Electrode process of deposition and dissolution of the Al—Pb binary system in an organic electrolyte
III. Anodic effects in Al—Pb binary system dissolution in ethylbenzene electrolyte

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Two peaks are observed on the anodic branch of cyclic voltammogram during the study of anodic dissolution of binary metallic Al—Pb system in organic electrolyte consisting of $AlBr_3 + PbBr_2 + KBr$ in ethylbenzene. The current, potential, and shape of both peaks are influenced predominantly by the time period starting with the onset of cathodic deposition and ending with the start of anodic dissolution of metallic phase. This time period is given by the following parameters: rate of the voltage scan, potential of reversing the polarity, *i.e.* switching potential, and time of retaining the potential on the constant switching potential value, *i.e.* retention time. The results point out the fact that at the sufficiently long time period both metals interact and the product of this interaction dissolves in one single peak.

При изучении анодного растворения бинарной металлической системы Al—Pb в органическом электролите, состоящем из раствора $AlBr_3 + PbBr_2 + KBr$ в этилбензоле наблюдались два пика на анодной ветви циклической вольтаммограммы. Величины тока и потенциала, а также вид обоих пиков определяются, главным образом, временем, прошедшим с начала катодного осаждения до начала анодного растворения металлической фазы. Этот период времени задается следующими параметрами: скоростью сканирования напряжения, потенциалом обращения полярности, т.е. потенциалом переключения, и временем сохранения постоянной величины потенциала, равной потенциалу переключения, т.е. временем удерживания. Полученные результаты свидетельствуют о том, что в течение достаточно продолжительного промежутка времени оба металла взаимодействуют между собой, и растворение продукта этого взаимодействия регистрируется в виде одного одиночного пика.

Aluminium belongs to the group of metals the deposition potential of which is much more negative than that of hydrogen. Consequently, they cannot be deposited in the form of coating from aqueous electrolyte since the deposition

of hydrogen precedes. A medium hindering the hydrogen deposition must be used, *i.e.* melt or organic aprotic electrolyte. Although lead may easily be obtained as coating from aqueous medium, a binary coating consisting of both lead and aluminium must be deposited from aprotic electrolyte. Solutions based on aromatic hydrocarbons (benzene, toluene, their mixtures or derivatives) as solvents proved to be suitable for preparing electrolyte for Al—Pb binary coating deposition [1]. Owing to a very low relative permittivity of these solvents, the solubility of commonly used ionic solutes suitable for basic electrolyte preparation is also very low. Waterfree aluminium halides, however, are of special importance in solving this problem due to unsaturation of their orbitals leading to the formation of stable ionic compounds of the type $M^+AlX_4^-$ or $M^+Al_2X_7^-$ with polar substances MX [2]*. Really, the conductivity values in the solution $AlBr_3 + KBr$ in ethylbenzene (ETB) are sufficiently high for the purpose of using this system as basic electrolyte in electrochemical studies [3].

In all electrochemical investigations in the present and preceding works [4, 5] the aluminium halide played two roles: as a component of basic electrolyte and as electroactive substance for aluminium deposition. The foregoing parts of the contribution were devoted to the study of cathodic deposition of aluminium and lead from ethylbenzene electrolyte [4] and to the study of stability of the deposited coating in this electrolyte [5]. In the present part, the attention is paid to the effects occurring during anodic dissolution of the Al—Pb binary system which may serve as indirect information source about the situation in the metallic coating.

Experimental

Cyclic voltammetry (CV) on a solid stainless steel electrode with $0.102\,cm^2$ surface area was used for the study. Other two electrodes of the three-electrode system were aluminium wires with a diameter of 3 mm. Measurements were carried out in inert atmosphere on a GWP 673 Polarograph. Further experimental conditions as well as experimental details on chronopotentiometric measurements were described in [4] and [5].

