ANODIC DISSOLUTION OF DEEPLY PASSIVATED ZINC IN ALKALINE SOLUTION SUPERSATURATED WITH ZINCATE

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The independence of the rate of dissolution of deeply passivated metals on potential, determined with the help of potentiostatic measurements, has been explained by many authors [1] by the fact that in this region of potentials, the rate of anodic oxidation of metal is limited by the rate of chemical dissolution of the film formed on the surface of the electrode. In the case of iron covered with a passivating oxide layer and in an alkaline solution of chloride, an alternative mechanism was proposed for anodic dissolution, according to which, in the electrochemical act, positively changed ions of metal are transferred into the solution from the oxide film [2].

In our investigations [3] it has been established that, in the case of zinc, during depassivation in solutions of pure alkali, and also in solutions of alkali containing zincate, the rate of anodic dissolution of zinc in a definite region of potentials also does not depend on the value of the potential. The task of the present investigation was to study the mechanism of anodic dissolution of a metal in this region of potentials using the example of zinc. In some of the experiments, the conditions were chosen so that chemical dissolution of the film was excluded. In fact, supersaturated solutions of zincate were used in which the oxide film did not dissolve. Potentiostatic curves were recorded on rotating disc zinc electrodes. Prolonged passivation of the zinc electrodes was carried out at various constant potentials from −0.9 to 1.0 V (normal hydrogen electrode) with the analysis of the zincate solution before and after passivation, and also with the determination of the weight losses of the zinc electrode during the removal from them of the oxide film by dissolution in the alkaline solution. On the basis of these data, a balance was established for the consumption of electricity in the formation of the film and in the anodic dissolution of zinc. Also, measurements were carried out of the capacitance and ohmic constituents of impedance of the zinc electrode at various frequencies of alternating current from 500 to 50,000 cps. The impedance was measured using an ac bridge R-568 by the method used for solid electrodes [4]. The electrodes had the form of a wire of diameter 1 mm pressed in a teflon holder.

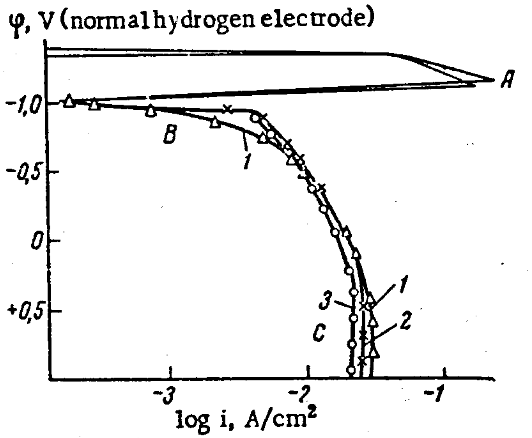

Fig. 1. Potentiostatic anodic curve recorded on a Zn electrode in supersaturated solutions of zincate with various concentrations of free alkali with mixing of 1000 rev/min: 1) 0.65 mole/kg ZnO, free alkali 2.05 mole/kg KOH; 2) 6.2 mole/kg ZnO, free alkali 9.1 mole/kg KOH; 3) 6.7 mole/kg ZnO, free alkali 9.1 mole/kg KOH (curve obtained analytically).

Figure 1 shows potentiostatic anodic curves recorded on a rotating zinc electrode in solutions of zincate saturated in relation to the material of the oxide film forming on the surface of the zinc electrode. The solutions contained free KOH from 2 to 9 mole/kg. During the setting in of passivation (point A Fig. 1) a decrease in the rate of dissolution of the passive zinc took place at approximately four times the rate found by extrapolation of this potential for the direct dependence of log I on φ for dissolution of active zinc. At point B (Fig. 1) from −1.0 to −0.8 V (normal hydrogen electrode) there is observed a linear dependence between φ and log I with a gradient of 0.15-0.2 V. It has been proposed that in this region the rate of the process is limited by the electrochemical dissolution of metallic zinc. During deep passivation in the region of potentials from 0.2 to 1.0 V (point C), the rate is practically independent of potential. In the region C, the rate of dissolution does not depend either on the composition of the solution (Fig. 1) or on the rate of mixing of the electrolyte.

