JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 590–595

# The modification of aromatic electrolytes for electrodeposition of aluminium

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Received 27 April 1989; revised 15 August 1989

With the purpose of obtaining finer-grained and more-compact aluminium coatings from aromatic solutions, the influence of some organic additives was studied. It was found that only the presence of dipyridyl (0.1–0.3 wt %) in the solution improved the coating resistance against corrosion. A small amount of $SnBr_2$ added to the solution and the use of reverse-pulse deposition also increased the protective properties of the coatings.

## 1. Introduction

Aluminium coatings have become extremely important for the corrosion protection of steel in recent years. The advantage of Al over Zn and Cd coatings has been shown, for example, by Kautek [1]. Unfortunately, aluminium cannot be electrodeposited from protic solvents because decomposition of the solvent with hydrogen evolution occurs at the potentials required to deposit the metal, so the current efficiency, $W$, of Al is essentially zero. Attempts to employ aprotic solvents led to three main groups of organic electrolytes from which aluminium coatings can be deposited:

(1) $AlCl_4$ and $LiAlH_4$ (5 : 1) in diethyl ether (DEE) or tetrahydrofuran (THF) (for example [2, 3]);
(2) $NaF \cdot 2Al(C_2H_5)$ in toluene [4];
(3) 2 M $AlBr_3$ in aromatic solvents (for example [5–8]).

The last of these electrolytes has the advantage of being the simplest, not pyrolitic and not very sensitive to moisture. Unfortunately, Al deposits obtained from $AlBr_3$ solutions in aromatic solvents have an inclination to dendritic growth, so these coatings are usually rather thin, up to 20 μm, and protect the basic metal against corrosion poorly. As was shown in [9], the Al deposits have very coarse crystal grains and were not compact, which explains their poor protective behaviour. The aim of the work presented here was to study the possibility of improving the protective properties of the Al coating by obtaining more-compact fine-grained deposits.

It is known that in order to obtain finer grained deposits it is necessary to increase the overpotential, $\eta$, of the cathodic depostion of the metal. The most popular ways of achieving this effect are (1) to bind the metal cation in more-stable complex ions or (2) to introduce into the electrolyte small amounts of organic additives, which have the ability to absorb on the cathode surface and act as inhibitors of the electrocrystallization process. Only the latter method can be used in the case of Al electrodepositions from $AlBr_3$ solution in aromatic solvent, because in these solutions ions already exist in the complex form, $Al_2Br_7^-$ or $Al_2Br_5^+$. Efforts have been made to apply organic substances as additives to xylene or toluene solutions of $AlBr_3$ by some authors [5, 8]. They studied a larger number of organic substances, but only a few additives positively influenced and improved the appearance of the aluminium coating; however, the protective properties of the coating were generally worse [5]. Information about the modification of the protective properties and the appearance of the coating due to the presence of an organic additive given previously [5, 8] is only descriptive. Improvement of the galvanic coating may also be achieved by the introduction in the electrolyte of a small amount of an inorganic salt of a metal, which can be deposited in the much more positive region of potential than the basic metal. The microcrystallites of supporting metal then operate as nucleation centers for the basic metal being obtained. The results of employing $SnBr_2$ as an inorganic additive are presented below. The last method of improving the corrosion resistance of the Al deposit was to apply reverse-pulse current (rpc) for electrolysis. It is known that applying rpc in the electrolytic deposition of Li suppresses the growth of dendrites [10], so it might be expected that an improvement of the quality of the coating and a better corrosion resistance might be achieved.

