ANODIC SOLUTION OF METALS AT HIGH CURRENT DENSITIES. I

A. D. Davydov, V. D. Kashcheev, and B. N. Kabanov

UDC 621.357.8

Some problems associated with the anodic solution of iron at high current densities in solutions containing activating ions are examined in this communication. These problems arise in studying the processes which occur during the electrochemical machining of metals. Obtaining high solution rates, which is necessary for the industrial use of this method of treatment, presents some difficulties. We studied some factors limiting the working current density by plotting polarization curves.

In order to clarify the role of concentration polarization studies were made using a rotating disc electrode. Because of the possible appearance in this case of passivation phenomena (which could have resulted in polarization phenomena in the sector with an unfavorable relation of potential to current strength) it was essential to use a potentiostat. Since, too, at high current densities a rapid dissolution of metal occurs which can change, during a prolonged run, not only the magnitude of the electrode area but also the distance between the electrode studied and the reference electrode, we plotted the dynamic potential polarization curves with a rate of change in potential of 2 V/min. For this purpose a P-9 potentiostat was used. This has been designed and made in the Institute of Electrochemistry of the Academy of Sciences. This instrument allows the potential of the main electrode to be controlled over the range ± 4V at a voltage ±20 V and a maximum current output of 5 A. A one-directional extension of the output voltage up to 40V is possible by the connection between the output of the potentiostat and an auxiliary electrode of a supplementary voltage booster. The instrument provides a means of eliminating variations in potential caused by a drop in voltage in parasitic intermediate resistances between the electrode and the grounded busbar, as shown by Knots et al. [1], since this error can be significant at high current values and when the current is supplied to the electrode by brushes or contact rings.

In measuring electrode potentials with current flow, particularly at high current densities, it is necessary to apply a correction to the measured value thus allowing for the ohmic drop in potential in the electrolyte layer between the main and the reference electrodes. In this work we measured values of potential at a fixed current with the capillary of the reference electrode at different distances measured along the normal to the center of the disc electrode [2-4]. These values were then extrapolated to zero distance. The extrapolated values of potential so obtained at different current densities make it possible to plot a complete polarization curve. (The values of potentials were measured relative to a saturated calomel element.) The experiments were carried out in unbuffered neutral (pH = 7) solutions of NaCl, since high solution rates were most likely to be obtained in these solutions.

The role of the chlorine ion in the iron ionization process is one of the main problems in this study: does the Cl^- play a direct part in the electrochemical event, or are hydrated iron ions bonded to Cl^- when in solution? In order to clarify this we first plotted polarization curves with a stationary Armco iron disc electrode in sodium chloride solutions of varying concentrations. It is evident from Fig. 1 that in the region of active dissolution where concentration changes do not yet have a decisive effect, the rate of the anodic process in the same potential depends on the NaCl concentration.

At a certain potential and current density, the values of which also depend on the electrolyte concentration, a slowing-down in the rate of solution appears, which is associated with the partial passivation of the electrode. A current, only a little less than the maximum for the active state, flows through the electrode in the passive state. With the same potential the rate of iron ionization in the active dissolution region increases with an increase in the NaCl concentration, but in the passive region the reverse is true. It can be concluded from this that the role of the chlorine anions in dissolution differs in the active and passive states, and therefore, separate examinations of the process in different parts of the dynamic potential curve should be made. Since, however, the changes in the layer close to the electrode and on the electrode surface which lead to passivation perhaps build up even during

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 5, No. 2, pp. 221-225, February, 1969. Original article submitted July 16, 1968.

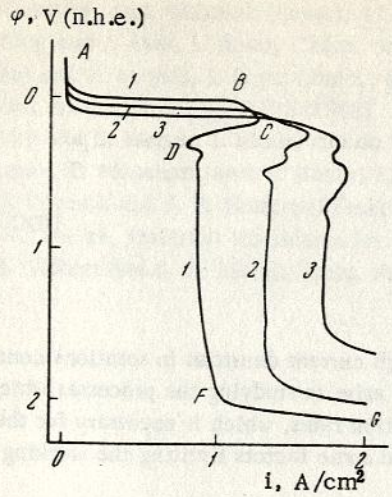

Fig. 1. Dynamic potential polarization curves plotted for an iron electrode in NaCl solutions: 1) 4; 2) 2; 3) 1 N solution.