Since, in supersaturated solutions of zincate, the rate of chemical dissolution of the oxide film on passive zinc is zero,

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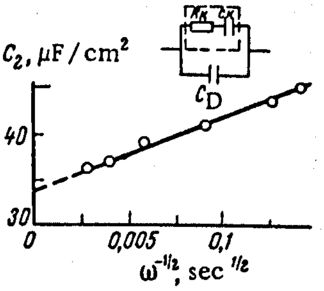

Fig. 2

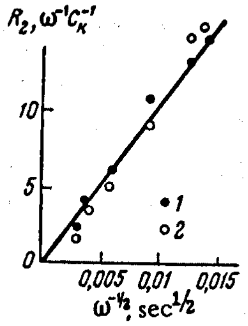

Fig. 3

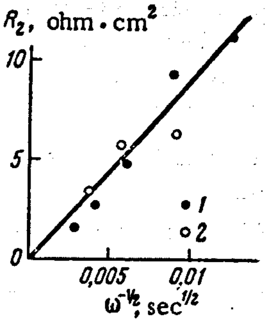

Fig. 4

Fig. 2. Relationship of capacity C_2 with $\omega^{-1/2}$ for the zinc electrode at a potential of 0.2 V.

Fig. 3. Relationship of resistance R_2 (1) and $\omega^{-1}C_K^{-1}$ (2) with $\omega^{-1/2}$ for the zinc electrode at a potential of 0.2 V.

Fig. 4. Relationship between the resistance R_2 and $\omega^{-1/2}$ for a zinc electrode at a potential of 0.2 V in 1 M KOH saturated with zincate (1) and 11.7 M KOH saturated with zincate (2).

we may accurately determine the consumption of electricity in the formation of the solid phase—oxide film—and in direct electrochemical dissolution of zinc, not passing through the stage of formation of zinc oxide.* Calculations of the balance of the quantity of material and the electricity show that, in direct electrochemical dissolution of zinc in saturated solutions of zincate, about 80% of the total quantity of electricity is consumed and the remaining 20% goes into the thickening of the film. From the above it follows that in the region C, in which there is formed on the electrode relatively thick phase films, the direct electrochemical dissolution of metallic zinc, in spite of the presence of the film, is not stopped, and takes place with a constant rate not depending on potential.

It is natural to propose that the rate of anodic dissolution of zinc in saturated solutions is limited by the rate of the processes of diffusion in the film.

The proposed existence of diffusion limitations in the solid phase may be detected by measurements of the impedance of the electrode at various frequencies of alternating current [5]. The resistance, characterizing the rate of the electrochemical process in this region of potentials, calculated from the gradient of the overpotential curve, was in our case equal to about 0.1 ohm · cm². As will be seen later on, the value of this resistance may be neglected in comparison with the value characterizing the diffusion resistance. Therefore, the electrical scheme of the investigated system zinc/oxide/solution in the indicated region of potentials may be presented (after deducting the resistance of the solution) in the form of parallel connected capacities C_D (Fig. 2, circuit), characterizing the capacity of the double electrical layer at the oxide/solution boundary† and the concentration impedance containing the values R_K and C_K. If such a scheme actually characterizes the investigated system, then during the measurements of the parallel circuit for capacity and ohmic constituents of impedance we must observe the following dependence of the measured values R_2 and C_2 with the frequency of the alternating current [5]:

$$R_2 = R_K = A/\sqrt{\omega}, \tag{1}$$

$$C_2 = C_D + 1/(A\sqrt{\omega}), \tag{2}$$

$$R_K = 1/(\omega C_K), \tag{3}$$

where $C_K = C_2 - C_D$.

