MECHANISM FOR THE FORMATION OF INTERMETALLIC COMPOUNDS DURING THE CATHODIC PENETRATION OF ALKALI METALS

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The decomposition of cathodically formed intermetallic compounds of sodium and cadmium in 1N NaOH has been studied. The amount of sodium during the anodic decomposition of the compound changes periodically as the duration of the penetration is increased. The nature of the periodicity is found to depend directly on the structure of the cathode metal, particularly on the size of the crystal grains. It is concluded on the basis of the experimental data that the intermetallic compound forms during the cathodic instrusion of an alkali metal in the following manner: the alkali-metal atoms penetrate into the cathode interior along intercrystalline boundaries, where plane crystals of the intermetallic compound form. When the crystal grows to a point where it intersects a new grain boundary, its growth becomes retarded. The sodium penetration coefficient into cadmium during cathodic penetration is calculated to be $5 \cdot 10^{-10}$ cm^2/sec on the basis of an approximate parabolic equation for the growth during reactive diffusion.

The intermetallic compound which forms during the cathodic penetration of an alkali metal into a solid metal [1] decomposes when this metal is anodically polarized. The decomposition, like that in similar systems [2], apparently occurs through the ionization of only the alkali atoms—the more negative component.

The amount of alkali metal Q_a which ionizes can be determined from the potential vs time [$\varphi(t_a)$] curve. As was shown in [3], Q_a has a complicated dependence (including a maximum) on the duration t_c of the preliminary cathodic polarization, during which the alkali metal penetrates into the other metal.

In a continuation of the study of the formation mechanism of the intermetallic compounds, we have used the procedure of [3] to measure* the amount of anodically dissolved metal over a wider range of cathodic-polarization times, from 15 min to 5 h. Figure 1 shows the curve for cadmium, which has several maxima. The results will be discussed below in a comparison with our ideas about the mechanism for the diffusion of the alkali metal into the cathode metal.

To explain the periodic changes in the amount of alkali metal which ionizes during a monotonic increase in the duration of the cathodic polarization, we have assumed a reactive diffusion to occur along grain boundaries. The concept of a limiting reactive diffusion was used earlier to explain experimental data found in a study of alkali metal atoms through a zinc membrane [4, 1]. As is known, reactive diffusion differs from other diffusion mechanisms in that: 1) the concentration of the diffusing component does not change smoothly along the diffusion direction, but shows a jump; 2) the component usually moves through a compound much faster than through a pure metal (i.e., the process is faster than self-diffusion) [5].

*P. I. Tyaglaya assisted in the experiments.

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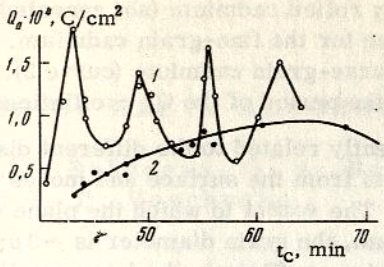

Fig. 1

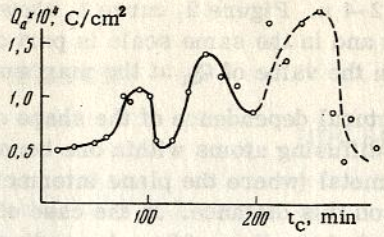

Fig. 2

Fig. 1. Dependence of the amount of anodically ionized sodium on the duration of the preliminary cathodic polarization of cadmium (in 1 N NaOH): 1) fine-grain cadmium; 2) coarse-grain cadmium.

Fig. 2. Dependence of the amount of anodically ionized sodium on the duration of the preliminary cathodic polarization of coarse-grain cadmium in 1 N NaOH.

One may suppose the following situation for the cathodic formation of an intermetallic compound and the anodic ionization of the alkali metal. As a result of ionic discharge at atomic vacancies during the penetration, the alkali atoms move into the lattice of the cathode metal and diffuse into the interior from the surface. Since the diffusion occurs primarily along grain boundaries, the crystals of the new phase are thin plates located between grains. The intermetallic crystal begins to form with the appearance of individual alkali atoms in the boundary plane. Their number at first increases (this requires an excess of energy) and then decreases, because the new alkali atoms which arrive bind the atoms already there, forming lattice nuclei which convert into structural elements of the compound having a lower molar energy.

The amount of alkali metal which dissolves during the anodic polarization is governed by the concentration of alkali metal at the electrode surface and in the interior of the elctrode; it is also governed by the alkali diffusion rate along grain boundaries of the electrode metal. This diffusion rate depends on the state of the lattice along the diffusion path, and thus on the stage at which the cathodic process stopped. If it stopped in the first stage (when the lattice elements had not yet formed), the diffusion rate* should be larger than if the cathodic process had been stopped during the second stage (when the intermetallic compound was formed), since additional energy is required in the latter case to remove the alkali metal, to disrupt the intermetallic lattice. Thus the amount of dissolved alkali metal should also depend on the stage in which the crystallization was stopped during the cathodic polarization.

