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# Electrodeposition of aluminium in the presence of some chromium compounds.

## 3. The XPS analysis of electrodeposits

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Elementary analysis of electrodeposits obtained from  $\text{AlBr}_3$ -dimethylethylphenylammonium bromide solutions in toluene containing chromium(III) acetylacetonate or oleate has been carried out by means of X-ray photoelectron spectroscopy. The contents of aluminium, chromium, oxygen, carbon, nitrogen, bromine and copper were determined on the surface of deposits as well as in their depth. A considerable amount of aluminium oxide was detected not only on the surface of electrodeposits but also in the depth of the coating. The major portion of carbon compounds was found to be concentrated on the surface of coatings, whereas nitrogen, on the contrary, in their depth.

**Key words:** aluminium, chromium, electrodeposits, elementary analysis, XPS spectra

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### INTRODUCTION

In the previous article [1] we have demonstrated a possibility to obtain aluminium coatings containing up to 10 wt. % chromium. The dependency of chromium amount in electrodeposits on the chromium concentration in solutions and on the cathodic current density has also been examined.

This paper reports results of XPS analysis of aluminium electrodeposits obtained in solutions containing chromium(III) acetylacetonate or, in some cases, chromium(III) oleate. All ingredients of the electrolyte, except hydrogen, were determined at the surface of electrodeposits and in their depth.

### EXPERIMENTAL

Preparation of aluminium electrolyte, synthesis of chromium compounds and conditions of electrodeposition are described in our previous articles [1, 2]. Aluminium coatings had been electrodeposited on both sides of copper specimens (total area  $4 \text{ cm}^2$ ). The thickness of the electrodeposited layer was about  $10 \text{ }\mu\text{m}$ .

The elementary analysis of the surface layer of Al deposits was carried out by means of X-ray photoelectron spectroscopy (XPS). The X-ray photoelectron spectrum was taken from the Al surface layer *ex situ*, using an ESCALAB-MK II spectrometer (VG Scientific, Great Britain) interfaced to an IBM

PC/XT computer for data acquisition. Achromic  $\text{MgK}_\alpha$  (1253.6 eV) radiation (15kV, 20 mA) as the excitation source was used for recording the XPS of the elements Al  $2p$ , O  $1s$ , Cr  $2p_{3/2}$ , C  $1s$ , N  $1s$ , Br  $3d_{5/2}$  and Cu  $2p_{3/2}$ . The data on the values of the relative intensity of XPS signals for standard compounds [3] and of the relative sensitivity factors [4] were used to determine the contents in at. % of Al, O, Cr, C, N, Br and Cu on the surface of deposits or in their depth.

The depth profile of elements was obtained from XPS measurements with an argon ion sputtering (ultra-high pure argon ion beam, 10 keV). The etching current of the aluminium specimen by  $\text{Ar}^+$  ions was maintained at the level of *ca*  $100 \text{ }\mu\text{A}$ . Etching time was 5 min and etching rate  $10 \text{ nm/min}$ . Consequently, after bombardment by  $\text{Ar}^+$  ions the information on the contents of elements from the depth of about  $50 \text{ nm}$  was obtained.

### RESULTS AND DISCUSSION

As is shown in Fig. 1, X-ray photoelectron spectra for aluminium coatings exhibit two clearly defined maxima of relative intensity: in the Al  $2p$  binding energy region of  $72.6 \pm 0.1 \text{ eV}$  and  $74.8 \pm 0.1 \text{ eV}$ . The first maximum corresponds to the binding energy of metallic aluminium  $E_B \text{ Al } 2p = 72.6 \text{ eV}$  and the second one – to the binding energy of aluminium oxide  $E_B \text{ Al } 2p = 74.7 \text{ eV}$  [3]. The second