## 2. Experimental details

The electrolytes were prepared by dissolution of $AlBr_3$ (pa, anhydrous) and additive in xylene. All reagents, excluding $AlBr_3$, and the solvent were carefully purified before use. Traces of $H_2O$ were removed from the xylene by distillation with $P_2O_5$. All solution preparation procedures were carried out in a dry box. A single compartment cell was used. The anode was an aluminium spiral (99.99%) with a surface area about 100 times larger than that of the cathode. The working electrode in the voltammetric methods was a Pt wire sealed in glass with a circular geometrical area of

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0.785 mm$^2$, or a Cu sheet (99.99%) with a geometrical surface equal of 1 cm$^2$ in all other experiments. The surface of the platinum cathode was polished on emery paper of 800–1000 grades, cleaned in concentrated $H_2SO_4$, rinsed in redistilled water and acetone and then dried carefully. An aluminium wire served as a reference electrode. Measurements were carried out at 303 K. Linear-scan voltammetry (va), rpc polarization and galvanostatic electrolysis, as well as scanning electron microscopy were employed. In the case of the rpc method the frequency, $\nu$, of the pulsation was changed over the range 0.1–1000 Hz, and the time ratio of cathodic to anodic polarization was 3 : 1.

A more detailed description of the experimental techniques was given in [9, 11].

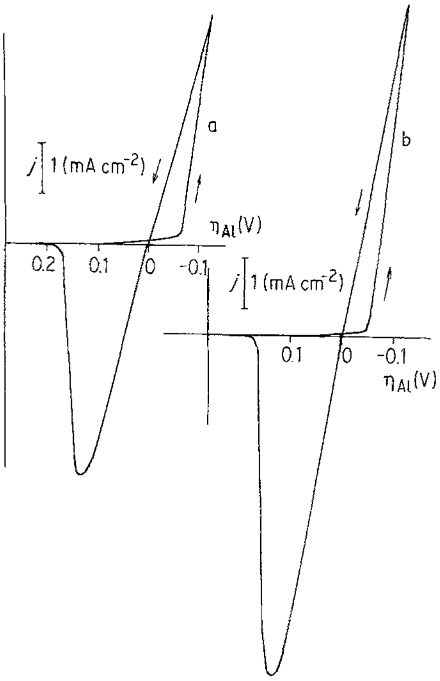

Fig. 1. Typical voltammetric curves recorded in the solution of 2 M $AlBr_3$ (a) in xylene and (b) with 0.1 wt% 2, 2′-dipyridyl as an additive on Pt electrode. Scan rate $v$ = 0.01 V s$^{-1}$.

## 3. Results and discussion

In Table 1 organic substances, which were tested by other authors as additives to the solution of $AlBr_3$ in aromatic electrolytes, are listed. The table gives information about the influence of the additive on the properties of the deposited Al coating. Unfortunately, the information given in the quoted papers has only a qualitative character, and deals mainly with the appearance of the coatings. According to [5, 12] the presence of the organic additives results in worse corrosion resistance of the Al coatings. It can be seen that the tabulated organic substances have various chemical characters, and there is no correlation between their chemical properties (for example, acid–base behaviour) and their ability to improve Al deposits.

At present there is no posssibility of predicting which organic substances might improve the protective properties of the coating, because information on the adsorption of organic molecules on Al is scant. Hence, the choice of an appropriate additive must be made in an empirical way. The additives which enhance the protective properties of the coating act mostly as inhibitors of the electrocrystallization of metals, and the overpotential of the cathodic deposition of metal usually rises in the presence of those substances. In order to discover which additives operate as inhibitors of cathodic deposition of Al, voltammetry has been employed. Some examples of the va curves are shown in Fig. 1. The curves recorded in $AlBr_3$ solution in xylene are typical for the cathodic depostion of metals. The characteristic crystallization loop on the cathodic branch and very sharp anodic peak in the reverse scan appear. The $i$–$E$ curve in the cathodic region is practically straight on the forward and backward run. The slope d$i$/d$E$ is of order $10^{-4}$ A cm$^{-2}$ V$^{-1}$ regardless of the presence or absence of additives in the electrolyte. Thus, it can be concluded that the process of Al electrodeposition proceeds with ohmic control when $\eta_{Al}$ is sufficiently high.

