KINETICS OF β-PHASE FORMATION DURING THE CATHODIC INCORPORATION OF LITHIUM INTO ALUMINUM FROM NONAQUEOUS SOLUTIONS

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It had been shown previously that lithium diffusion in the intermetallic compound LiAl is very fast. Values of 10^{-8} [1], 7×10^{-6} [2], and even 5×10^{-5} cm^2/sec [3] are reported for the diffusion coefficient of lithium in LiAl at temperatures around 500°C.

In the present work we report results obtained when studying the kinetics of formation of the intermetallic compound LiAl (β-phase) during the cathodic incorporation of lithium into aluminum from propylene carbonate solutions of lithium perchlorate at room temperature.

The electrodes were made from aluminum wire (0.12 cm diameter) and foils (thicknesses of 930 and 10 μm). The purity of the aluminum was 99.99%. The procedures used to purify lithium perchlorate and propylene carbonate have been described in the preceding paper [4]. Reference electrode was a silver–silver chloride electrode in 1 N lithium perchlorate solution in propylene carbonate saturated with lithium chloride. The potential of this electrode against the Li/Li^+ electrode is 2.85 V. All values of potential in the work are reported relative to the Li/Li^+ electrode. The measurements were done with potentiostats P-5848 and P-5827M. Current and potential were recorded as functions of time with potentiometers KSP-4 and PDP4.

The growth rate of the layer of intermetallic compound LiAl was determined from the time of complete conversion of the aluminum electrode to intermetallic compound during the cathodic incorporation of lithium into aluminum. Electrodes made of foil with thickness $\delta = 930$ μm had a surface area of 1.0×0.5 cm^2, those made of foil with thickness $\delta = 10$ μm had an area of 1.3×0.5 cm^2.

Incorporation was performed at potentials between 0.050 and 0.250 V. The average current density of incorporation was 1.5×10^{-3} A/cm^2. The time taken for complete conversion was determined from the cessation of cathodic current. For an electrode of 930 μm thickness this time was found to be 158 400 sec, for the other electrode (10 μm) it was 3300 sec.*

Considering that the electrodes were polarized from both sides and hence the thickness of the LiAl layer on each side was 0.5 δ, we found that the average linear rate of advance of the intermetallic compound/metal boundary during incorporation, $\nu = 0.5\,\delta/t$, was 5×10^{-7} cm/sec. Such a high rate of solid-phase formation at room temperature can be due to the fact that the process occurs without diffusion control. This was the conclusion drawn in [2] on the basis that the cathodic current remains constant for a long time during cathodic formation of β-phase in melts. However, according to [1], diffusion control is lacking in the beginning only, while with increasing time of polarization and, hence, thickness of the layer of β-phase, diffusion of lithium through this layer becomes the rate-limiting step. In fact, for the multi-step process of cathodic incorporation, a great variety of forms of kinetic control is characteristic. Depending on the changing conditions under which the process occurs, these forms may interchange [5, 6].

The nature of the slow incorporation step can be inferred from the dependence of process rate i_c on potential φ. In the case of incorporation under diffusion control, these quantities usually are linked by a quadratic relation [6]:

$$i_c = k_i \sqrt{\varphi}. \quad (1)$$

* In the experiment with foil ($\delta = 10$ μm) we measured the amount of charge consumed for LiAl formation (6.0 C). It practically coincides with the amount of charge (6.2 C) calculated to be required to transform 1.7 mg of aluminum into LiAl. This coincidence implies that LiAl formation is not attended by other electrochemical reactions.

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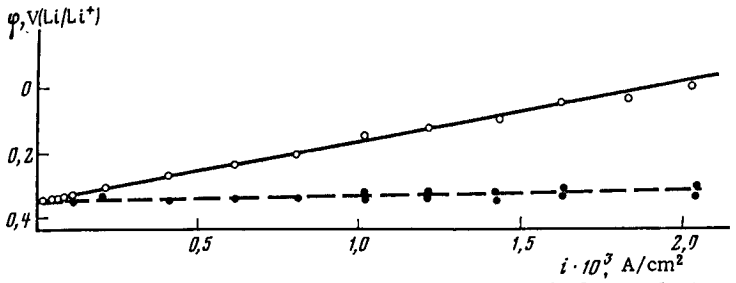

Fig. 1. Polarization curve obtained at a LiAl electrode in 1 N lithium perchlorate solution in propylene carbonate. The LiAl was obtained by prior cathodic polarization of the aluminum to a potential of 0.25 V (relative to a Li/Li^+ electrode in the same solution) lasting 90 min.

