Electrode process of deposition and dissolution of the Al—Pb binary system in an organic electrolyte
II. Stability of the aluminium and aluminium-lead metallic coating in ethylbenzene electrolyte

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The stability of Al and Al—Pb coating obtained from ethylbenzene electrolyte was studied in this electrolyte. The study was carried out by comparison of chronopotentiometrically obtained cathodic and anodic charge densities. It was observed that in electrolyte with lower $AlBr_3$ concentration around $1 \, mol \, dm^{-3}$ both Al and Al—Pb coatings underwent spontaneous chemical dissolution. At $AlBr_3$ concentration approx. $2 \, mol \, dm^{-3}$ this effect was minimalized. At long enough electrolysis time the anodic to cathodic charge density ratio approached one. The conditions were found leading to the depression of the spontaneous dissolution of the coating. Reactions explaining this effect were suggested.

Устойчивость Al и Al—Pb покрытий, полученных из этилбензольного электролита, изучена в этом электролите. Исследование проводилось путем сравнения хронопотенциометрически полученных величин катодной и анодной плотности заряда. Наблюдалось, что в электролите с низкой концентрацией $AlBr_3$ около 1 моль $дм^{-3}$ как Al, так и Al—Pb покрытия подвергались самопроизвольному химическому растворению. При концентрации $AlBr_3$ около 2 моль $дм^{-3}$ этот эффект был минимален. При достаточно продолжительном времени электролиза отношение величин анодной и катодной плотностей заряда достигало единицы. Определены условия, в которых подавлялось самопроизвольное растворение покрытия. Предложены реакции, с помощью которых можно объяснить данный эффект.

In the preceding part of this contribution [1] the attention was paid to the electrode reaction of aluminium and lead deposition from electrolyte consisting of $AlBr_3 + PbBr_2 + KBr$ in ethylbenzene (ETB) and to the accompanying effects. The choice of electrolyte was given by its practical applicability for Al or Al—Pb coating deposition [2]. The study of the stability of obtained coating in the electrolyte used and of factors causing its worsening is important both

from theoretical and practical standpoints. This is the subject of the present paper.

Experimental

The chronopotentiometric measurements were realized on the GWP 673 Polarograph (GDR) with a stainless-steel working electrode (surface area $0.102\ cm^2$) in three-electrode arrangement. All experiments were carried out in closed cells in inert atmosphere of dry argon. Last traces of oxygen were removed by Cherox 4300 catalyst and those of humidity by molecular sieves Nalsit A4. Purification and drying of other chemicals as well as further experimental details are given in the preceding part [1].

Results and discussion

Typical chronopotentiometric (ChP) record of the $AlBr_3 + KBr$ solution in ETB is presented by curve *1* in Fig. 1. Aluminium is deposited on the working electrode during the whole time t_K of application of the cathodic current pulse.
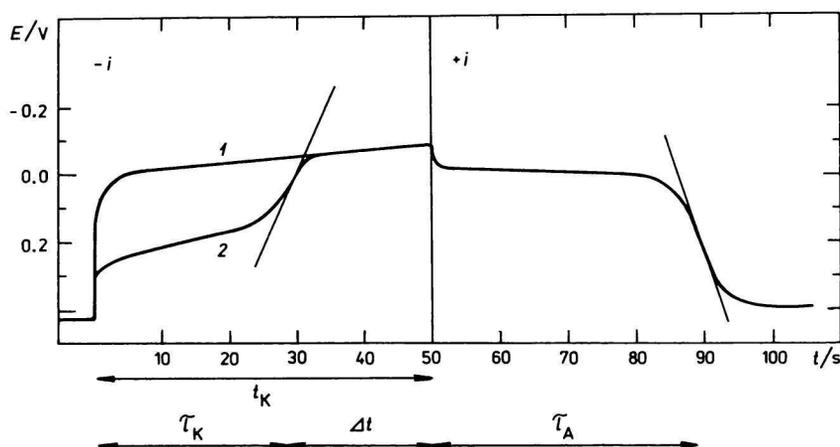
Fig. 1. Chronopotentiometric record of deposition and dissolution of aluminium (*1*) and lead (*2*). Current density pulse: $0.59\ mA\ cm^{-2}$; $c(AlBr_3)$: $1.86\ mol\ dm^{-3}$; $c(PbBr_2)$: $3.13 \times 10^{-3}\ mol\ dm^{-3}$.