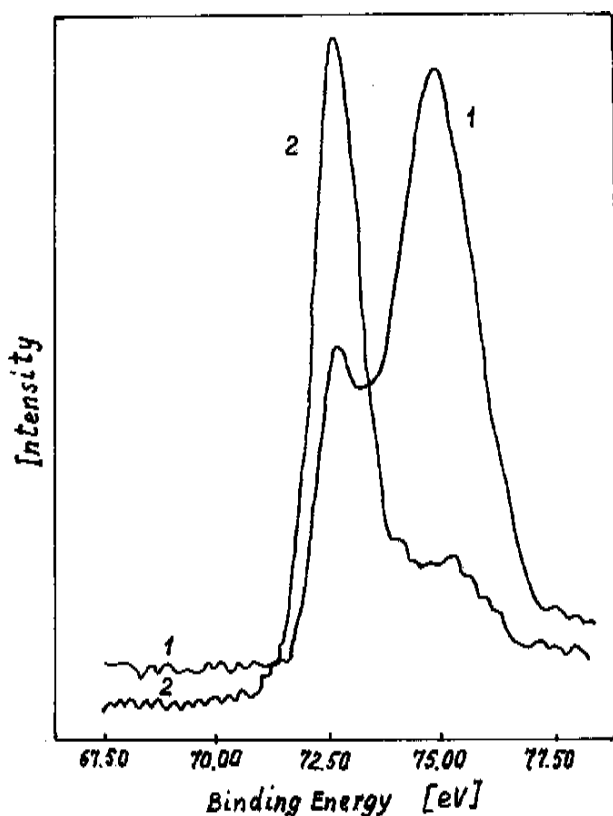


Fig. 1. XPS spectra for Al 2p: 1 – from surface of electrodeposit obtained at  $i_c = 2.5 \text{ mA cm}^{-2}$  in toluene solution of 0.935 M  $\text{Al}_2\text{Br}_6$  DMEPAB and 5.7 mM  $\text{Cr}(\text{Acac})_3$ ; 2 – the same after etching for 5 min by ionized argon

maximum becomes most pronounced in the XPS spectra for the surface of deposits, what would be expected provided the surface of aluminium is always covered with an oxide layer. In the XPS spectra for the deeper layers of electrodeposits, this maximum is reduced substantially but does not vanish completely. Since the aluminium coatings undoubtedly are not compact absolutely, but are somewhat porous and have intercrystalline cavities, formation of aluminium oxide is unavoidable not only on the surface of electrodeposits, but also in their depth in the course of their rinsing in water as well as during exposure to the atmosphere.

Beside these two maxima of relative intensity, the XPS spectra for the surface of electrodeposit exhibit one more maximum in the binding energy region of 75.0–75.8 eV which may be attributed, according to [3], to various aluminium oxy-compounds.

After five-minute etching of aluminium deposit by ionized argon, in the XPS spectra (Fig. 1) the maximum of the relative intensity is observed to dominate in the binding energy region of  $72.6 \pm 0.1 \text{ eV}$  attributed to metallic aluminium and the other one, considerably weaker, in the region of  $74.7 \pm 0.2 \text{ eV}$  attributed to  $\text{Al}_2\text{O}_3$ .

By the way, the height of the second maximum tends to increase with increasing the triethylaluminium (TEA) concentration in electrolyte. It seems likely that TEA penetration into the coating increases the  $\text{Al}_2\text{O}_3$  content in the latter.

As may be seen in Fig. 2, the XPS spectra for O 1s from aluminium deposits have also two maxima of relative intensity: in the binding energy region of  $531.7 \pm 0.2 \text{ eV}$  and  $533.4 \pm 0.4 \text{ eV}$ . The first of these maxima probably corresponds to the binding energy of oxygen in  $\text{Al}_2\text{O}_3$  molecule  $E_{\text{B O}1s} = 531.6 \text{ eV}$  [5] and the second one is close to the value of the binding energy for oxygen in  $\text{Al}(\text{OH})_3$  molecule ( $E_{\text{B O}1s} = 533.3 \pm 0.1 \text{ eV}$ ) and also in molecules of some other hydroxy-compounds including organic ones [3]. As is evident from Table 1, the amount of oxygen on the surface of aluminium deposit averages even between 40 and 50 at. %. That much oxygen on the surface of coating is quite comprehensible, taking into account that aluminium in the air is always covered by an oxide or hydroxide layer and in addition water molecules may be adsorbed on its surface. (By the way, the binding energy for oxygen in the  $\text{H}_2\text{O}$  molecule is close to detected 533 eV value [6]).