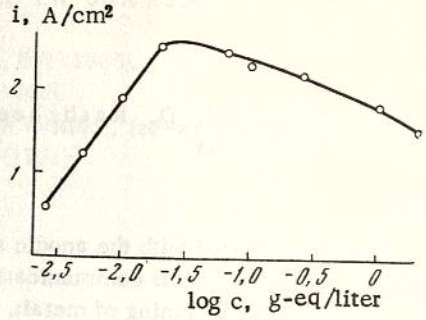

Fig. 2. Current maximum, before the onset of passivation, during dissolution of an iron electrode, as a function of the concentration of NaCl additions to a 2 N solution of $NaClO_4$.

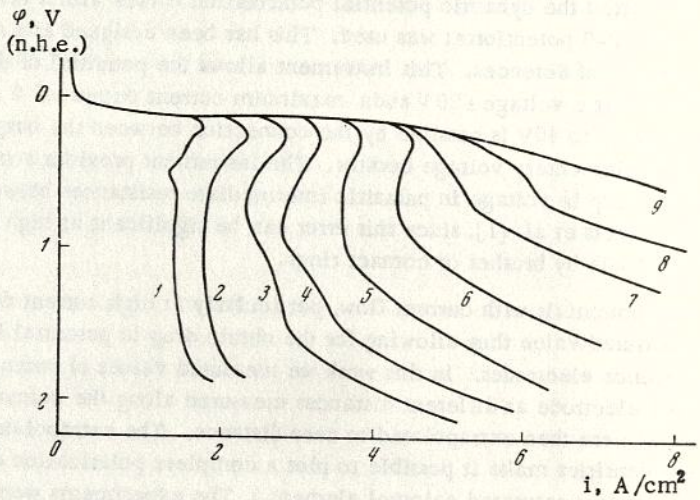

Fig. 3. Dynamic potential polarization curves, plotted for a rotating iron disc electrode in a 2 N solution of NaCl at the following rotation rates, rev/min: 1) 0; 2) 310; 3) 550; 4) 700; 5) 1000; 6) 1300; 7) 1850; 8) 2200; 9) 4400.

active dissolution, the connection between the process in the active and passive states may be found to explain the reasons for the transition from one state to the other.

In a number of experiments it was observed that the stage of anion adsorption occurs prior to the stage at which the metal passes into the solution [5-7]. The anodic dissolution rate of the metal at a constant potential is thus found to be proportional to the concentration of these ions in the electrolyte. It can be assumed that, during the passage of the current, the chlorine ions are adsorbed on the surface of the iron (in this case the anion can displace the oxygen from the surface and in this way activate the iron electrode), and form, with the surface iron atoms, particles of an activated complex which are also destroyed on the electrode. If this mechanism is accepted then the deficiency of Cl^- ions must be taken as the first possible reason for the limitation in current. An explanation is then required for the inverse dependence of the current density at which the abrupt slowing-down of the process occurs on the electrolyte concentration.

It should be noted that we observed this in the region of high NaCl concentrations. It was not possible in our apparatus to use less-concentrated solutions because of their high specific resistances. We therefore conducted experiments with low NaCl concentrations in a supporting electrolyte of 2 N sodium perchlorate, in a range of potential more negative than that at the onset of anode activation of the iron by ClO_4^- ions [8]. ClO_4^- ions can be considered in the first approximation as unreactive with respect to the iron electrode in this region of potential. It was found that the dependence of the maximum current value, before electrode passivation, on the Cl^- concentration of the solution passes through a maximum. With low concentrations of the NaCl additions (up to 0.02 g-eq/liter) the maximum current value increases rapidly with the Cl^- concentration, but at high concentrations it slowly decreases (Fig. 2). It was found that the chlorine ions facilitate the dissolution of iron, but at a sufficiently high concentration their presence causes a deceleration in the process thus facilitating passivation. This indicates, in support of the hypotheses, the direct part played by the Cl^- ion in the electrochemical reaction.