Since the $AlBr_3$ concentration in the solution is remarkably high, the limiting conditions are not reached as regards the depletion of diffusion layer by depolarizer. Consequently, the cathodic transition time for Al deposition τ_K could not be observed. After reversing the current polarity, anodic dissolution of the deposited aluminium starts. The termination of this process in time τ_A is expressed by change of the working electrode potential towards the more positive values — to the steady potential of steel. If metal or other insoluble product is deposited on the electrode, the anodic transition time equals the cathodic one

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provided that both current densities are identical [3]. If the product of deposition is engaged in some follow-up reaction, *i.e.* spontaneous chemical dissolution, the τ_A/t_K ratio could not reach the value of unity. In Fig. 2 are shown the statistically treated results of a great number of ChP measurements in the above described solution. Curve *1*, corresponding to the lower $AlBr_3$ concentration shows that the τ_A to t_K ratio is constant within experimental errors with changing the electrolysis time but differs remarkably from unity: it fluctuates around the value 0.42. In more concentrated $AlBr_3$ solutions, the τ_A/t_K ratio increases with increasing deposition time and approaches the value 1 as it is demonstrated by curve *2* in Fig. 2.
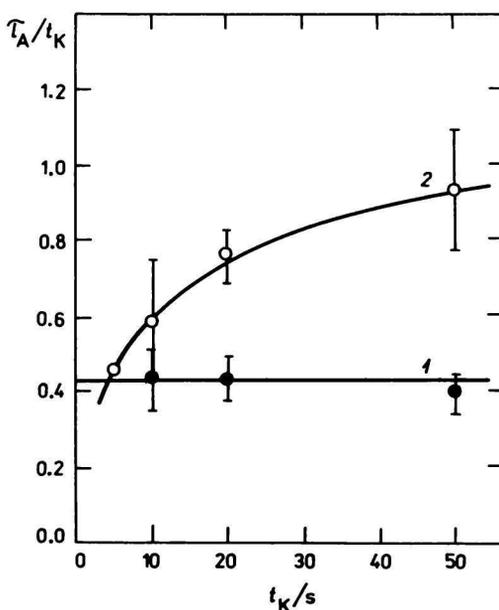
Fig. 2. Change of the ratio of dissolution time τ_A to deposition time t_K with the duration of electrolysis. $c(AlBr_3)$: *1.* $1.27\ mol\ dm^{-3}$; *2.* $1.86\ mol\ dm^{-3}$.

The calculation of the formal value of current density j_N corresponding to the follow-up chemical reaction is based on the assumption that the follow-up process proceeds during the whole time of ChP experiment, *i.e.* during the cathodic as well as anodic current pulse application. The appropriate charge densities balance equation can then be written as follows

$$Q_K - Q_A = Q_N \tag{1}$$

$Q_K = t_K \cdot j_K$ is the cathodic charge density,
$Q_A = \tau_A \cdot j_A$ is the anodic charge density,

$Q_N = (t_K + \tau_A) \cdot j_N$ is the formal charge density corresponding to the follow--up process,

j_K, j_A, and j_N are the respective current densities.

Provided that $j_K = j_A = j$, the relationship (1) may be written in the form

$$\frac{\tau_A}{t_K} = 1 - \frac{j_N(t_K + \tau_A)}{j \cdot t_K} \qquad (2)$$

The τ_A/t_K ratio differs the more from unity the higher is the rate of the follow-up reaction formally expressed by the j_N value. In order to calculate the j_N value, the following relationship was used

$$j_N = j \frac{t_K - \tau_A}{t_K + \tau_A} \qquad (3)$$

The rate of the follow-up reaction is thus proportional to the current density used. The rate of the spontaneous dissolution of Al metallic coating, *i.e.* corrosion as follow-up reaction in ETB electrolyte was calculated according to eqn (3). The statistically treated results for ETB electrolyte with lower $AlBr_3$ concentration are summarized in Table 1. The rate of chemical dissolution of Al was calculated from the formal j_N values by Faraday's law. The results obtained are given also in Table 1.