As follows from a comparison of results presented in Tables 1 and 2, the oxygen amount in the depth of coatings decreases roughly double and yet more often than not exceeds 20–25 at. %. It should be pointed out that a greater amount of oxygen has

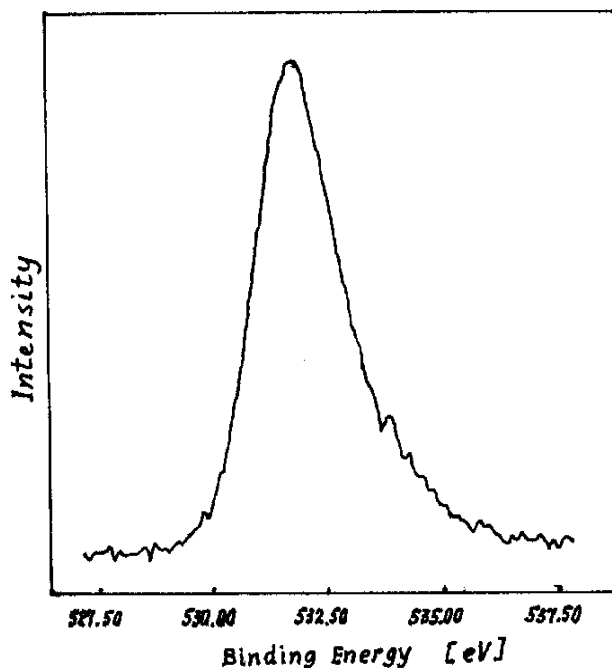


Fig. 2. XPS spectrum for O 1s from the depth ca. 50 nm of electrodeposit obtained at  $i_c = 2.5 \text{ mA cm}^{-2}$  in toluene solution of 0.935 M  $\text{Al}_2\text{Br}_6$  DMEPAB and 17.1 mM  $\text{Cr}(\text{Acac})_3$

been defined in the less compact, more porous coating when more favourable conditions exist for the formation of oxides or hydroxides as well as for H<sub>2</sub>O adsorption into pores.

As may be seen from XPS spectrum (Fig. 3), chromium in the deposits predominates with the Cr 2p<sub>3/2</sub> binding energy of 573.6 ± 0.2 eV. This value is somewhat less than the binding energy in me-

Table 1. Amounts of elements, in at. %, in the surface layer of aluminium coatings (according to the XPS data)

Cr(Acac) <sub>3</sub> conc. in solution, mM	i <sub>c</sub> , mA cm <sup>-2</sup>	Elements, in at. %						
		Al	O	Cr	C	N	Br	Cu
Electrolyte without TEA								
5.7	2.5	14.63	51.02	0.07	33.18	0	1.02	0.07
5.7	5.0	9.58	36.72	0.14	51.69	0.28	1.37	0.23
5.7	10.0	12.24	47.28	0.06	36.78	0.87	2.58	0.19
11.4	2.5	19.12	51.52	0.20	27.84	0	1.05	0.28
11.4	5.0	11.21	55.04	0.03	33.30	0.10	0.25	0.06
11.4	10.0	21.24	43.63	0.17	33.43	0.09	0.79	0.64
In 2.2 mM chromium(III) oleate solution								
–	5.0	19.12	41.62	0.16	38.35	0.24	0.27	0.24
Electrolyte with 0.56 M TEA								
5.7	2.5	21.11	44.37	0.46	33.61	0.28	0	0.17
5.7	5.0	20.38	42.02	0.47	36.14	0.28	0.18	0.54
5.7	10.0	17.97	39.93	0.24	40.60	0.34	0.76	0.16
11.4	2.5	11.07	49.56	0.34	36.25	0	2.45	0.32
11.4	5.0	21.16	48.21	0.69	28.12	0.21	1.61	0
11.4	10.0	15.60	41.20	0.48	41.88	0	0.78	0.06