*Table 1. The influence of some organic additives on the appearance of Al deposits*

| *No influence* | *Deterioration* | *Little improvement* | *Improvement* | *Reference* |
|---|---|---|---|---|
| Alkanes | Methyl bromide | Phenanthren | 2-Hexanon | [8] |
| Isopropyl bromide | Methyl ether | Anthracene | Diethylamine | |
| Isoamyl bromide | Dimethylaniline | Napthalene | Diphenylamine | |
| Octyl bromide | 2-Aminophenol | α, β-Naphthyloamine | | |
| Ethers | Piperidine | α-Naphthylamaine | | |
| Nitroaniline | Morpholine | Chinoline | | |
| Thiourea | Dioxan | Tetramethylammonium iodide | | |
| | 2-Sulphobenzoic acid | | | |
| | Salicylic acid | | | |
| | | Ethylbenzene | Quaternary ammonium bromide* | [5] |
| | | Mesitylene | | |
| | | Triethylamine | Derivatives of benzene and napthalene | |
| | | Anthracene and its derivatives | Naphthalene | |

* Corrosion resistance is poor.

*Table 2. Some characteristic data for electrodeposition of Al obtained by voltammetry in 2 M $AlBr_3$ solution in xylene with different additives*

| *Additive* | *($mV s^{-1}$)* | $E_l$ | $E_{nuc}$ | $E_{pa}$ | $j_{100}$ | $j_{pa}$ |
|---|---|---|---|---|---|---|
| | | *Versus Al (V)* | | | *($mA cm^{-2}$)* | |
| None | 10 | −0.125 | −0.065 | +0.120 | 2.8 | 4.59 |
| | 100 | −0.125 | −0.095 | 0.09 | 0.92 | 2.65 |
| | 200 | −0.125 | −0.100 | 0.08 | - | 1.79 |
| 2, 2′-dipyridyl (0.1%) | 10 | −0.125 | −0.050 | 0.120 | 4.59 | 6.38 |
| $(C_2H_5)_3N$ (1%) | 20 | −0.130 | −0.080 | 0.08 | 0.32 | 0.7 |
| n-Butylamine (1%) | 20 | −0.180 | −0.08 | 0.140 | 0.25 | 0.9 |
| $(C_4H_9)_4NI$ (0.15%) + 0.5 M KBr | 20 | −0.120 | −0.04 | 0.135 | 3.81 | 3.49 |
| 8-Oxychinoline (0.1%) + 0.5 M KBr | 10 | −0.160 | −0.095 | 0.125 | 0.32 | 3.56 |
| $SnBr_2$ ($7 \times 10^{-5}$ M) | 10 | −0.125 | −0.06 | 0.06 | 3.18 | 2.29 |
| | 100 | −0.105 | −0.08 | 0.05 | 1.48 | 1.28 |

As found in previous experiments [9], the crossover potential on the reverse scan of the cathodic branch, $E_x$, corresponds to the equilibrium potential of Al. For this reason $j^0$ can be calculated from the slope of the cathodic and anodic va curves, when $\eta_{c,a} < 0.01$ V. It is equal to $0.001 \pm 3 \times 10^{-5}$ A cm$^{-2}$, with correction for ohmic drop. A sharp increase of cathodic current is noticeable when the cathodic polarization reaches a certain potential. This is also typical for metal electrocrystallization processes and is connected with the rapid growth of the cathodic surface as a result of the creation and growth of metal nuclei. Therefore, the potential at which the cathodic current increases rapidly, may be called 'the nucleation potential', $E_{nuc}$. Hence, if the additive has the ability to adsorption on the cathodic surface, the value of $E_{nuc}$ will shift toward more negative potentials. Unfortunately, the additives under consideration have not changed the value of $E_{nuc}$ above 0.05 V (see Table 2).