Table 1

Values of the current density corresponding to the spontaneous chemical dissolution of the Al coating (corrosion) and rate of this chemical reaction in ETB electrolyte
$c(AlBr_3)$: 1.27 mol dm^{-3}; current density applied, j: 9.82 mA cm^{-2}

Electrolysis time t_K/s	10	20	50	
Number of experiments	12	11	17	$\emptyset$
Mean corrosion current density $j_N/(mA\ cm^{-2})$	4.62 ± 0.26	3.73 ± 0.68	4.00 ± 0.17	4.12 ± 0.37
Ratio $\frac{j_N}{j}$	0.47 ± 0.03	0.38 ± 0.08	0.41 ± 0.01	0.42 ± 0.04
Mean value of the corrosion reaction rate $v_m \cdot 10^9/(g\ cm^{-2}\ s^{-1})$	43.9 ± 2.5	35.4 ± 6.4	38.1 ± 1.6	39.1 ± 3.5
$v_n \cdot 10^9/(mol\ cm^{-2}\ s^{-1})$	1.62 ± 0.10	1.31 ± 0.24	1.41 ± 0.05	1.45 ± 0.13

Similar effect in molten salts electrolyte $AlCl_3$—butylpyridinium chloride at ambient temperature was observed on tungsten [4] as well as glassy-carbon [5] electrodes; the corrosion reaction rate values in these cases were even higher

than those given in Table 1. The authors [4, 5] agree in the statement that the observed Al corrosion effects may be ascribed to the impurities present in the melt.

In electrolyte containing higher $AlBr_3$ concentration the situation is rather different. Curve 2 in Fig. 2 shows that at longer cathodic deposition times t_K the τ_A/t_K ratio approaches unity, i.e. the spontaneous corrosion reaction is suppressed under the condition of high metal concentration in the electrolyte. The difference from unity at shorter deposition times may be caused by yet another effect, for instance by formation of non-adherent aluminium coating in the early stages of electrolysis. Such effect, however, seems not to play a decisive role in the electrolyte with lower $AlBr_3$ concentration. The possibility of forming non-adherent coating at the beginning of electrolysis in electrolytes with high metal concentration is known from the galvanotechnic praxis. Thus, for practical purposes it is necessary to find the proper $AlBr_3$ concentration in order to form well adherent coating on the one hand and to avoid its spontaneous dissolution on the other.

Spontaneous dissolution of Al coating was observed also by the ChP method: after applying a certain cathodic current pulse the working electrode was left on zero current density and yet, the anodic transition time τ_A denoting the end of dissolution of the deposited aluminium appeared. Such anodic ChP curve was logarithmically analyzed and the result is shown in Part I of this contribution — curve 1 in Fig. 2 [1]. Further effect confirming the spontaneous dissolution of aluminium in ETB electrolyte was observed when leaving the aluminium counter-electrode in the electrolyte for several weeks: its corrosion was obvious and at long enough time its complete dissolution took place. Another important practical conclusion may be drawn from this effect: in the aluminium coating process from ETB electrolyte, the coated parts must be taken out from the electrolyte as soon as possible after the end of electrolysis.

The stability of the Al—Pb coating was also studied chronopotentiometrically by comparing the total deposition time t_K for both metals with the anodic transition time τ_A, as well as by comparing the corresponding charges Q_K and Q_A. The ChP record changed after adding $PbBr_2$ to the electrolyte: a cathodic transition time τ_K appeared corresponding to the deposition of Pb. On the anodic part of the ChP curve, mainly at longer deposition times, only one transition time appeared in most cases. This effect will be discussed in Part III of this contribution.

Table 2 shows that the Al—Pb coating also undergoes spontaneous dissolution. Rate of this process is independent within the experimental error of the $PbBr_2$ concentration in the electrolyte, as it is shown in part a) of the table. The ratio of the apparent current density corresponding to the rate of spontaneous corrosion process to the current density used decreases with the time of elec-

Table 2

Values of the corrosion current density for Al—Pb coatings in ETB electrolyte in dependence on PbBr$_2$ concentration, time, and current density of the coating deposition

