INVESTIGATION OF THE MECHANISM OF THE CORROSION OF ZINC USING A ROTATING DISC ELECTRODE WITH A RING

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Application of the method of a rotating disc electrode with a ring for determining the rate of the chemical dissolution of zinc and of the oxide layer on it is proposed and examined, using the example of zinc in alkali solutions.

The method of a rotating disc electrode with a ring permits separating out from the total current of an electrochemical reaction that part which is accompanied by the formation of ions in the solution [1, 2]. In corrosion investigations by this method, in principle, qualitative and quantitative determinations can be made of the intermediate and final corrosion products, if they are found in the solution, as well as the rates of chemical and electrochemical dissolution of the metal and the oxide layer on it, and of the mechanism of steady state dissolution. * In conjunction with oscillographic and polarographic methods, it becomes possible to investigate unsteady-state transitory processes which, in many cases, yield information on the mechanism of the process (for example, on the mechanism of passivation [4], and on the step-wise mechanism of dissolution [5]). We shall consider here certain corrosion problems, using the example of zinc in an alkali solution.

METHOD

The apparatus used was analogous to that described in [4]. The rotating disc electrode and the ring were made of Brand TsO zinc. The diameter of the disc was 0.5 cm, and the inner and outer diameters of the ring were 0.55 and 0.72 cm, respectively. In the ring, using a type TsLA PO 51-22 oscillographic polarograph, oscillograms were taken of the reduction of zincate ions formed during the dissolution of the zinc. A second such polarograph was used for the polarization of the disc. This polarograph had a device permitting it to complete previously determined jumps from one potential to another after a time of 0.05 sec. The auxiliary electrodes were large plates made of platinized platinum, located beyond the stopcocks. The potentials measured and given below are referred to an oxide–mercury electrode in a 0.1 N solution of KOH.

The experiments were carried out in an atmosphere of purified argon. The reagents used were chemically pure, and the caustic potash was specially pure. The electrode being investigated was cleaned before the experiment with a fine moist glass powder; it was then reduced with a cathode current at a potential of −1.4 V. In carrying out the work, special attention was paid to maintaining laminar conditions and steady-state convective flow conditions, to the polishing of the surface of the electrode, and to the elimination of vibration in the rotation, etc. The coefficient of convective transfer N from the disc to the ring was calculated using the equation of Levich and Ivanov [6], with the additions proposed later [7]:

$$N = 0.133 \ln \frac{K^3 + X^3}{(K + X)^3} + 0.266 \sqrt{3} \arctan \frac{2x - K}{K\sqrt{3}} + 0.241,$$

where $K^3 = 1 - 3/4\ (r_1/r_2)^3$, $X^3 = (r_3/r_2)^3 - 1$, r_1 is the radius of the disc; r_2 and r_3 are the inner and outer radii of the ring. For an electrode of our parameters, N = 43%.

In view of the fact that the steady-state rate of transfer established itself in only 1 sec after the potential was switched on, the comparison of the currents in the disc and in the ring was made at $t > 1$ sec (this question will be examined in more detail in a subsequent communication).

* In a recently published work [3] a description is given of the application of a disc with a ring to an investigation of the mechanism of the selective corrosion of binary alloys.

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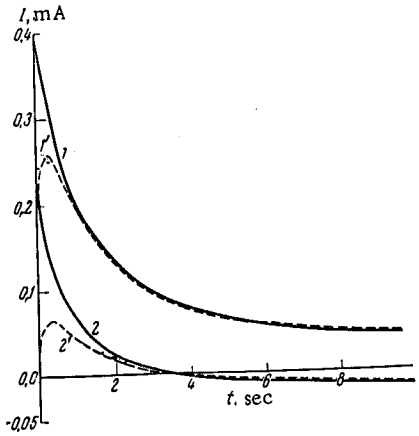

Fig. 1

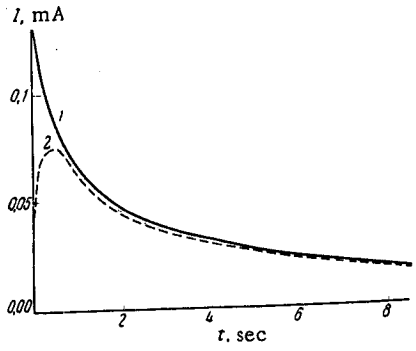

Fig. 2

Fig. 1. Surges of the current in the disc (1, 2) and in the ring (1', 2') with switching of the potential of the disc from −1.20 to −1.15 V (1 and 1') and from −1.15 to −1.10 V (2 and 2').