Also given in Table 2 are the values of the cathodic current density, $j_c$ calculated for $\eta_c = 0.1$ V, which can be used for comparative purposes of the rates of the cathodic electrodeposition processes from the electrolyte with or without and additive. The value of the anodic peak current gives information relevant to the amount of the deposited Al and its activity, but the values may be compared provided that curves are recorded with the same scanning rate, $v$, and the same limit potential of the cathodic scan, $E_l$.

It is clear from the data in Table 2 that only in the presence of some amines does the rate of deposition of Al decrease. However, in these solutions the shape of the va curves changes and a prewave appears (see Fig. 2). It can be assumed that this is caused by electroreduction of the organic additive, which occurs in the more electropositive region than $E_{nuc}$ of Al. This assumption is confirmed by the fact that in the case of the Al coatings obtained from a solution containing the amines or napthalene, the existence of a black, non-metallic, powdered sublayer under the Al coating

*Table 3. The effect of some organic additives on the properties of the Al deposit obtained from a solution of 2 M $AlBr_3$ in xylene*

| *Additive* | *Concentration (wt %)* | $j_c$ *($mA cm^{-2}$)* | *Yield (%)* | *Notes about deposits* |
|---|---|---|---|---|
| Naphthalene | 1 | 10 | > 80 | Light grey ps* in NaOH |
| | 10 | 10 | 90 | Black, poor adherence, ps in NaOH |
| Tetrabutylammonium iodide | 0.05 | 10 | > 80 | Light grey, without dendrides ps in NaOH |
| | 0.15 | 10 | > 80 | Dark grey, ps |
| Triethylamine | 1 | 10 | 80 | Dark gray, ps in NaOH |
| sec-Butylamine | 1 | 10 | - | Passivation of Al anodes |
| 8-Oxychinoline | 0.1 | 5 | - | Coarse-grained, ps in NaOH |
| Dimethylformamide | 5 | 6 | - | Black powder, insoluble in NaOH |
| Tetrahydrofuran | 4 | 10 | - | Black powder, insoluble in NaOH |
| 2, 2′-dipyridyl | 0.1 | 10–30 | > 80 | Light grey, |
| | 0.4 | 10–30 | 80 | dendrites appear when $t_c > 0.5$ h, 100% soluble in NaOH |

* ps, partially soluble in 5% NaOH.

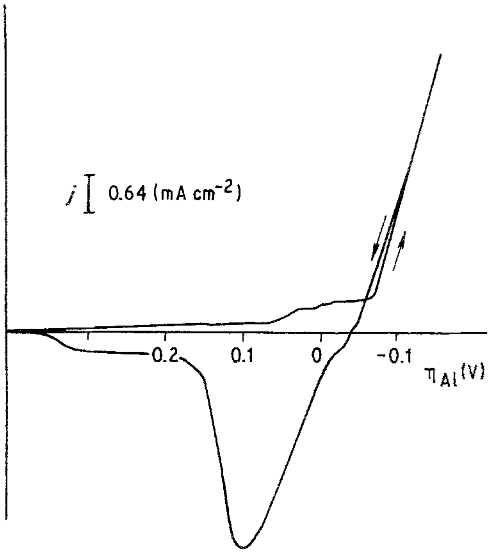

Fig. 2. Cyclic voltammogram on Pt electrode for 2 M $AlBr_3$ in xylene with 0.15% $(C_4H_9)_4NI$ as an additive, $v = 0.01\ V s^{-1}$.

was observed after the stripping of Al by dissolution in 5% NaOH. Of course, the Al coating deposited under these conditions possesses very poor corrosion resistance.

The influence of some organic additives on the appearance and properties of aluminium coating is described in Table 3. The values of corrosion potentials, $E_{cor}$, measured for samples of Cu covered by Al, after 1 h exposure in aqueous $Na_2SO_4$ solution ($c$ = 1 M) are listed in Table 4. If the coating is nonporous, $E_{cor}$ should be equal to $E_{cor}$ of Al used as a reference electrode. Among the organic additives only 2, 2′-dipyridyl (dipy) improved the corrosion resistance of the coatings. The deposits were studied by scanning electron microscopy. Some representative micrographs are shown in Figs 3–6. It is evident that an addition of dipy to the solution leads to the formation of a compact adherent layer. In a solution without any additives the deposits were granular and not compact (see Fig. 3).