Table 2. Amounts of elements, in at. %, in aluminium coatings after etching with ionized argon at beam current of 100 mA during 5 min

Cr(Acac) <sub>3</sub> conc. in solution, mM	i <sub>c</sub> , mA cm <sup>-2</sup>	Elements, in at. %						
		Al	O	Cr	C	N	Br	Cu
Elektrolyte without TEA								
5.7	2.5	40.25	42.13	0.49	5.17	9.37	0	2.19
5.7	5.0	67.73	24.62	0.33	4.11	2.20	0.09	0.92
5.7	10.0	41.60	45.59	0.20	1.54	7.93	0	3.14
11.4	2.5	62.83	22.12	1.36	9.15	2.62	0	1.90
11.4	5.0	58.81	26.05	0.86	8.62	3.13	0	2.53
11.4	10.0	63.77	17.68	0.82	7.65	7.10	0	2.97
17.1	2.5	64.44	21.86	0.75	6.31	5.94	0.05	0.65
17.1	5.0	65.84	19.01	1.02	6.17	6.60	0.06	1.36
In 2.2 mM chromium (III) oleate solution								
5.0	67.36	26.08	0.40	4.58	0	1.36	0.22	
Elektrolyte with 0.56 M TEA								
5.7	2.5	48.80	25.93	4.79	9.50	10.90	0	0
5.7	5.0	62.61	20.74	4.42	5.12	6.07	0	1.04
5.7	10.0	41.32	42.33	1.52	2.94	10.91	0	0.98
11.4	2.5	36.63	50.28	1.24	2.91	5.68	0	3.27
11.4	5.0	53.64	24.64	7.69	12.31	1.56	0	0.16
11.4	10.0	50.37	29.96	6.08	11.61	1.63	0	0.35
17.1	2.5	50.58	32.15	9.37	5.72	2.12	0.07	0
17.1	5.0	59.41	21.39	9.92	5.40	3.07	0.12	0.69
17.1	10.0	51.31	25.73	6.69	9.16	6.96	0.15	0
Speciment wetted 5 h in water								
17.1	5.0	54.51	23.13	7.24	10.52	2.87	0.17	1.57

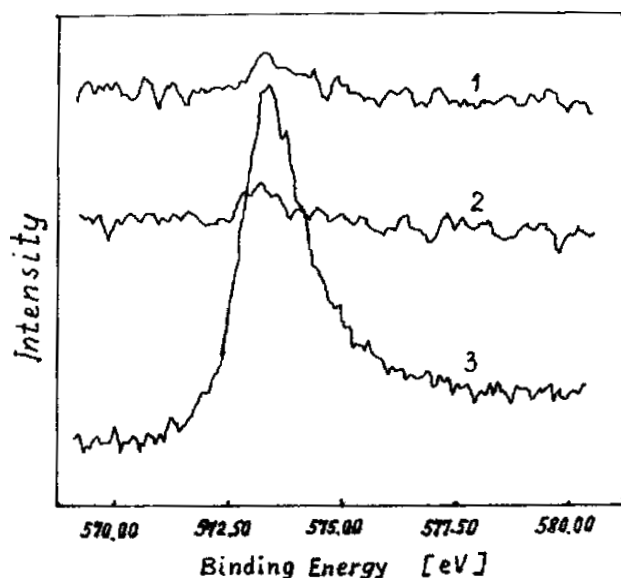


Fig. 3. XPS spectra for Cr  $2p_{3/2}$  from the depth *ca.* 50 nm of electrodeposit obtained at  $i_c = 5 \text{ mA cm}^{-2}$  in toluene solution of 0.935 M  $\text{Al}_2\text{Br}_6$  DMEPAB and: 1 – 2.2 mM chromium(III) oleate, 2, 3 – 5.7 mM  $\text{Cr}(\text{Acac})_3$ ; 3 – with addition of 0.56 TEA