Results

The CV record of the basic electrolyte, *i.e.* $AlBr_3 + KBr$ solution in ETB has already been described [4]. Assuming that the switching potential is sufficiently negative, the anodic branch of the cyclic voltammogram in basic electrolyte consists of one peak only corresponding to the dissolution of deposited aluminium. In the presence of $PbBr_2$ the

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*X^- — halide anion, M^+ — potassium, sodium or other suitable cation.

situation is more complicated. First of all, the anodic part is obviously influenced by the cathodic switching potential value. With switching potential value equal to zero or -0.1 V (vs. aluminium reference electrode — AlRE) the deposition potential of aluminium is not yet reached. Evidently only one peak would be expected on the anodic branch under these conditions. Fig. 1 shows that this peak appears only when the potential is kept for a certain retention time on the constant switching potential value — cf. curves 1 and 2 with no retention time applied with curves 3 and 4 with retention time 10 and 50 s, respectively. With switching potential value -0.2 V the deposition of aluminium has already begun — see curves 5 and 6 in Fig. 1 — thus, on the anodic side two peaks would normally be expected but only one peak appears although higher than in the previous cases of curves 3 and 4. (Note: As to the retention time, curve 3 should be compared to curve 5 and curve 4 to curve 6.)
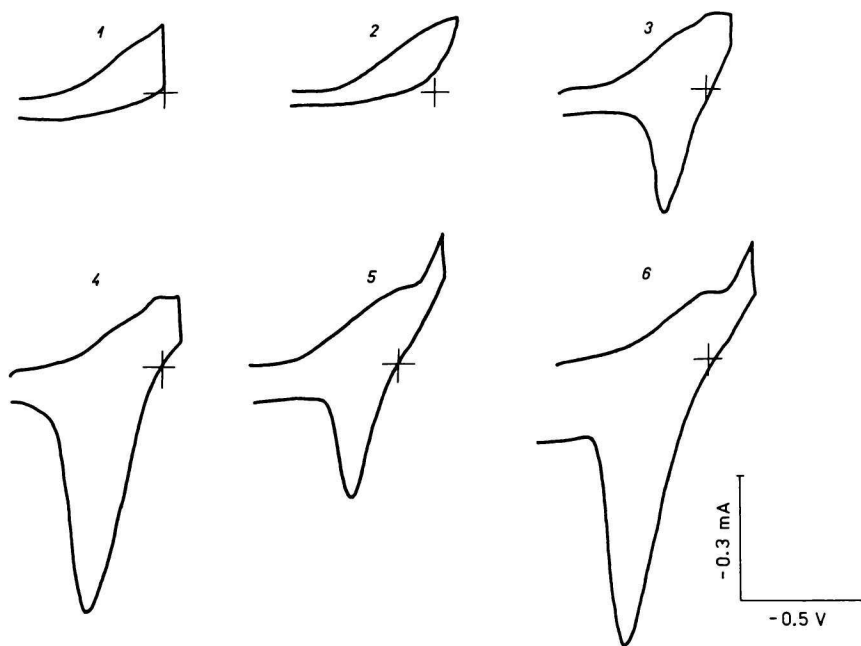

Fig. 1. Cyclic-voltammetric records of deposition and dissolution of lead in ethylbenzene electrolyte. $c(AlBr_3) = 1.82 \, mol \, dm^{-3}$; $c(KBr) = 0.8 \, mol \, dm^{-3}$; $c(PbBr_2) = 3.13 \times 10^{-3} \, mol \, dm^{-3}$. Scan rate $v = 0.166 \, V \, s^{-1}$. Switching potential E_λ: 1. 0 V; 2, 3, 4. -0.1 V; 5, 6. -0.2 V. Retention time: 1, 2. 0 s; 3, 5. 10 s; 4, 6. 50 s.

Two peaks on the anodic branch of CV record appear only when the switching potential overreaches the aluminium deposition potential of at least 0.2 V negatively. The current, potential and shape of these peaks are influenced, in addition to the switching potential and retention time values also by the rate of the voltage scan. This is clearly seen

by comparison of Fig. 2 recorded with low scan rate 0.0166 V s^{-1} and Fig. 3 recorded with higher scan rate 0.25 V s^{-1}. (*Note*: The anodic peaks are marked in the direction of polarization, A$_1$ — negative peak, A$_2$ — positive peak.) Fig. 2 shows that at a low rate of voltage scan mainly the negative peak A$_1$ increases with the cathodic shift of the