According to the classification proposed by Despič [12] the Al deposits obtained from the solution of $AlBr_3$ in xylene belong to a special category of granular isolation-type (GI), which can account for their poor corrosion protection properties. (Note that according to Despič the GI type of deposits appear when the growth of crystallites is suddenly stopped; for example, by occlusion of by-products of cathodic reaction.) It may be assumed that these originate from the electroreduction of the solvent molecules, which form a polymeric by-product on the cathode, due to the appearance of ionic radicals during the cathode process [13, 14]. It is noticeable that the rate of growth of the aluminium coating is higher when accompanied by dipy. This is seen from the comparison of the corresponding values of $j_c$($\eta$ = 0.01 V) and $j_{pa}$ listed in Table 2. The SEM observation shows that the Al obtained from solution with dipy is more compact and has a different structure. It is not a GI-type deposit. On this base it might be assumed that in the presence

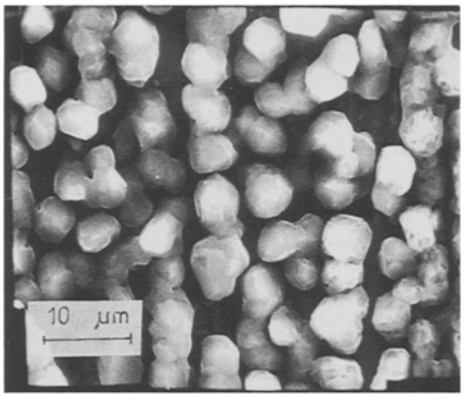

Fig. 3–6. Scanning electron micrographs of an aluminium deposit obtained from 2 M $AlBr_3$ in xylene on Cu electrode.

Fig. 3. $j_c$ = 15 mA cm$^{-2}$, $t_c$ = 1 h.

*Table 4. The corrosion potentials of Cu samples covered by Al from xylene solutions measured at 1 h exposure in 1 M $Na_2SO_4$ aqueous solution*

| *Metal* | *Composition of the solution in xylene and time of polarization* ($t$) | $j_c$ (*mA cm*$^{-2}$) | $E_{corr}$ *versus SCE* ($V$) | *Remarks about coating and cathodic efficiency W* |
|---|---|---|---|---|
| Al (99.997%) | – | – | −0.470 | – |
| Cu | – | – | −0.060 | – |
| Al/Cu | 2 M $AlBr_3$<br>$t$ = 2 h | 15 | −0.34 | Light,<br>coarse-grained,<br>$W$ = 70% |
| Al/Cu | 2 M $AlBr_3$<br>$t$ = 0.5 h<br>rpc = 1000 Hz | 12 | −0.61 | Light,<br>without dendrites,<br>$W$ = 40% |
| Al/Cu | 2 M $AlBr_3$<br>+0.26% dipy<br>$t$ = 1.5 h | 17 | −0.53 | Light,<br>fine-grains,<br>$W$ = 80% |
| Al/Cu | 2 M $AlBr_3$<br>7 × $10^{-5}$ $SnBr_2$<br>$t$ = 1 h | 15 | −0.49 | Grey, fine<br>grains,<br>$W$ = 70% |

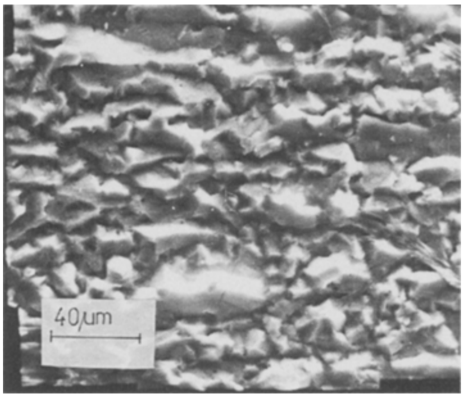

Fig. 4. In the presence of 0.26 wt % dipy. $j_c = 15\,\mathrm{mA\,cm^{-2}}$, $t_c = 1\,\mathrm{h}$.