Fig. 2. Surges of the current in the disc (1) and in the ring (2) with switching of the potential in the disc from −0.9 to 0.8 V.

Determination of the rate of Chemical Dissolution of the Oxide Films on the Electrode

If the previously oxidized disc is not subjected to polarization, then, from the polarogram of the dissolution products, taken in the ring, it is easy to calculate the rate of the chemical dissolution of the oxide. In this case, we neglect the effect of short-circuited galvanic elements, which can act in the absence of a current in the outer circuit, if the layer is insufficiently thick and dense. In our case, with Brand TsO zinc, continuously oxidizing from the surface, such elements are evidently absent. The limiting currents in the ring, determined by this method, and the corresponding rates of the chemical dissolution of the oxide formed in air on the surface of the zinc disc in different solutions, are given in Table 1.

As is evident, the rate of dissolution of the oxide layers increases with the transition from LiOH to NaOH to KOH, and falls sharply with a decrease in the activity of the alkali.

The data given in Table 1, particularly those obtained at small concentrations of the alkali, are slightly on the high side, due to the small cathode current of the background, which is very difficult to get rid of completely, but which can be partially taken into account by measuring it separately. If measures are taken to strongly decrease the background current, or to take into account, the current in the ring in 0.1 N KOH is found to be equal to 0.05 ± 0.01 mA. In the case when the oxide layers on the disc are formed by anode oxidization of the zinc, the current in the ring does not depend on the potential at which the oxide was formed, and is 0.04 mA.

TABLE 1

Solution	Current in ring, mA	Rate of chemical dissolution, mole/cm^2·sec
1 N LiOH	0,40	$2{,}0\cdot10^{-8}$
1 N NaOH	0,45	$2{,}2\cdot10^{-8}$
1 N KOH	0,81	$4{,}0\cdot10^{-8}$
0.1 N KOH	0,07	$3{,}5\cdot10^{-9}$

The rate of dissolution does not depend on agitation (at a rate of rotation of the disc greater than 350 rpm). Consequently, under the given conditions, the process of chemical dissolution takes place with kinetic control.

Investigation of the Mechanism of Dissolution of Passive Zinc

Two possible mechanisms are known for the dissolution of passive metals. In one case the process consists of two stages: electrochemical formation of the oxide, and its chemical dissolution. In this case, it is usually assumed that the steady-state rate

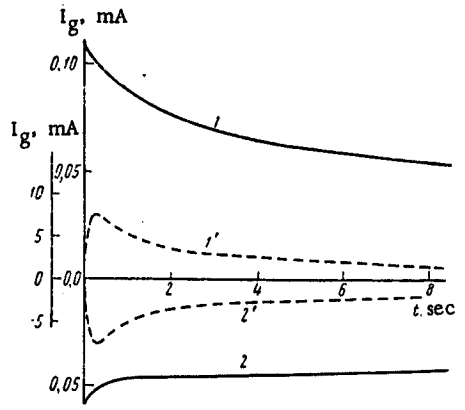

Fig. 3

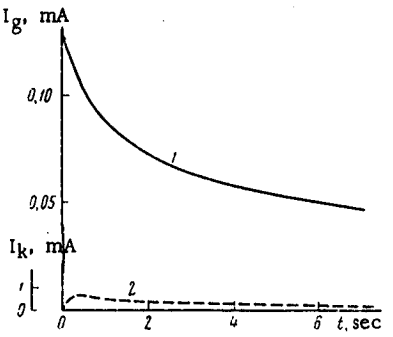

Fig. 4

Fig. 3. Surges in the current in the disc (1, 2) and in the ring (1' and 2'), with switching of the potential in the disc from 0.4 to 0.5 V (curves 1 and 1') and from 0.5 to 0.4 V (curves 2 and 2').