Fig. 2. Cyclic-voltammetric records of deposition and dissolution of lead and aluminium in ethyl-benzene electrolyte for various switching potential values at scan rate 0.0166 V s^{-1}. $c(AlBr_3) = 1.82$ mol dm^{-3}; $c(KBr) = 0.8$ mol dm^{-3}; $c(PbBr_2) = 8.65 \times 10^{-3}$ mol dm^{-3}. Switching potential E_λ: *1.* -0.2 V; *2.* -0.4 V; *3.* -0.6 V.
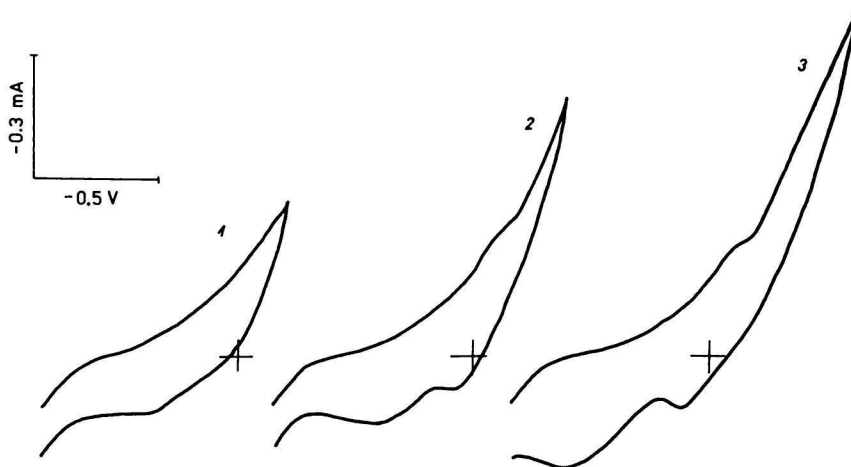

Fig. 3. Cyclic-voltammetric records of deposition and dissolution of lead and aluminium in ethyl-benzene electrolyte for various switching potential values at scan rate 0.25 V s^{-1}. Electrolyte composition and switching potential values are the same as in Fig. 2.

switching potential E_λ. The positive peak A_2 appears only when reaching the E_λ value -0.5 V. At higher scan rates the anodic peak A_2 is observed already at $E_\lambda = -0.3$ V (Fig. 3). Both peaks increase with the cathodic shift of E_λ but entirely differently: whereas at a low scan rate the peak A_1 shows remarkable increase, at higher scan rate it is the peak A_2 increasing with the cathodic shift of E_λ. Fig. 4 presents the dependence of both anodic peak heights on the square root of the scan rate.
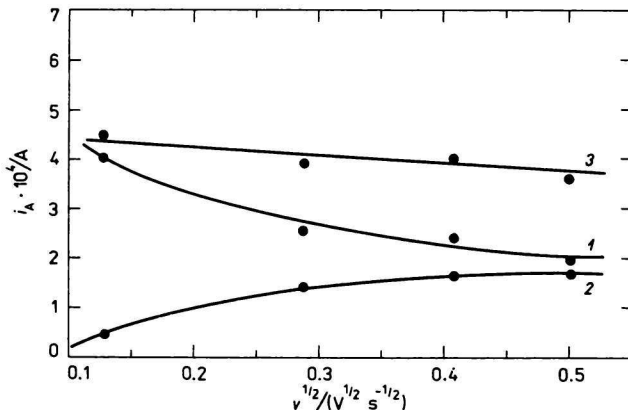

Fig. 4. Dependence of the anodic peak currents during dissolution of the Al—Pb binary system in ethylbenzene electrolyte upon the scan rate.
$c(AlBr_3) = 1.82$ mol dm^{-3}; $c(KBr) = 0.8$ mol dm^{-3}; $c(PbBr_2) = 6.75 \times 10^{-3}$ mol dm^{-3}. Switching potential $E_\lambda = -0.6$ V. $1.\ i(A_1)$; $2.\ i(A_2)$; $3.\ i(A_1) + i(A_2)$.