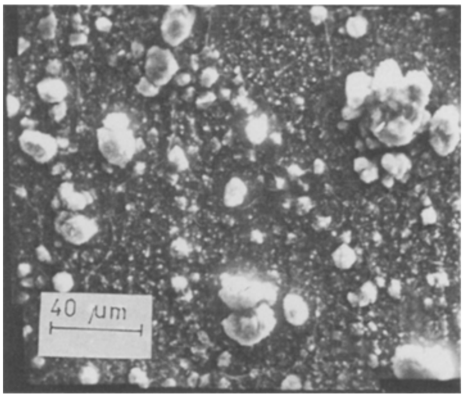

Fig. 5. In the presence of $7 \times 10^{-5}$ M $SnBr_2$, $j_c = 10\,\mathrm{mA\,cm^{-2}}$, $t_c = 1\,\mathrm{h}$.

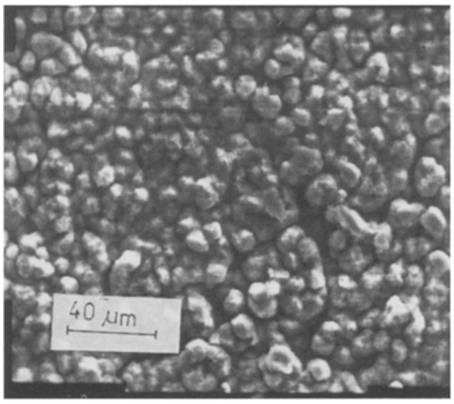

Fig. 6. Aluminium coating deposited by the rpc method, $j_c = j_a = 15\,\mathrm{mA\,cm^{-2}}$, $t_c : t_a = 3:1$, $t = 0.5\,\mathrm{h}$, $\nu = 0.1\,\mathrm{Hz}$.

of dipy the process of formation of the undesired by product is suppressed.

The quality of the cathodic deposits can also be improved by the use of inorganic additives. In the case of electrodeposition of Al from molten salts, $SnBr_2$ acts as an inorganic additive [15], and thus it was chosen for investigation. The concentration of $SnBr_2$ was of the order $10^{-5}\,\mathrm{mol\,dm^{-3}}$. In Fig. 7 the V–A curve is recorded in the solution with higher concentration of $SnBr_2$. The cathodic prewave results from Sn deposition. In the anodic scan of this curve the two peaks indicate that the electrodeposition of Sn proceeds before the deposition of Al. The characteristic dependence of $j_l$ of the prewave on the concentration of $SnBr_2$ and on the scan rate proves that the electrodeposition of Sn proceeds with diffusion control. The coating obtained in the presence of small amounts of $SnBr_2$ in the solution is shown in Fig. 5. The deposit is more compact and much finer-grained. Its protective properties are better than those of the Al coating deposited from basic solution (see Table 2).