tallic state  $E_B \text{ Cr } 2p_{3/2} = 574.1 \text{ eV}$  as well as binding energy in chromium(III) oxide  $E_B \text{ Cr } 2p_{3/2} = 576.6 \text{ eV}$  [3]. In all probability this is due to interaction between metallic chromium and metallic aluminium at alloy formation. As regards  $\text{Cr}_2\text{O}_3$ , close values of the binding energy ( $\sim 575.5 \pm 0.1 \text{ eV}$ ) were defined, even if of low intensity, for the surface of deposits as well as for the depth of coating, moreover, irrespective of plating conditions (composition of electrolyte, current density). In addition, in some cases the values of binding energy corresponding to  $\text{CrN}$  ( $\sim 575.6 \text{ eV}$ ),  $\text{CrO}_3$  ( $\sim 578.1 \text{ eV}$ ),  $\text{CrBr}_3$  ( $\sim 576.0 \text{ eV}$ ) were defined.

As may be inferred from Tables 1 and 2, the XPS analysis supports the conclusions drawn earlier [1] from scanning probe microanalysis data about an increase of chromium amount in electrodeposits with increasing the chromium concentration in solution, with adding TEA to electrolyte and with decreasing the cathode current density. Besides, as is evident from Tables 1 and 2, the relative amount of chromium on the surface of deposit is several times less than in the depth of coating, what may be attributable to accumulation of oxides and analogous compounds on the surface.

Also, a reasonably large amount of carbon was found on the surface of electrodeposits (Table 1). In parallel with the carbon adsorbed from various components of electrolyte, it is possible that some amounts of carbon (from 4 to 12%, as was noticed in [6]) get into the surface of the deposit from a diffusive pump in the course of analysis. As may be

inferred from XPS spectrum (Fig. 4), carbon in the electrodeposits to be studied exists in the form of various compounds, namely, as the elementary carbon (graphite) with binding energy  $E_{B\text{C}1s} = 284.6 \text{ eV}$  [1], as  $\text{CO}_2$  ( $E_{B\text{C}1s} = 291.7 \text{ eV}$  [1]) and other unidentified compounds. However, as the maximum of relative intensity in the region of 285.2 eV (Fig. 2) suggests, the dominant bulk of carbon probably exists in the form of organo-metallic compounds whose binding energy is generally in the region of 285.3–287.7 eV [1]. Such conclusion is well grounded when it is considered that aluminium as well as chromium in the electrolyte composes organic compounds, and consequently, while these compounds or their partial degrading products are included into the electrodeposit, carbon would still retain certain bonds with the mentioned metals. When the data of Table 1 are compared with these of Table 2, it is apparent also that the major portion of carbon is concentrated on the surface of coating, *i.e.* it is most likely to originate exclusively from the electrolyte in the course of reaction between the electrodeposit and the electrolyte remaining on its surface, the washing liquid or the atmosphere. Meanwhile, the amount of carbon in the deeper layers of coating decreases on the average by a factor of five.

