



# LOW - TEMPERATURE ELECTROLYTE (MELT) FOR THE PREPARATION OF CORROSION AND HEAT-RESISTANT ELECTROPLATINGS BY ALUMINUM

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The composition of the melt was described in which, primarily the preparation of aluminum electroplatings at low - temperatures: 95-110 °C is possible on hardware and steels such as: ST-3, Cr-18 and ST-40, as well as on screw like hardware (bolts, nuts), manufactured from steels 25CrMoFe and 35MoFe. Optimum conditions of the process of plating preparation and electrochemical parameters were also determined. The effect of various metal-modifier (Pb, Sn, Bi, Mn, Zr, Cr) on plating process and quality of the melt has also been studied.

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## INTRODUCTION

The service period of hardware, machines-plants, constructions and others etc. depends upon corrosion-resistance and heat stability of the metals. Unfortunately, most of them are not characterized by these properties. All over the world the annual losses, caused by corrosion, estimated as 20 million tons in terms of pure metals in the form of machines-plants, equipment, constructions and others etc. The replacement of these old ones with new material requires the enormous expenses. The losses, caused by corrosion, comprise 2.5-4 % of annual national income in industrially developed countries. For example, in USA this estimated value is about 3.1 % (276 million dollars, annually, by the data of the year 2011), in Germany – 2.8 % and etc. Therefore, all over the world it's a matter of great importance to search the new methods of corrosion prevention and improvement of existing ones. Comprehensive development of electro-deposition is of considerable importance for metal protection against corrosion by efficient methods.

Preparation of electroplatings is possible by electrolysis of aqueous solutions, non-aqueous solutions and of the melts. From aqueous solutions the production of the majority of metals and their platings is impossible because of high electronegative potential (for example,  $E=-1,7$  V for Al). The use of organic compounds is limited because of their instability, toxicity and high costs.<sup>1,2</sup> The preparation of more than a half of the metals and, respectively, of their electroplatings is possible from the molten electrolytes. High temperature, huge power consumption and costly

materials used for the corrosion resistance are the difficulties faced during the implementation of such processes. Despite of above mentioned difficulties there is no alternative for the preparation of the platings of the majority of the metals and their alloys from molten electrolytes. Prepared platings are characterized by high adhesion with a base metal which, every so often, is due to the surface diffusion of plated metal into base metal or to the formation of intermetallides. Although in some cases an existence of intermetallides on the base surface is harmful (for example, FeAl<sub>3</sub>, formed on iron surface, impairs iron properties).

Protective coatings on the basis of organic (paints-varnishes, polymeric materials and etc.) and inorganic (metals, oxides and etc.) compounds occupies an important place in unified system of corrosion control of hardware and other construction etc.

Protection of metals by metals (Zr, Sn, Ni, Cr) plating against corrosion is used since centuries. Due to this world reserves of these metals are to be exhausted. Availability of aluminum resources in the world is the specific reason to use it for plating for corrosion world wide. Aluminized metals are corrosion-resistance and heat stabile also, they are unaffected by corrosion even at high temperatures. The surface of aluminized iron is unchanged at 470 °C and is characterized by 85 % reflection of heat and light. It is corrosion – resistant at 700 °C over several thousand hours. Sulfur-containing hot gases also have no effect on aluminum plating even at high temperatures.

Aluminum platings protect the base metals not only mechanically but also electrochemically (anodic). In the case of mechanical damage of aluminum plated surface the corrosion “couple” is formed where the base metal becomes a cathode and is not oxidized.

Presently various methods are used for the plating of aluminum such as: high-temperature spraying; obtaining of aluminum electroplatings from organic solutions; colorizing (hot aluminizing) – immersion of large size hardware iron sheets in molten aluminum at 700-800 °C for some time. These methods are characterized by considerable disadvantages. They are unsuitable for aluminizing of complex-profile hardware as well as of screw-surface bolts and nuts, on which the durability of various constructions as well as of the masts of high-voltage line is highly dependent. Thus there is a huge demand of these materials.