Fig. 4. Surges of the current in the disc (1) and in the ring (2), with switching of the potential in the disc from 1.0 to 1.1 V.

of dissolution is determined by the rate of the chemical reaction [8-10]. The second path is electrochemical passage of ions from the crystal lattice of the metals into solution. Here the role of the oxide film consists of a change in the rate of the basic process [10-14].

Comparison of the current passing through the passive anode under consideration and of the rate of the direct passage of the ions of the metal into solution in certain cases offers the possibility of indicating by which of the above mechanisms the dissolution of the passive metals takes place, and what the role of the oxide layer is in this process [15]. Actually, if it is a question of the first path, the steady-state anode current of the dissolution of the passive metal, determined in the disc, should be equal to the rate of the chemical dissolution of the oxide layers. If the process takes place even partially by the second path, then the steady-state anode current in the passive disc should exceed the rate of chemical dissolution of the oxide film, and the current in the ring should increase with the application of the anode current for the passive disc. Such a result was obtained by this method for the case of zinc in 0.1 N KOH, in the region of potentials from −1.3 to −0.2 V.

Steady-state measurements, however, are rendered difficult by the smallness of the currents in the dissolution of difficultly-soluble oxides, and by the necessity for the careful exclusion of background currents. In this sense, the most convenient variant of the method is that using steady-state currents [3], since in this case background currents are automatically eliminated.

As an example, Figs. 1-4 show typical curves of the change in the unsteady-state component of the current with time, taken in the ring and in the disc in 0.1 N KOH, with an abrupt shift of the potential of the disc by 50-100 mA to the side of more positive or more negative values. The potential in the ring electrode was always equal to −1.45 V, and the speed of rotation to 1000 rpm. The currents in the ring shown on the graphs for convenience of comparison with the currents in the disc (solid lines), are converted by 100% (dotted lines) (taking account of the transfer coefficient and of the number of electrons participating in the reaction).

In the region of active dissolution (Fig. 1), and with shallow passivation (Fig. 2) almost all of the unsteady-state current (with an accuracy up to 5%) is expended in the direct electrochemical dissolution of zinc, and not in the formation of the oxide layer. In the region of deep passivation, from 0.5 to 1.1 V (Figs. 3 and 4), on the contrary, there is not registered in the ring a large part of the surge of the unsteady-state current in the disc. This and analogous data (not shown on the graphs) point uniquely to the fact that, in the region of potentials from −0.1 V (the start of the passive region) up to approximately −0.2 V, in contrast to the more anode region, dissolution of the zinc takes place mainly directly, by passing the stage of the formation of a surface oxide. The boundary between the above regions is not sharply marked. Its

position can change depending on the prehistory of the sample. In the transition region of potentials, under certain conditions, there can exist such a state of the surface that the reactions proceed by the two mechanisms in a parallel manner. The transition to the second region in 0.1 N KOH is irreversible. In order that in an electrode, stabilized in the second passive region, there may exist the dissolution mechanism distinctive of the first region, the metal must be cleaned of oxides.

CONCLUSIONS

The expediency of using the method of a rotating disc electrode with a ring for investigating corrosion processes has been shown.

By this method, the difference in the mechanism of the dissolution of passive zinc in 0.1 N KOH has been demonstrated. In the region of potentials from the start of passivation up to approximately −0.2 V, almost all (with an accuracy up to 5%) of the unsteady-state anode current goes into the direct passage of the metal ions into solution. In the region of potentials more positive than +0.5 V, on the contrary, a large part of the unsteady-state anode current goes into a change of the thickness of the oxide. Consequently, at these potentials, dissolution of passive zinc takes place mainly through the stage of the electrochemical formation and chemical dissolution of the surface oxide.

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