Figure 3 shows the polarization curves for iron dissolution in a 2 N NaCl solution at various rotation rates of the disc electrode. With an increase in the rotation rate, on the one hand, the region of active dissolution is extended to higher current densities. The potential at the beginning of passivation shifts slightly towards positive values and the current density for the passive iron dissolution increases. On the other hand, and this is particularly interesting, the region of potentials in which the dissolution of passivated iron occurs with a comparatively steady current density is retained; and high current densities can be obtained with less positive potentials. As a result of the simultaneous appearance of these two tendencies with an increase in the mixing rate in the solution, the dynamic potential curve is straighter and at the highest rotation rates used by us an almost complete removal of passivation limits occurs up to a current density of 8 A/cm^2.

From the results of such experiments it is possible to evaluate the optimum value of the electrolyte flow rate for the removal of the passivation limits. This can be used in calculating the flow rate necessary for obtaining a given current density using a specific power source. From this point of view (neglecting the role of the flow in cooling the working zone and clearing a narrow interelectrode gap from the slurry and gas bubbles formed during the operation of an electrochemical lathe) it is not expedient to increase this electrolyte flow rate.

It should be noted that during rotation, started not at the beginning of the experiment but at those potentials at which passive iron dissolution occurs, on uneven current increase is observed. Considering this, it must not be assumed that passivation here is caused by the formation on the iron conductivity or by a change in the properties of the surface oxide phase. Evidently, the transition of the iron electrode into the passive state occurs during the accumulation of dissolution products in the layer close to the electrode.

Some similarity to zinc passivation in alkali solutions described in [9] is observed in our experiments. It was found in [9] that the transition into the passive state is associated with the value of the relative concentration of reaction products (zincate and the original material, the alkali). But in the case of iron passivation in NaCl solutions, as well as the decelerating effect of the reaction products (basically divalent iron), there is a decelerating effect of the Cl^- ions if their concentration is too great. The role of the concentration changes in the electrolyte layer close to the electrode is significantly greater than in the case of the zinc. The presence of chlorine ions, instead of the OH^- ions in the case of zinc, also contributes to the significant differences.

Thus, the rate of anodic solution of an iron electrode in NaCl solutions is determined by the rate of discharge of the iron ions from it and by the supply of salt anions to it; i.e., by conditions of convective diffusion.

LITERATURE CITED

1. L. L. Knots, A. G. Pshenichnikov, V. V. Kushnev, and V. N. Alekseev, Author's Certificate No. 208324, Report No. 3 (1967).
2. B. N. Kabanov, Zh. Prikl. Khim., 11, 1424 (1938).
3. E. Lange, Proc. CITCE, Milan, 1950, 2, 391 (1951).
4. M. Breiter and T. Guggenberger, Z. Elektrochem., 60, 594 (1956).
5. B. V. Érshler, Zh. Fiz. Khim., 18, 131 (1944).
6. B. N. Kabanov and D. I. Leikis, Dokl. Akad. Nauk SSSR, 58, 1685 (1947).
7. V. V. Losev and A. I. Molodov, Dokl. Akad. Nauk SSSR, 130, 111 (1960).
8. V. D. Kashcheev, B. N. Kabanov, and D. I. Leikis, Dokl. Akad. Nauk SSSR, 147, 143 (1962); B. N. Kabanov and V. D. Kashcheev, Dokl. Akad. Nauk SSSR, 151, 883 (1963).
9. T. I. Popova, V. S. Bagotskii, and B. N. Kabanov, Dokl. Akad. Nauk SSSR, 132, 634 (1960); Zh. Fiz. Khim., 36, 1432 (1962).