation potential of chromium, recording curves of the dependence of the rate of its solution on potential. The rate of solution was determined radiometrically with continuous recording of the radioactivity of the solution [4]. We used vacuum-melted chromium containing (%): C < 0.003; Si < 0.01; Al < 0.005; Fe < 0.005; O < 0.005. Before the test, the working surface of the specimens (0.25-0.15 cm^2) was pickled for 20-30 sec in a hot 1 N solution of sulfuric acid and washed twice with distilled water. The solutions were prepared using sulfuric acid of special purity, twice-distilled water, and chemically pure ($K_2Cr_2O_7$) and pure (Na_2MoO_4) salts. The tests were conducted at room temperature.

It can be seen from Fig. 1 that, in concentrations up to 10^{-3} N, the bichromate does not affect the passivation potential of chromium. With a further increase in bichromate concentration, passivation potential is displaced in the negative direction, as in the case of addition of hydrogen peroxide [1].

The effect of molybdate is more complex (Fig. 2). In concentrations of 0.01 g-eq/liter, it causes a sharp (by 400 mV) negative shift in the passivation potential of chromium in 0.1 N sulfuric acid.* With a further increase in molybdate concentration, passivation potential remains almost unchanged. Chromium does not become passive within the entire range investigated, including very negative potentials, until a molybdate concentration of 0.3 N is achieved. As a result, the rate of the solution of chromium at potentials from −0.8 to −0.3 V falls by several orders and turns out to be lower than the limit of sensitivity of the analytical method used, which under the test conditions was approximately 10^{-6} A/cm^2. With an increase in solution acidity, the molybdate concentration required for the above-described passivation effect at fairly negative potentials increases and, e.g., is 2.5-3.0 N in a 1 N solution of sulfuric acid. This agrees with the corresponding data for hydrogen peroxide.

Together with the above-noted shift in the passivation potential, the introduction of molybdate increases the solution rate of chromium in the region of the Tafel dependence (Fig. 2).† The latter agrees with the change in the rate of electrochemical solution of chromium in the presence of hydrogen peroxide [5] and may be explained by the direct participation of molybdate ions in electrochemical stages of the process of chromium solution.

*With a concentration of molybdate below 0.01 N, the effect is poorly reproducible; the passivation potential either remains generally unchanged or immediately shifts, as in 0.01 N molybdate solution.

†The section of potential-independence of the chromium solution rate on the dashed curve reflects the solution of chromium by the chemical mechanism [5, 6].

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov, Vol. 13, No. 6, pp. 703-705, November-December, 1977. Original article submitted September 17, 1976.

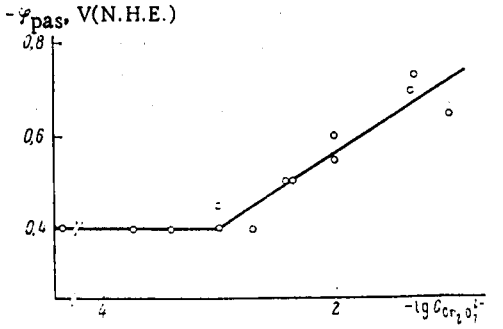

Fig. 1. Dependence of passivation potential of chromium in 0.01 N H_2SO_4 + 0.1 N Na_2SO_4 on bichromate concentration.

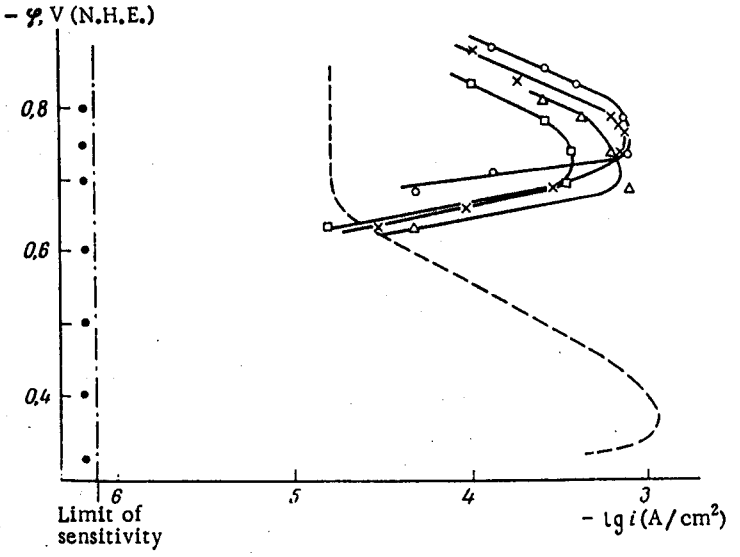

Fig. 2. Dependence of rate of solution of chromium in 0.1 N H_2SO_4 on potential at molybdate concentration (N) of : △) 0.01; ×) 0.04; ○) 0.07; □) 0.1; ●) 0.3; dashed line shows similar curve for pure sulfuric acid.