It is complicated to explain the origin of quite a large amount (as seen in Table 2, occasionally up to 10 at. %) of nitrogen in the electrodeposits, especially as this amount on the surface comes to only several tenths of at. %, and in some cases even

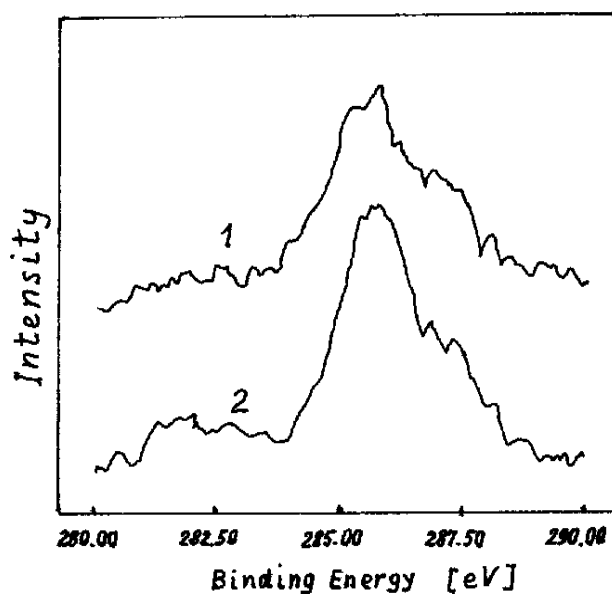


Fig. 4. XPS spectra for C  $1s$  from the depth *ca.* 50 nm of electrodeposit obtained at  $i_c = 2.5 \text{ mA cm}^{-2}$  in: 1 – toluene solution of 0.935 M  $\text{Al}_2\text{Br}_6$  DMEPAB and 5.7 mM  $\text{Cr}(\text{Acac})_3$ , 2 – in the same solution with addition of 0.56 TEA

escapes detection (Table 1). It is inconceivable that nitrogen should originate from its admixture in argon in the course of etching, because ultra-high pure argon was used. The sole contributor of nitrogen entering into the coating may be dimethylethylphenylammonium ions abundant in electrolyte, excluding the  $N_2$  atmosphere wherein the electrolyte was prepared and electrolysis was maintained. The quantities of N and C in dimethylethylphenylammonium ions are in the ratio of 1:10, meanwhile this ratio (even though the net amount of carbon is considered) is increased several times, and in some occasions the amount of nitrogen even exceeds the amount of carbon. Unfortunately, the electrochemical behaviour of quaternary ammonium ions has not been adequately studied. However, on the basis of present knowledge [7–11], only one conclusion suggests itself that quaternary ammonium ions would be expected to form larger conglomerates but not to decompose into simpler compounds in which the number of carbon atoms shall be very small. By the way, thermal decomposition of quaternary ammonium ions is also hampered at ambient temperatures [12].

As the data of Table 1 suggest, the amount of bromine determined from XPS spectra for the surface of deposits differs significantly for individual specimens and varies between 0 and 2.5 at. %. After surface etching by ionised argon only traces of bromine are found, and only in rare instances its amount reaches *ca.* 0.1 at. %. From this results the conclusion that bromine arises on the surface of coating through adsorption of compounds formed from

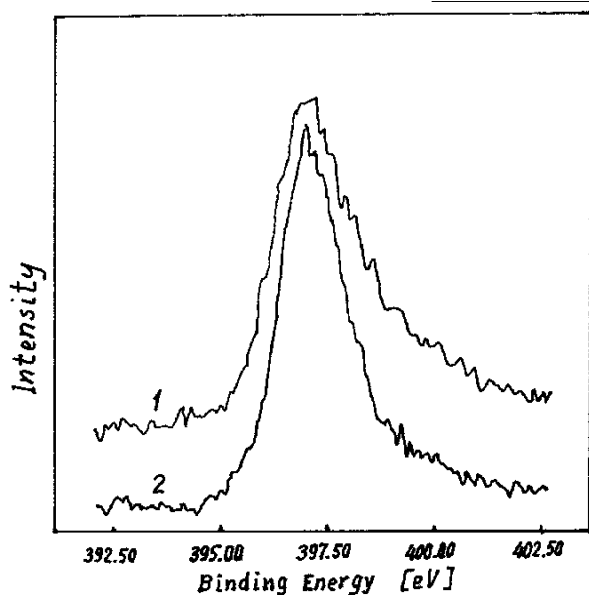


Fig. 5. XPS spectra for N 1s from the surface of electrodeposit obtained at  $i_c = 2.5 \text{ mA cm}^{-2}$  in toluene solution of 0.935 M  $Al_2Br_6$ , DMEPAB and 5.7 mM  $Cr(Acac)_3$ : 1 – with 0.56 TEA, 2 – without TEA

the solution remaining on the surface after withdrawing the plated specimen from electrolyte and during its washing.