The preparation of aluminum electroplatings is possible from cryolite - containing melts at the temperatures of 1000-1070 °C, in fluoride-chloride melts at 800-900 °C.<sup>3-6</sup> The use of chloride melt allows performing the process at relatively low (~200 °C) temperatures.<sup>7-9</sup>

On the basis of available literature data, it is observed that high volatility of AlCl<sub>3</sub> and the formation of large quantities of sludge – Al<sub>2</sub>O<sub>3</sub> is the main hurdle in promoting the present process in industries.

Our main aim is to create some eco-safe and technofriendly electrolyte, melting at low temperatures, for preparation of aluminum electroplatings on hardware. Molten chloride system is proposed in which, usually the preparation of mentioned platings is possible at “unusual” low (95-105 °C) temperatures. Low-temperature processes are characterized by less technological difficulties, there is no need in the use of heat-stable materials, evidently, power consumption is significantly less and etc. At ~100 °C the volatility of AlCl<sub>3</sub> is sharply decreased what is more important from ecological viewpoint. In proposed electrolyte one of the cations is a powerful acceptor of oxygen-ions<sup>10</sup> which hinders the formation of sludge - Al<sub>2</sub>O<sub>3</sub>. It should be also noted that at preparation of aluminum electroplatings on hardware in such conditions the above-mentioned undesirable inter-metallide – FeAl<sub>3</sub> is not formed.

Proposed electrolyte allows obtaining aluminum electroplatings at hardware (steels) which are widely used in power engineering, agriculture, food, chemical and oil - refineries etc.

Galvanic aluminizing for metals of strategic importance (Pb, Ti, Zr, Hf, Ta, Nb, Mo, W and etc.) is topical for use on various fields of engineering. These metals are heat-resistant at high temperatures (400-1500 °C) and have load bearing capacities also. As a result they become corrosion-resistant at the temperatures of (400-1500 °C). Previously, aluminizing of mentioned metals was carried out in the melts at the temperatures of (800-1070 °C).

Because of thermal in-stability of plastic materials their plating by aluminum is not possible at high – temperature. In low-temperature (~100 °C) melt, proposed by us, in a usual practice, the galvanic aluminizing of various plastic materials was made possible with heat stability up to more than 100 °C.

The results of the investigations, performed on the present problems, strongly suggest possible solutions in proposed electrolyte by galvanic aluminizing.

In present paper the results of the investigation of low-temperature galvanic aluminizing of hardware are given.

## EXPERIMENTAL

The experiments were performed in the beakers of glass, corundum or porcelain. An electrolyte was prepared by fusion of chemically pure and preliminary dehydrated salts. In the beaker an anode of aluminum and metal-modifier were hung. The properly treated plates of low-grade steels, including steel-3 (thickness: 0.2-2 mm) as well as screw-profile hardware (bolts and nuts, manufactured from the steels 25KhMF and 35MF) were used as the cathodes (base). Temperature was controlled by contact thermometer with an accuracy of ±1 °C. Cathode current density was varied in the range from 0.01 to 0,05A·cm<sup>-2</sup>, electrolysis duration: 15-35 min; temperature (105-110 °C±1<sup>0</sup>).

The preparation of the surface of a base metal is of a significant importance at obtaining of plating. The surface of the metal for aluminum plating was prepared by two ways: a)-mechanically, b)-electrochemically – by anodic treatment in a solution: H<sub>2</sub>SO<sub>4</sub> 150-200 g L<sup>-1</sup>; NaCl 20-40 g L<sup>-1</sup>; temperature: 20-25 °C, anode -- plated hardware, cathode - lead plate, anode current density – 0.02-0.1 A·cm<sup>-2</sup>, electrolysis duration: 5-10 minutes. Plated hardware was washed by water and acetone. Thereafter their aluminum electroplating was performed in selected melt.