Measurements of the constituents of impedance on the zinc electrode were carried out in a saturated solution of zincate (6.2 mole/kg ZnO in 11.7 M KOH, concentration of free alkali 9.1 mole/kg). The electrode was immersed in the solution and at the stationary potential, the resistance of the solution in the cell was measured at a high frequency ($5 \cdot 10^4$ cps). Afterwards, on the electrode, with the help of a potentiostat, a potential of 0.2 V

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*We are neglecting the slow process of precipitation of zinc oxide from supersaturated solutions of zincate on the surface of the passive electrodes.

†By analogy with the Ag/Ag_2O/solution system [6], we can consider that the capacity of the metal/oxide boundary is large and it may be neglected in comparison with the capacity of the oxide/solution boundary.

(normal hydrogen electrode) was established and maintained, corresponding on the potentiostatic curve to the part C (Fig. 1). When the electrode had been maintained for 1 h at a potential of 0.2 V, on the electrode there was formed a layer of oxide of thickness, on the average, of up to 10^{-4} cm and the impedance of the electrode was measured in the range of frequencies $5 \cdot 10^2$-$5 \cdot 10^4$ cps.

As can be seen from Fig. 2, the measured value of the capacity C_2 depended linearly on $1/\sqrt{\omega}$. The obtained straight line on extrapolating to the values $1/\sqrt{\omega} = 0$ intersects the section corresponding to the capacity of the double layer of the investigated boundary. Figure 2 shows the relationship of the measured value R_2 with $1/\sqrt{\omega}$. The obtained straight line passes approximately through the beginning of the coordinates. As can be seen from Fig. 3, the value of R_2 (spots), in agreement with Eq. (3), coincides with the values of $1/(\omega C_K)$ (circles).

Measurements of the impedance of the zinc electrode in saturated solutions of zincate of various concentrations (1 M KOH + 0.2 mole/kg ZnO and 11.7 M KOH + 6.2 mole/kg ZnO) at a potential of 0.2 V showed that the value of the concentration resistance R_2 did not change on changing the concentration of the alkali (Fig. 4). In addition, the obtained value of the concentration resistance (15 ohm $\cdot$ cm^2 at the least frequency used) was more than an order greater than the value of the concentration resistance measured at the same frequency in 0.001 N solution of the diffusing ion [7].

On the basis of the obtained data the proposed scheme (see above) for an electrical model of the Zn/zinc oxide/solution system during the anode process at a potential of 0.2 V can be considered.

The process of anodic oxidation of zinc in the region of frequencies 500-50,000 cps is limited by the diffusion of atoms of zinc in the layer of oxide. The electrochemical process of direct transition of the metal from the oxide film into the alkaline solution by reaction (1), first proposed in a previous investigation [2], takes place at the boundary of the oxide with the solution.

LITERATURE CITED

1. K. Bonhöeffer and U. Frank, Z. Elektrochem., 55, 180 (1955).
2. L. V. Vanyukova and B. N. Kabanov, Dokl. AN SSSR, 59, 917 (1948).
3. T. I. Popova, V. S. Bagotskii, and B. N. Kabanov, Zh. Fiz. Khimii, 36, 1432 (1962); T. I. Popova, N. A. Simonova, and B. N. Kabanov, Élektrokhimiya, 2, 1476 (1966).
4. D. I. Leikis and B. N. Kabanov, Tr. In-ta fiz. khimii, No. 6, 5 (1957); E. A. Budnitskaya, D. I. Leikis, É. S. Sevast'yanov and A. I. Shurpach, Élektrokhimiya, 2, 501 (1966).
5. D. I. Leikis, Élektrokhimiya, 1, 472 (1965); G. L. Vidovich, D. I. Leikis, and B. N. Kabanov, Dokl. AN SSSR, 412, 109 (1962).
6. G. L. Vidovich, Dis., In-t Élektrokhimii AN SSSR, Moscow (1962).
7. B. V. Érshler and K. H. Rozental', Tr. Soveshchaniya po Élektrokhimii, Moscow (1953), p. 446.