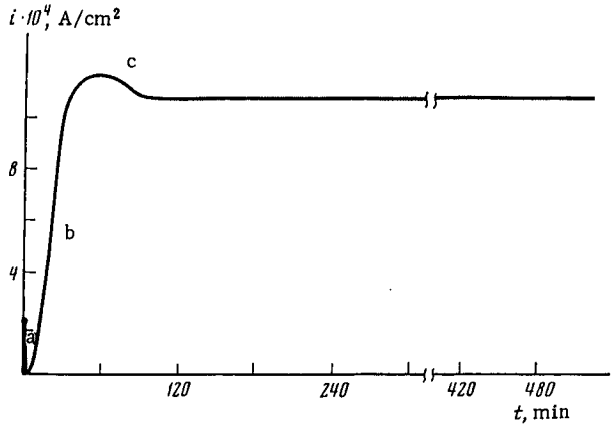

Fig. 2. Time variation of the current during cathodic polarization of the aluminum electrode to a potential of 0.11 V (n. l. e.).

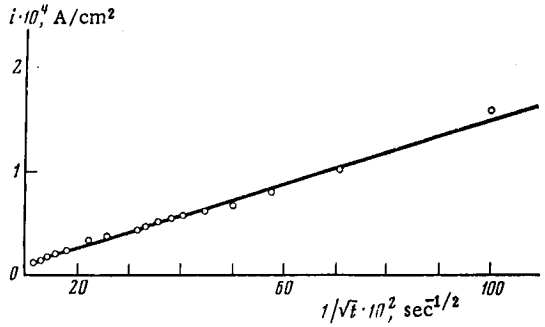

Fig. 3. Time variation of the current plotted as i_c against $t^{-1/2}$ in the initial section of the i_c vs. t curve shown in Fig. 2.

But in the case of a slow chemical reaction governing the formation of intermetallic compound at the intermetallic compound/metal interface, i_c is a linear function of φ:

$$i_c = k_2\varphi. \qquad (2)$$

Quantities k_1 and k_2 in (1) and (2) are kinetic coefficients.

For the purposes of defining the slow step of β-phase formation in the cathodic incorporation of lithium into aluminum at room temperature, we studied the incorporation rate as a function of potential in the present work, together with the time variation of the rate of incorporation of lithium into aluminum from nonaqueous solutions.

Figure 1 shows a polarization curve recorded on a preformed layer of intermetallic compound (β-phase) on the surface of an aluminum cathode. The intermetallic compound on the electrode surface was obtained by cathodic polarization of an aluminum electrode in a lithium perchlorate solution in propylene carbonate under potentiostatic conditions at a potential less positive than the equilibrium potential of LiAl. The polarization curves were recorded under steady-state conditions in the galvanostatic mode. The open-circuit potential of the electrode was measured between potential measurements under current in order to check the state of the electrode. A stable value of the open-circuit potential throughout the experiment (the dashed line in Fig. 1) implies that there was essentially no change in the state of the electrode. One can see from Fig. 1 that the incorporation current is a linear function of potential. Such a dependence indicates that the slow step of the process is the chemical step of intermetallic compound formation at the metal/intermetallic-compound interface [6, 7].

An examination of the time variation of the rate of the cathodic process also indicates that except for the initial time period, the rate of the cathodic process is limited by a chemical reaction. A general view of the time dependence of the rate of lithium incorporation into aluminum at 0.11 V is presented in Fig. 2. We see that the character of the dependence is changing with time. The complicated shape of the i_c vs. t curve indicates that the nature of the rate-limiting step is changing as the process evolves. One must note first of all that after a certain period of changes, a constant process rate is established. This is evidence that a chemical reaction rather than diffusion is limiting the growth rate of the β-phase. Before reaching a stationary mode the process exhibits a decrease in rate, then an increase and a renewed decrease (corresponding to sections a, b, and c of Fig. 2). Figure 3 shows the initial section (a) of the curve as a plot of i_c against $t^{-1/2}$. Here one can see a nicely developed linear dependence, which is evidence for diffusion control of the process in the initial period.

The change in the form of kinetic control can be explained by observing that diffusion as a reaction mechanism is possible only when the phase of intermetallic compound LiAl is present, at least in minimum quantities. It appears that generation of these minimum quantities of intermetallic compound phase constitutes the nucleation process suggested in [1].

Thus, formation of β-phase occurs without diffusion limitations (except for the initial period) during lithium incorporation into aluminum from nonaqueous solution at room temperature, just as had been found for temperatures around 500°C. The limiting step of the process is formation of the intermetallic compound LiAl. This reaction occurs with a high linear rate ($\nu = 5 \times 10^{-7}$ cm/sec). It is difficult to compare the rates of this reaction in solution and in the melt, since diffusion coefficients rather than chemical reaction rates are reported for melts in the literature; moreover, the diffusion coefficients diverge by three orders of magnitude. However, if we assume that in molten salts, the rate of lithium incorporation into aluminum also is governed by the rate of the chemical reaction and calculate the linear rate of advance of the interface from the diffusion coefficients reported in these papers, we find that our value of the rate is intermediate between the values following from the early work and somewhat closer to the results of [1].

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