Figs. 5 and 6 represent the dependence of anodic peak heights upon the switching potential value E_λ and $PbBr_2$ concentration, respectively. The negative shift of E_λ (Fig. 5) causes at first remarkable increase of the A_1 peak current up to the value of $E_\lambda = -0.4$ V; beyond this value the A_1 peak current remains roughly constant. The A_2 peak current changes very slightly up to $E_\lambda = -0.4$ V but beyond this value it increases remarkably. The sum of both peak currents increases, as can be expected, linearly with the negative shift of the switching potential. Fig. 6 shows that the increase of the $PbBr_2$ concentration in the electrolyte results in almost linear increase in the A_2 peak current whereas the A_1 peak current is influenced only slightly by this parameter.

As to the shift of potential of both peaks A_1 and A_2 the following may be stated: with increasing scan rate and negative shift of the switching potential both anodic peaks shift positively. The effect is, however, almost negligible for peak A_1 but quite remarkable in case of peak A_2. Actual values are given in Table 1.

Discussion

The experimental results point out the fact that dissolution of binary Al—Pb system in ETB electrolyte is significantly influenced by the time period from the

beginning of deposition to the beginning of dissolution of the metallic phase which, in turn, is given by the following experimental parameters: scan rate, switching potential, and retention time. The effect of this time period which represents the duration of deposition process, however, is not entirely faradaic, *i.e.* longer time means larger charge passing and thus higher amount of deposited material. The faradaic influence of the time period is the most decisive as to the sum of both anodic peak currents. But another effect appears, too: at sufficiently long time period mutual interaction occurs between both metals in
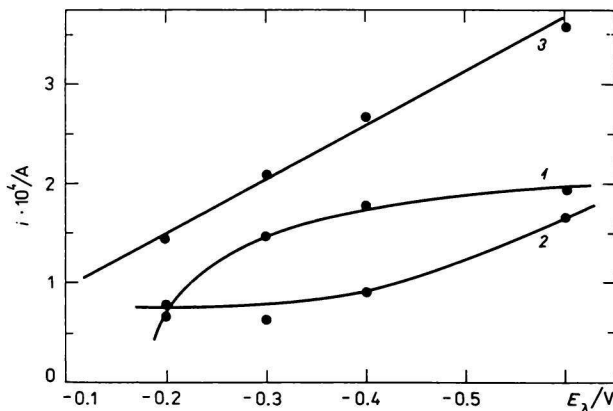

Fig. 5. Dependence of the anodic peak currents during dissolution of the Al—Pb binary system in ethylbenzene electrolyte upon the switching potential.
Electrolyte composition as in Fig. 4. Scan rate $v = 0.25 \text{ V s}^{-1}$. *1.* $i(A_1)$; *2.* $i(A_2)$; *3.* $i(A_1) + i(A_2)$.
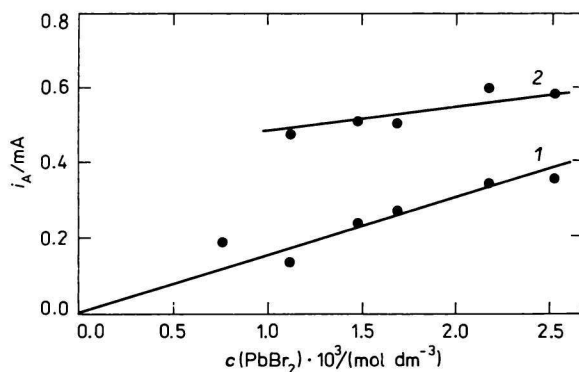

Fig. 6. Dependence of the anodic peak currents during dissolution of the Al—Pb binary system in ethylbenzene electrolyte upon the PbBr$_2$ concentration.
Basic electrolyte composition: $c(\text{AlBr}_3) = 1.92 \text{ mol dm}^{-3}$; $c(\text{KBr}) = 0.8 \text{ mol dm}^{-3}$. Scan rate $v = 0.25 \text{ V s}^{-1}$. Switching potential $E_\lambda = -0.6 \text{ V}$. *1.* $i(A_1)$; *2.* $i(A_2)$.