The crystallization of the intermetallic compound presumably occurs in layers: the growth of each crystal plate begins only after the crystal growth in the preceding layer has been completed. As a result of this process, there is a periodic change in the number of disordered alkali atoms at the edge of the diffusion zone. This should result in a repeated wave-shaped change in the amount of anodically dissolved alkali metal which is measured (Fig. 1). The ascending branches of the $Q_a(t_c)$ curve corresponds to the stage in which nuclei are accumulating at the edge of the zone, while the descending branches correspond to a decrease in the number of such nuclei because of the formation of the ordered intermetallic lattice.†

This mechanism is in agreement with the $Q_a(t_c)$ curve's dependence on the grain size of the cathode metal. The curve shown in Fig. 1 refers to an electrode of coarse-grain cadmium. The samples were made from a metal which had been annealed after rolling, at a temperature near 200°C for 70 h. The linear

*Diffusion through a compound without a change in the latter's properties offers no difficulties in a discussion of the process as a whole.

†The slow increase of Q_a at the start of the penetration is due to the particular conditions for the formation of the first layer of the compound. This layer begins to form in a manner different from the succeeding ones: as the disordered atoms of the alkali metal accumulate, they evidently cannot be in a stable state at the electrolyte boundary, even if alkali ions are discharging. Under these conditions, only those atoms which penetrate to vacancies at sites favorable for formation of the intermetallic lattice are stable. Accordingly, Q_a increases slowly and monotonically during the formation of the first layer. It is also possible that the formation of the first crystal plates is also retarded.

dimensions of the grains of these samples reached 20 μ. For freshly rolled cadmium (not annealed), the grain size was 2-4 μ. Figure 2, curve 1, shows the $Q_a(t_c)$ dependence for the fine-grain cadmium. Shown for comparison and in the same scale is part of the curve for the coarse-grain cadmium (curve 2). Curves 1 and 2 differ in the value of Q_a at the maximum and, especially, in the period of the Q_a oscillations.

The structural dependence of the shape of the curves is apparently related to the different distances covered by the diffusing atoms within one boundary plane which starts from the surface and moves into the interior of the metal (where the plane intermetallic crystal forms). The extent to which the plane crystal grows depends on this distance. In the case of the fine-grain cadmium, the grain diameter is $\sim 3\mu$; for the coarse-grain cadmium, it is $\sim 20\mu$. Accordingly, for the same diffusion coefficient, the intermetallic crystals in the fine-grain cadmium should grow an average of seven times as fast as in the coarse-grain cadmium. Figures 1 and 2 reflect this expected dependence of the $Q_a(t_c)$ curve on the structure: the oscillation periods differ by a factor of about seven. In light of the assumptions made, this agreement may be considered semiquantitative confirmation of the mechanism outlined above.

According to the known parabolic growth law for the intermetallic phase during reactive diffusion [6], the thickness a of the growing layer has the time dependence

$$a^2 = Pt, \tag{1}$$

where P is the penetration coefficient, which is of the same order of magnitude as the diffusion coefficient, and t is the duration of the diffusion. Neglecting diffusion into the interior of the small metal crystals, assuming that the thickness a is essentially equal to the diameter of the cathode-metal grain, and assuming that the time required to form a layer of this thickness is governed by half the distance between the two minima on the $Q_a(t_c)$ curve, we can determine the sodium penetration coefficient into cadmium from Eq. (1). For coarse-grain cadmium, we have

$$P_c = \frac{a^2}{t} = \frac{(2\cdot 10^{-3})^2}{45\cdot 60} = 14\cdot 10^{-10}\ \text{cm}^2/\text{sec};$$

for fine-grain cadmium, we have

$$P_f = \frac{a^2}{t} = \frac{(3\cdot 10^{-4})^2}{3\cdot 60} = 5\cdot 10^{-10}\ \text{cm}^2/\text{sec}.$$

Accordingly, the penetration coefficient calculated for the fine-grain cadmium is approximately $5\cdot 10^{-10}$ cm^2/sec, and that for the coarse-grain cadmium is slightly higher, if this mechanism for the growth of the intermetallic phase is assumed (i.e., that it grows, not monotonically, at a grain boundary, but is stopped at intersections of grain boundaries).

There are experimental data available for the rate at which a cathodically-penetrating alkali metal diffuses into a cathode metal. According to these data, the sodium diffusion coefficient in lead is $4\cdot 10^{-11}$ cm^2/sec [7], and that for potassium in zinc is $7\cdot 10^{-12}$ cm^2/sec [4]. Taking into account the great difference between the diffusion coefficients for various metals, we can conclude that these experimental values are close to that calculated in this paper for sodium in cadmium. This supports the use of the above mechanism for the formation of an intermetallic compound during cathodic penetration to calculate the penetration coefficient P.

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