$c(AlBr_3)$: 1.84 mol dm^{-3}

a) Current density j: 0.98 mA cm^{-2}
Deposition time t_K: 20 s

$c(PbBr_2) \cdot 10^3/(mol\,dm^{-3})$	$j_N/(mA\,cm^{-2})$	$\dfrac{j_N}{j}$
3.13	0.324	0.33
5.10	0.478	0.49
6.75	0.422	0.43
8.67	0.520	0.53

b) Current density j: 0.98 mA cm^{-2}
$c(PbBr_2)$: 5.1×10^{-3} mol dm^{-3}

Deposition time t_K/s	$j_N/(mA\,cm^{-2})$	$\dfrac{j_N}{j}$
10	0.634	0.646
20	0.478	0.487
50	0.416	0.424

c) $c(PbBr_2)$: 5.1×10^{-3} mol dm^{-3}
Deposition time t_K: 50 s

Deposition current density $j/(mA\,cm^{-2})$	$j_N/(mA\,cm^{-2})$	$\dfrac{j_N}{j}$
0.393	0.321	0.816
0.786	0.393	0.500
0.982	0.416	0.424

trolysis — see part b) of the table, and with the applied current density — part c) of Table 2. Thus, the more the electrolysis conditions prefer or fasten the electrode process itself, the less chances there remain for the proceeding of the spontaneous chemical dissolution.

The effects described may no doubt be ascribed mainly to the presence of impurities in the electrolyte. They may, however, occur also in pure electrolyte in case that an oxidizing agent is formed during the electrode process. For instance, Br$_2$ may be formed in consequence of the counter-electrode passivation or during the anodic polarization of the working electrode. The anodic dissolution of Al and Pb proceeds according to the following summary equations

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$$2Al \quad \rightleftharpoons \quad 2Al^{3+} + 6e \qquad (Aa)$$

$$2Al^{3+} + 6Al_2Br_7^- \quad \rightleftharpoons \quad 7Al_2Br_6 \qquad (Ab)$$

$$Pb \quad \rightleftharpoons \quad Pb^{2+} + 2e \qquad (Ba)$$

$$Pb^{2+} + Al_2Br_7^- \quad \rightleftharpoons \quad PbBr^+ + Al_2Br_6 \qquad (Bb)$$
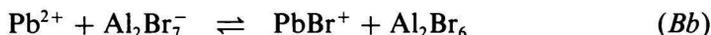
If, in consequence of low electrolyte concentration or unsuitable Al_2Br_6 to KBr ratio, the $Al_2Br_7^-$ concentration at the electrode is insufficient, concentration polarization of the electrode occurs and the process (A) cannot proceed. The electrode is passivated for Al dissolution but, for Br_2 formation in the reaction

$$2Al_2Br_7^- \quad \rightleftharpoons \quad 2Al_2Br_6 + Br_2 + 2e \qquad (C)$$
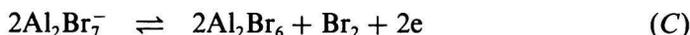
the $Al_2Br_7^-$ concentration in the electrolyte may suffice. The reaction (C) proceeds also at the counter-electrode if the Al dissolution reaction cannot proceed. The Br_2 formed passes to the working electrode by diffusion or convection.

The main impurities in the electrolyte causing the same effect of spontaneous dissolution of aluminium coating are oxygen and water molecules. Oxygen causes passivation of the aluminium electrode by forming insulating Al_2O_3 layer not to mention the possibility of direct oxidation of Br^- or $Al_2Br_7^-$ ions to Br_2 in solution. Water molecules react with Al_2Br_6 forming HBr which may attack the aluminium coating directly

$$Al_2Br_6 + H_2O \quad \rightleftharpoons \quad Al_2Br_5OH + HBr \qquad (D)$$

$$2Al + HBr \quad \rightleftharpoons \quad Al_2Br_6 + 3H_2 \qquad (E)$$
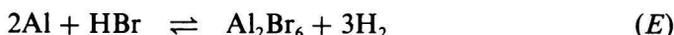
The most important conclusions that may be drawn from the results presented for practical application of the process can be summarized as follows: in order to obtain the best coating and to avoid its spontaneous chemical dissolution it is necessary to keep the electrolyte concentration sufficiently high ($AlBr_3$ at least $2 \, mol \, dm^{-3}$), the mole ratio of the components suitable ($AlBr_3$ to KBr not higher than 2), and the inert atmosphere and purity conditions rigorous. These experimental requirements were already listed in an earlier publication [6] without explaining the chemical and electrochemical nature of the corresponding processes.

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