The acceleration of the electrochemical solution of chromium under the influence of molybdate leads to the fact that the above-examined effect of the strong inhibiting action of this oxidant on active solution at sufficiently high concentrations is manifest only on the positive side of a certain potential (a potential close to the passivation potential in the presence of molybdate).

It follows from the data obtained that molybdate and bichromate, like hydrogen peroxide, may reinforce the passivating ability of a solution, shifting the passivation potential of the metal in the negative direction. In accordance with conclusions made earlier [1], this allows us to suggest the possibility of direct participation of the investigated anions in the formation of passivating layers on the metal. Such participation may amount to adsorption of molybdate and bichromate on the chromium surface. A similar conclusion was reached by Cartledge [7] in a study of the inhibiting action of oxidants of the type XO_4^{n-} on the solution of iron. The complex character of the dependence of the passivation potential of chromium on the concentration of molybdate may also be related to the possible effect of products of molybdate reduction on the passivation process [8].

The results obtained on the effect of bichromate on passivation of chromium allows us to examine yet another problem. According to a widely held view, this anion may affect the rate of solution of passive metal through the formation on the metal surface of a compound oxide of dissolved metal and chromium [9]. It follows from such an assumption that an improvement in the passivation properties of the metal in the presence of chromate is connected

with the precipitation of chromium onto its surface from the chromate. The data that we obtained lead us to conclude that such a mechanism of chromate action is not generally obligatory: chromium from chromate naturally cannot form compound oxides with chromium, although the chromate does make passivation of chromium easier. This shows that the effect of chromate is connected with the formation of protective surface layers by the interaction of the metal with oxygen atoms included in the chromate.

We thank Ya. M. Kolotyrkin for his valuable advice in conducting and discussing the results of this work.

LITERATURE CITED

1. V. A. Goryachkin, G. M. Florianovich, and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 218, 604 (1974).
2. Ya. M. Kolotyrkin, G. M. Florianovich, and G. S. Raskin, Rev. Roum. Chim., 17, 161 (1972).
3. G. H. Cartledge, Corrosion, 24, 233 (1968).
4. V. V. Losev, M. A. Dembrovskii, and A. I. Molodov, Tr. Nauchno-Issled. Fizikokhim. Inst., Problems of Physical Chemistry [in Russian], No. 3, Goskhimizdat (1963), p. 46.
5. Ya. M. Kolotyrkin, G. M. Florianovich, V. A. Goryachkin, and F. M. Mikheyeva, J. Electroanal. Chem., 69, 407 (1976).
6. Ya. M. Kolotyrkin and G. M. Florianovich, Zashch. Met., 1, 7 (1965).
7. G. H. Cartledge, J. Electrochem. Soc., 113, 328 (1966).
8. Chemistry of Rare and Trace Elements, Vol. 1, Vysshaya Shkola, Moscow (1965), p. 282.
9. D. M. Brasher and A. D. Mercer, Trans. Faraday Soc., 61, 803 (1965).

ELECTROCHEMICAL BEHAVIOR OF COPPER IN DESALINATED WATER

I. K. Marshakov, A. V. Vvedenskii, and A. P. Karavaeva

UDC 620.193.2

The electrochemical characteristics of metals in desalinated water has received very little study, even though their corrosion behavior under such conditions is often unique [1]. A serious obstacle to obtaining polarization curves in desalinated water is the presence of a large ohmic component of potential E_{om} arising from the high resistivity of water (up to 10 mΩ·cm). To eliminate E_{om}, we used the commutator method of measuring potential [2] by means of a unit [3], a block diagram of which is shown in Fig. 1a.

Apparatus and Method

The test electrode, polarized from the source 1, is constantly grounded. Connected to the platinum electrode circuit is quick-acting microrelay RÉS-49 (R1), commutating the polarization current after a period ⩾1 msec.

The total signal

$$E_{tot} = E + E_{om} \quad (1)$$

enters the input of high-resistance cathode follower 2, having an input resistance of $\sim 10^{10}$ Ω in a dynamic range of ±50 V with a band of ∿5 mHz. Microrelay RÉS-49 (R2) commutates the potential recording circuit with a controlled (within the range 10 μsec–10 msec) delay relative to the moment the polarizing circuit is broken, so that only the electrode potential E enters the input of oscillograph S1-54 (3 in Fig. 1). Zero drift of the cathode follower does not exceed 5 mV/h and is checked periodically. The communication frequency in all tests was 5 Hz, time of commutation was 2-3 msec, and exposure time in plotting one point was 30 min. Overall synchronization of the unit was accomplished by means of control unit 4 and generator G5-6A (5 in Fig. 1), and transients were compensated by a diode–capacitive circuit. The test electrode and the reference electrode, made of M1 copper, were placed coaxially in an organic glass holder (Fig. 1b), sealed with epoxy resin, and screwed in flush with the flow-type, rectangular (80 × 6 × 1 cm) unit. The quantity being directly measured in this case is polarization

Voronezh State University. Translated from Zashchita Metallov, Vol. 13, No. 6, pp. 706-709, November-December, 1977. Original article submitted April 5, 1976.