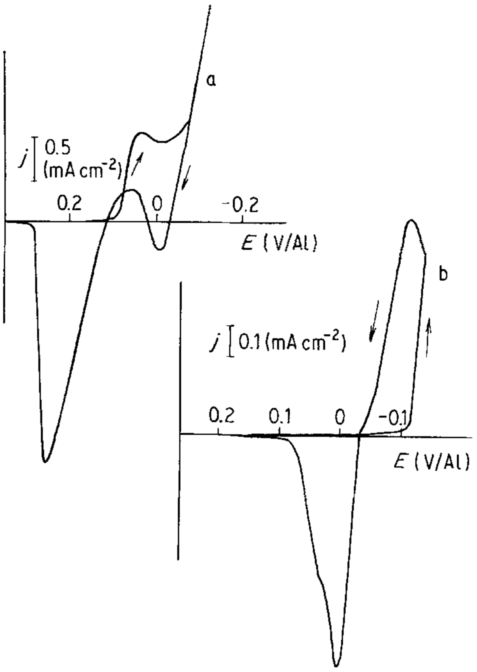

Fig. 7. Cyclic voltammetric curves recorded on Pt electrode in the solution of 2 M $AlBr_3$ in xylene with (a) $2 \times 10^{-2}$ M $SnBr_2$ and (b) $7 \times 10^{-5}$ M $SnBr_2$. $v = 0.01\,\mathrm{V\,s^{-1}}$.

The application of some small amounts of additive does not have any influence on the cathodic efficiency of Al.

The third method of improving the quality of the protective coating and suppressing the dendrite formation may be to employ rpc polarization. The deposits formed in this case are also compact and with

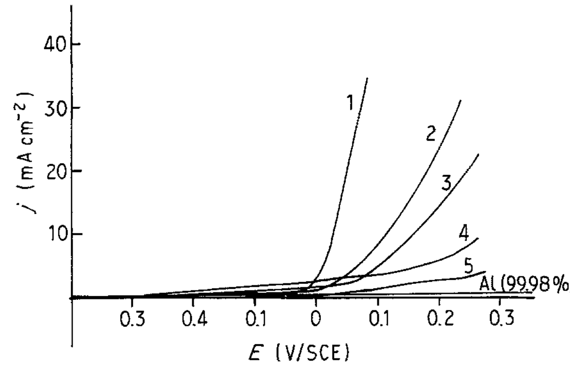

Fig. 8. Anodic polarization curves obtained in 1 M $Na_2SO_4$ on Cu electrode (curve 1), Cu sheet covered with Al deposited from 2 M $AlBr_3$ in xylene at various conditions of electrolysis. (curve 2) dc: $j_c = 12\,\mathrm{mA\,cm^{-2}}$, $t_c = 0.7\,\mathrm{h}$; (curve 3) dc: $j_c = 12\,\mathrm{mA\,cm^{-2}}$, $t_c = 0.5\,\mathrm{h}$ and then rpc: $j_c = j_a = 25\,\mathrm{mA\,cm^{-2}}$, $\nu = 1000\,\mathrm{Hz}$, $t = 0.1\,\mathrm{h}$, and $j_c = j_a = 20\,\mathrm{mA\,cm^{-2}}$, $\nu = 1\,\mathrm{Hz}$, $t = 0.1\,\mathrm{h}$; curve 4) dc: $j_c = 15\,\mathrm{mA\,cm^{-2}}$, $t_c = 0.7\,\mathrm{h}$ and then rpc: $j_c = j_a = 15\,\mathrm{mA\,cm^{-2}}$, $t = 0.5\,\mathrm{h}$, $\nu = 50$ and 1500 Hz alternately; (curve 5) anodic polarization curve of Cu sheet covered with Al in 2 M $AlBr_3$ in mesitylene, electrolysis as above.

good adherence (see Fig. 6), but their protection against corrosion in the electrolyte solution is not good (see Fig. 8).

To conclude, it may be said that Al coatings deposited from xylene solutions with appropriate additives or by the use of rpc may be useful in protection against atmospheric corrosion.

## 4. Conclusion

The results of this study show that at present it is impossible to predict which organic additives enhance the protective properties of Al deposited from organic solutions. In the case of xylene electrolyte the addition of dipyridyl, in a concentration of 0.1–0.3 wt%, makes it possible to obtain a more compact coating whose resistance against corrosion is much improved. It has been found that the improvement in the protective properties of the coating can also be achieved if rpc deposition of aluminium is applied and a small amount of $SnBr_2$ is added to the solution.

## Acknowledgements

The authors are indebted to the Coordination Committee of CPBP 01-11 for financial support.

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