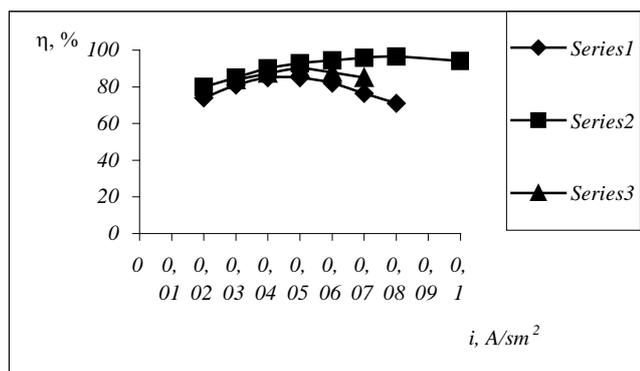
Structure and composition of obtained platings were determined by metallographic, X-ray crystallographic and chemical analyses. Plating thickness was measured by weight increment too.

Detection of the microstructure of aluminum and its alloys is very difficult because of high plasticity and relatively low – hardness of pure aluminum. The surface of the samples has pale color after grinding-polishing. For its elimination the sample was brushed with 0.5 % acid (HF) moistened cotton. Thereafter the sample was placed in 5-20 % aqueous solution of NaOH over 30-60 seconds for “pickling”. Dark color, formed after pickling, was removed by concentrated nitric acid. Thereafter the sample was washed by hot distilled water and was dried. The presence of diffusion layer was determined by microscope MIM-7. Micro-hardness was measured by device PMT-3.

## RESULTS AND DISCUSSION

The experiments have shown that the reasonable aluminum electroplatings were obtained at the following conditions: temperature: 100-110 °C, electrolysis duration: 25-45 minutes, cathode current density 0.03-0.1 A·cm<sup>-2</sup>. In this conditions the light, silvery platings were obtained with a good adhesion with a base; a thickness comprises 20-30 μm. Dependence of current efficiency on current density is shown in Fig. 1.

The experiments were also performed for aluminizing of other complex-profile hardware. Angle-bars, manufactured from low-grade steels and other small – size complex- shape hardware were used as a cathode. The results are identical (Picture 1).



**Figure 1** Dependence of current efficiency of the process of preparation of aluminum electroplating on the cathode current density without modifier. 2. modified by Pb. 3. modified by Zr.

Since the dendrites are formed at a cathode in a course of long-term electrolysis, therefore in many cases the preparation of the plating of desirable thickness has not met with success. For this reason metals – “modifiers” were added to a melt.



**Picture 1.** Various aluminized complex-profile hardware.

There are three reasons about the mechanism of the effect of small amounts of metals ions-additives on the process of aluminum electroplating:<sup>8-11</sup>

- In the course of electrolysis the atoms of metals-additives are deposited on active centers of a cathode, cause their passivating and in doing so are favorable for the formation of new crystallization centers;
- Because of mixing of separated atoms of metals-additives with aluminum the surface energy of crystalline formations is reduced, increasing the probability of their generation;

Metal ions positively affect on plating quality if the potentials of separation of metal-additive and main metal are closely related or their separation proceeds in equilibrium (quasi - equilibrium) regime. Along with it the sizes of the atoms of metals-additives must differ significantly from the sizes of the atom of main metal or it must form a chemical compound with it. Two or more metals, separated in quasi-equilibrium regime, in many cases form inter-metallides.<sup>10-11</sup>

The effect of the ions of metals-modifiers (Pb-1,75 Å, Sn-1,27 Å, Bi-1,82 Å, Mn-1,30 Å, Zr-1,60 Å, Cr-1,27 Å) on the process of preparation of aluminum electroplatings and on plating quality in proposed melt was studied.

Ionic compounds of the metals (0,01-0,1 wt. %) were used as the additives in terms of existing aluminum halide or metals ions were introduced into a melt by anodic dissolving of a metal. Current strength on anode-modifier was smaller by a factor 500-600 than cathode current strength and varied with increase of the amount of metal ions-additives, when the occasion requires. By this way their concentration was controlled in molten electrolyte in the course of the overall process.