And finally, along with the elements present in the components of electrolyte, also a certain amount of substrate metal (copper) was determined in the coatings. As is evident from Table 1, the amount of copper on the surface of coating, excepting rare instances, does not exceed 0.1–0.2 at. %. Meanwhile, this value in the deeper layers of a coating, closer to its back, increases by a whole order of magnitude and in some instances reaches even 3%. This demonstrates that aluminium coatings are not compact but, occasionally can contain a considerable number of pores in which various products of reaction between copper back and electrolyte are found. In addition, it can be seen that in the case when a great body of copper is found in the coating, *i.e.* when the coating is more porous, the relative quantities of all other elements stand out against the definite sequence of a specified trend.

## CONCLUSIONS

1. The elementary analysis of Al-Cr electrodeposits has been carried out by means of X-ray photoelectron spectroscopy, and the amounts of aluminium, chromium, oxygen, carbon, bromine and copper were determined both on the surface of deposits and in their depth.
2. A considerable amount of aluminium oxide was detected not only on the surface of electrodeposits, but also in the depth of coatings.
3. The conclusion was confirmed that chromium content in Al-Cr electrodeposits increases with increasing the chromium concentration in solution, with adding triethylaluminium to electrolyte and with decreasing the current density.
4. The major portion of carbon in form of various compounds is concentrated on the coating surface.
5. An unexpectedly large amount of nitrogen was detected in the electrodeposits, whereas its amount on the surface was negligibly small.

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**ALUMINIO ELEKTROLITINIS NUSODINIMAS  
ESANT KAI KURIEMS CHROMO JUNGINIAMS.  
3. ELEKTROLITINIŲ DANGŲ XPS ANALIZĖ**

S a n t r a u k a

Rentgeno spindulių fotoelektroninių spektrų pagalba nustatyta elementinė sudėtis elektrolitinių dangų, gautų

AlBr<sub>3</sub>-dimetiltilfenilamonio bromido toluoliniuose tirpaluose su chromo(III) acetilacetonu ar chromo(III) oleatu. Nustatytas aliuminio, chromo, deguonies, anglies, bromo ir vario kiekis ir dangų paviršiuje, ir jų gilumoje. Aliuminio oksido pastebimas kiekis nustatytas ne tik dangų paviršiuje, bet ir jų viduje. Anglies junginių didžioji dalis yra susikaupusi dangų paviršiuje, tuo tarpu azoto, atvirkščiai, dangos viduje.

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**ЭЛЕКТРООСАЖДЕНИЕ АЛЮМИНИЯ В  
ПРИСУТСТВИИ НЕКОТОРЫХ СОЕДИНЕНИЙ  
ХРОМА  
3. XPS-АНАЛИЗ ЭЛЕКТРОЛИТИЧЕСКИХ  
ПОКРЫТИЙ**

Р е з ю м е

С помощью рентгеновских фотоэлектронных спектров определен элементный состав электролитических покрытий, осажденных из толуольных растворов AlBr<sub>3</sub>-бромид диметилэтилфениламмония, содержащих ацетилацетонат или олеат хрома. Определено количество алюминия, хрома, кислорода, углерода, брома и меди как на поверхности покрытий, так и в их глубине. Заметное количество оксида алюминия обнаружено не только на поверхности покрытий, но и в их глубине. Основная часть соединений углерода накапливается на поверхности покрытий, в то время как азот, наоборот, в их глубине.