USE OF A ROTATING DISC ELECTRODE WITH RING TO STUDY THE MECHANISM OF THE PASSIVATION OF METALS

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The production of passivity when a quantity of electricity corresponding to the adsorption of only a monolayer of oxygen on the active metal electrode is passed through the electrode is usually taken as proof of an adsorption mechanism of passivation [1]. This criterion is not quantitative in those cases where the true magnitude of the surface area of the metal is unknown. Moreover, it is inapplicable if the production of passivation on an oxide electrode is being studied. Another method recently proposed for studying the mechanism of passivation involves comparison of the nonstationary anodic current with the rate of the direct transfer of metal ions to the solution, determined using radioactive isotopes. By this method it has been possible to obtain quantitative proof of the adsorption mechanism of passivation on iron in sulfuric acid [2]. Unfortunately, this method can be applied only to metals which have a suitable radioactive isotope.

In the present paper we propose a method which is free from the above disadvantages. It is based on the use of a rotating disc electrode with ring [3] to determine the nonstationary rate of dissolution of metals. The latter is readily determined quantitatively if the dissolving metal is used as the disc, and the products of dissoltuion are recorded polarographically at the ring. It is convenient to maintain throughout at the ring electrode a potential corresponding to the limiting current on the polarogram, and to compare the current peaks above their stationary values on the two electrodes, produced when the potential is switched over on the disc.

The measurements were made on Ts-0 grade zinc electrodes in 0.1 N KOH solution saturated with argon in the cell represented in Fig. 1. "Highly pure" grade alkali was used. The rate of rotation of the electrode was 1000 rpm. The potential at the disc was applied by means of a potentiostat and three-electrode scheme relative to a large auxiliary electrode of platinized platinum. The current was recorded with an S1-4 oscillograph. A potential of −1.45 V (the potential was measured and given relative to a mercury oxide electrode in 0.1 N KOH), corresponding to the limiting current for the reduction of zincate ions, was applied to the ring electrode. The change in current with time was recorded using a modified 03 model PO 51-22 oscillographic polarograph. The polarograph was modified to make it possible to achieve a previously determined switch-over of potential from one value to another in 0.05 sec. Before the experiment the electrodes were cleaned with fine moist glass powder. In every case the measurements were begun in the range of active dissolution of zinc (from −1.3 to −1.1 V) and were gradually moved into the range of the passive state up to −0.1 V.

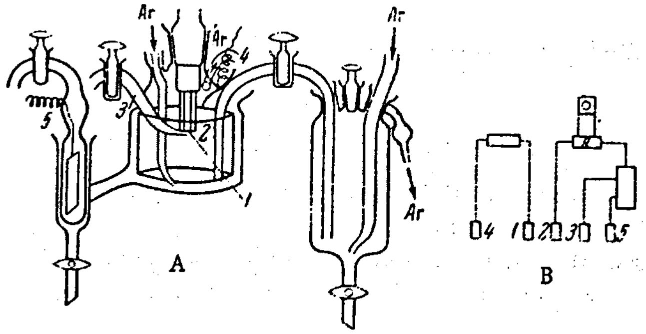

Fig. 1. A) Diagram of instrument; B) electrical circuit: 1) Ring, 2) disc, 3) reference electrode, 4, 5) auxiliary electrodes.

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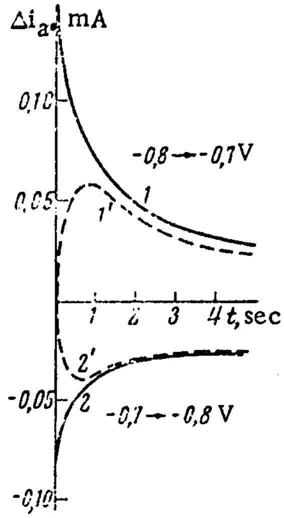

Fig. 2. Current peaks at the disc (solid lines) and at the ring (broken lines) when the potential at the disc was switched over from −0.8 to −0.7 V (curves 1 and 1') and from a potential of −0.7 to −0.8 V (curves 2 and 2').

Figure 2 gives typical current peaks obtained for the disc (solid curves) and for the ring (broken curves) when the potential at the disc was switched over towards more anodic (1 and 1') and more cathodic (2 and 2') potentials. These curves refer to the passive range (potential between −0.7 and −0.8 V). In all cases the potential was switched over by 100 mV. Hydrodynamic calculation for the rotating disc electrode with ring shows that under stationary conditions with laminar flow, convection ensures that 38-40% of the substance formed in solution at the disc electrode is supplied to the ring [3,4]. In view of this feature, the currents at the ring given in the figure are recalculated for 100% (multiplied by 2.5)* for convenience in carrying out the comparison with the current at the disc.

It can be seen from the figure that when the potential at the disc is switched over, the ring electrode shows a current peak which is directed in the same direction as that on the disc. At the same time, for zinc in the passive range (as in the dissolution of active metals) the flow of substance recorded at the ring corresponds to almost all the nonstationary anodic current passing through the disc electrode.† In the range of the start of passivation (from −1.1 to −1.0 V) the current at the disc, after increasing, decreases and acquires a value smaller than its initial value. In general, the changes in current at the ring repeat the changes at the disc. Change in the direction in which the potential at the disc is switched over produces a change in the direction of the peak on the ring, as can be seen from curves 2 and 2'. The picture observed in 0.25 and 0.5 N KOH solutions is analogous to that described above for 0.1 N KOH solution. The currents at the ring and at the disc were measured with an accuracy of up to 5-6% of the measured values.

On the basis of the results obtained it may be stated that on freshly-passivated zinc in the potential range from −1.0 to −0.1 V, with an accuracy of up to approximately 10%, the nonstationary current is used for the direct electrochemical dissolution of zinc, and not for increasing the thickness of the oxide layer. Reaction with the intermediate formation of oxide [5] is possible only within this 10%. Thus in the case of passive zinc, adsorbed oxygen for the most part is not a direct participant in the reaction, and its influence is indirect; it alters the activation energy of the dissolution process, i.e., and adsorption mechanism of passivity applies in the case of zinc. It should be emphasized that in this case the adsorption mechanism is observed under conditions in which the zinc surface may be covered with zinc oxide in quantities corresponding to a large number of monolayers [6], i.e., the presence of phase oxide on the zinc surface does not prevent the operation of an adsorption mechanism of passivation.

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*We confirmed the accuracy of this factor in our experiments with active electrodes.

†The reason for the discrepancy in the currents for times of less than 0.5 sec will be discussed in a subsequent paper.