Experimental results have shown that the small additives of the metals ( $10^{-6}$ - $10^{-5}$  g. at.  $mol^{-1}$ ) improve considerably the plating quality. The plating of better quality is obtained with the use of Pb and Zr, in comparison with other similar metals. The thickness increases to 60-70  $\mu m$ . The plating is dense, smooth and is characterized by high adhesion.

At the use of lead auxiliary electrode at electrode surface an interaction of absorption type takes place between aluminum growing crystals and lead additives. The small amount of lead additives acts as a surfactant allowing increase the plating thickness. Lead amount in the plating does not exceed 1 %.

The use of Cr and Mn made possible not only to increase a plating thickness but reduced the electrolyte volatility too, decreased dendrites amount and the rate of sludge formation respectively. These facts increase the electrolyte stability very considerably.

It was also established that Mn content in the plating comprises no more than 2 %. The plating of such type is used in chemical and food industries and etc. They replace success- fully the items of scarce tin in an industry.

At co-deposition of aluminum-tin the plating is smooth, but porous. In the case of small additives of bismuth the dendrites are formed, the plating is not thick and hard. Mechanical strength increases in series: Bi, Sn, Mn, Pb, Zr, Cr.

Literature reveals that the greater is the difference between the values of atomic radius of main metal and metal-additive, the plating is obtained by good mechanical strength. This observation is not always true, as in the case of Bi.

It was established that the grip of aluminum platings on ST-3 is reasonably large. Doping of the plating by chromium and manganese at the same base increases an increase in the grip and comprises 70-77  $kg\ cm^{-2}$  and at a steel Kh-18: 55-60  $kg\ cm^{-2}$ . The said grip of aluminum platings, doped by lead, comprises 50  $kg\ cm^{-2}$ .

Also the high-quality and corrosion-resistant platings are obtained on screw hardware (bolts and nuts) which are manufactured from the steels – 25KhMF, 35MF.

**Table 1.** Characteristics of aluminum platings

№	Base material	Anode-modifier	Ratio $I_C/I_A$	Current density, $i, \text{Acm}^{-2}$	Plating thickness, $\mu\text{m}$	Current efficiency, $\eta\%$
1	ST-3	-	-	0,02	16	74
2	Kh-18	-	-	0,04	25	85,5
3	ST-40	-	-	0,06	22	82
				0,08	18	72
4	ST-3	Pb	1/1000	0,02	20	80
5		Pb	1/1000	0,06	60	96
6		Zr	1/500	0,03	35	84
7		Zr	1/500	0,05	49	90
		Mn	1/500	0,04	52	89,5
		Cr	1/250	0,03	55	80,0
8	Kh-18	Pb	1/1000	0,04	27	90
9		Pb	1/1000	0,06	63	94
10		Zr	1/500	0,07	54	85
		Mn	1/500	0,04	55	91,5
11	ST-40	Pb	1/1000	0,08	68	96,5
12		Zr	1/500	0,05	57	90,0
13		Mn	1/500	0,05	60	91,0

Hardware, aluminized in various regimes as well as non-aluminized ones (bolts and nuts), were tested on corrosion resistance in humid atmosphere and in 5-10 % aqueous solution of NaOH (over 25-30 days). Un-plated hardware was subjected to strong corrosion but some aluminized hardware remained unchanged. This fact also became a reference point for selection of electrolysis conditions. Some characteristics of aluminum platings on the metals are presented in Table 1.

Thus the investigation, performed in proposed electrolyte, has shown that a high-quality aluminum electroplatings are obtained on above-listed base-metals. Doping of aluminum by other metals - modifiers allows to increase the current density, current efficiency and plating thickness.

The additives of selected metals have an encouraging effect on plating adhesion among which Cr and Mn additives must be marked off.

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