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Table 1

Shift of potential of the CV anodic peaks A_1 and A_2 during the dissolution of the Al—Pb binary system in ETB electrolyte with increasing scan rate and with negative shift of the switching potential

Switching potential $E_\lambda = -0.6$ V

Scan rate	Peak potential	
v/V s^{-1}	E_{A_1}/V	E_{A_2}/V
0.0167	0.079	0.453
0.0833	0.081	0.471
0.167	0.095	0.495
0.250	0.100	0.546

Scan rate $v = 0.25$ V s^{-1}

Switching potential	Peak potential	
E_λ/V	E_{A_1}/V	E_{A_2}/V
−0.2	0.027	0.323
−0.3	0.054	0.477
−0.4	0.077	0.518
−0.6	0.100	0.546

the surface. The interaction seems to be in fact a diffusion process of one metal into the other resulting in formation of homogeneous solid solution, alloy or intermetallic compound which dissolves in a single anodic peak. For instance, curves 5 and 6 in Fig. 1 present the CV record of deposition of both metals at −0.2 V with 10 and 50 s retention time, respectively; the anodic part of the record consists of one A_1 peak only, increasing with the increase of the retention time. Similarly, Fig. 3 recorded at a low scan rate shows the increase of peak A_1 with negative shift of the switching potential. When the experimental conditions allow deposition of both metals but on the anodic side only one peak appears then it is obvious that mutual interaction between the metals in the surface has taken place and the product of this interaction dissolves in one peak.

It is necessary to consider the possibility of such interaction occurring in the surface within a still relatively short time period. The situation at the electrode during the electrolysis of the binary Al—Pb system may be outlined as follows: during cathodic scan the deposition potential of lead is reached first and metallic lead is being deposited. The rate of this process reaches its limit after depletion of the diffusion layer. Then it proceeds further with constant diffusion-controlled rate also during the deposition of aluminium. The first layer of Pb metallic deposit is thus covered by a layer of metallic aluminium containing certain amount of lead. The lead/aluminium ratio in this layer decreases with negative shift of the cathodic potential. It is however, quite overestimated to speak about compact separated layers; at the lowest scan rate 0.0166 V s^{-1} the amount of

charge needed for deposition of the Pb layer is less than 1 mC, which on the electrode applied with the given surface area represents a layer of about 10 nm thickness with roughly 10—50 atomic plates. Although the diffusion coefficients of metals in solid state are rather low, the diffusion routes are also very short. In addition to this, the extremely high electric field conditions in the surface play a great role. It is known, for instance, that hardness of electroplated chromium is many times higher than that of ordinary metallic chromium [6]. All this may lead to the fastening of surface diffusion by as much as two orders of magnitude and result in formation of homogeneous solid solution or even alloy formed by lead and aluminium in the surface if long enough time period is available. Table 2 shows the measured time periods of metal deposition for the lowest and highest scan rates used; the difference is rather remarkable and, consequently, the assumption about interaction of metals in the surface may obviously be accepted. Comparison of the CV records in Figs. 2 and 3 confirms this hypothesis: In Fig. 3 CV record is presented with time period ranging from 1.6 s to 4.8 s; on the anodic scan both peaks A_1 and A_2 are equally developed whereas in Fig. 2 with time period ranging from 24 s to 72 s peak A_1 corresponding to the dissolution of binary phase, if not entirely single, is obviously dominant. Fig. 4 summarizes these results.

Table 2

Measured time period from the beginning of metallic phase deposition to the beginning of metallic phase dissolution for various scan rates and switching potential values

Scan rate $v/V\ s^{-1}$	Switching potential E_λ/V	Time period t/s
0.0167	−0.2	24
	−0.3	36
	−0.4	48
	−0.5	60
	−0.6	72
0.25	−0.2	1.6
	−0.3	2.4
	−0.4	3.2
	−0.5	4.0
	−0.6	4.8

The results of chronopotentiometric study of the deposition and dissolution of the Al—Pb binary system in ETB electrolyte partially presented in [5] point to the same effect: although during the cathodic current pulse two reduction processes may be identified corresponding to the deposition of Pb and Al, the

anodic part of ChP record differs according to the duration of cathodic pulse. If long enough cathodic electrolysis time is applied (20 s or 50 s), only one anodic process is observed corresponding to the dissolution of the homogeneous binary phase; the constant potential of this process is approximately the same as the potential of the A_1 peak in cyclic voltammetry. With shorter cathodic pulse duration — 5 s or 10 s — two transition times are observed on the anodic scan, which again points to the separate dissolution of both metals.

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