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B. N. Bushmanov and G. S. Vozdvizhenskii

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Abstract

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Study of the Exchange Process $\mathrm{Zn} \rightleftarrows \mathrm{Zn}^{++}$ on the Faces of a Zinc Single Crystal by the Method of Radioactive Tracers

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Recently it has become increasingly clear that electrochemical processes, including those that determine the sign and magnitude of the electrode potential, depend on the crystallographic direction of the specimen ([1,2]). Previously there were only contradictory data on the potentials of single crystals of zinc, aluminum, copper, iron, and others. At present it may be considered firmly established that different faces of these single crystals have different potentials both in the absence of current and under polarization ([3–7]). The difference in potentials for different faces may reach several tens of millivolts, increasing substantially in the case of polarization as the current density is increased.

Thus it is evident that atom ⇄ ion exchange processes on different faces of metallic single crystals differ substantially both in their nature and in their kinetics. One of the methods for the quantitative study of exchange currents is the method of radioactive tracers ([8,9]). With the aid of this method, sufficiently reliable data have been obtained for cases of exchange at the amalgam-solution boundary ([10,11]). More complex relationships occur on solid metallic surfaces. Taisinskii and co-workers carried out a series of studies (([12]) and others, cited in ([14])), the aim of which was to study the relation between exchange rates and the electrode potentials of metals. The authors concluded that the atom ⇄ ion exchange reactions themselves proceed very rapidly, that they are reversible and do not depend on the metallic surface; other investigations ([13]) found that the state of the surface affects the exchange rate. Changes in exchange rates are attributed to differences in crystal structure ([14]). At the same time, considerations are expressed that exchange between a metal and radioactive ions of that metal is not the result of simple displacement associated with the electrode potential ([14]), but that in the present case exchange is complicated by adsorption and other processes taking place on the metal surface.

Experimental Part

As the object of our investigation we chose zinc single crystals. This choice was determined by the circumstance that for zinc one may expect the greatest

Figure 1

Figure 1: Figure 1

difference in the properties of different crystallographic faces (^{15}). In addition, in our laboratories other electrochemical properties of zinc single crystals have also been studied (^{3,4}). Finally, zinc has a radioactive isotope, Zn^{65}, which is convenient for radiochemical measurements.

Zinc single crystals were obtained according to a variant of the Bridgman method developed by us (^{16,17}). The basal face was exposed by breaking specimens cooled in liquid oxygen, while the prism face was cut—

by etching. The samples were then treated with sandpaper Nos. 00, 000, and 0000 and subjected to electrolytic polishing in Faust electrolyte (18).

The entire surface of the samples, except for the surface of the face under investigation, was insulated with bakelite varnish. After electropolishing of the investigated surface, the samples were kept for a definite time in a 0.03 M solution of zinc sulfate labeled with the radioactive isotope Zn^65 and washed with distilled water. In each series of experiments, 7-10 samples of each crystallographic orientation were tested simultaneously.

Fig. 1. **A**—dependence of the activity of the faces of a zinc single crystal on time; **B**—the same for samples connected in pairs: 1—basal plane, 2—prism

To illustrate the suitability of the chosen measurement method, we give the results of one group of experiments (see Table 1. In each series, 8 pairs of samples with an area of 1 cm^2 were investigated.)

Graphically, these results are shown in Fig. 1A, beginning with an exchange duration of 1 min. At exchange durations of 5 and 30 sec, a large scatter of points is obtained, which does not allow the results of these measurements to be considered sufficiently reliable.

From Table 1 and Fig. 1A it is evident that the activity acquired by the prism face is approximately 10% higher than the activity acquired by the basal plane. In itself this result may appear insufficiently convincing, since the boundaries of the error ranges for the basal plane and the prism almost touch. Note, however, that as a result of 52 series of measurements the activity of 736 samples was measured, and the mean ratio $I_{\text{pr}}/I_{\text{bas}}$ was found to be 108%.

Table 1

Exchange duration	Basal plane $I \pm \Delta I$, imp/min	Basal plane $I \pm \Delta I$, %	Prism $I \pm \Delta I$, imp/min	Prism $I \pm \Delta I$, %
5 sec.	821$±41	100±5	674±107	79±13
30»	597±55	100±9	596±71	100±12
1 min.	421±15	100±4	485±	

Note. I—mean activities acquired by the samples during the exchange process; ΔI—mean square errors of the activity measurements (19).

According to our concepts, the surface of polycrystalline zinc (after removal of the deformed layer of metal) consists of a mosaic of areas of two crystallographic faces—the basal plane and the prism—short-circuited through the body of the sample itself. It is known that the basal-plane-prism galvanic couple possesses an electromotive force (3, 4), which probably has a corresponding influence on the course of the processes determining the activity of the samples.

To test this supposition, we studied the process on samples

basis—prism, connected into galvanic couples (see Table 2. In each series, 9 pairs of specimens with an area of 1 cm^2 were studied). In Fig. 1B these data are shown graphically (beginning with 1 min). In this case the anisotropy effect is expressed more clearly than in the preceding case, and amounts to approximately 25%.

Table 2

Exchange duration	Basis, $I \pm \Delta I$, imp/min	Basis, $I \pm \Delta I$, %	Prism, $I \pm \Delta I$, imp/min	Prism, $I \pm \Delta I$, %
5 sec.	565±64	100±11	575±93	102±16
30»	444±18	100±4	539±34	121±8
1 *min.*	412±9	100±2	511±1	

It follows from the foregoing that the course of the atom ⇄ ion exchange processes on the faces of a zinc single crystal depends on the crystallographic direction. On the less densely packed prism face, which has a more negative potential, exchange proceeds more intensively.

When specimens of the basal and prism faces are connected into short-circuited pairs, which always occurs on the surface of a polycrystalline metal, the exchange equilibrium on the prism face is shifted toward the formation of ions, and on the basal face toward the formation of atoms. The influence of crystallographic orientation on the activity acquired by the specimens is manifested more sharply in this case.

Kazan Aviation Institute

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