Metallization of aluminum alloys with electrodeposition by rubbing

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Abstract. The technology of metallization of duralumin alloy D16 and cast aluminum alloy AL4 with method of electrodeposition by rubbing has been developed, which allows excluding operations of chemical etching and clarification without reducing the adhesion of coatings. In these operations, such high-concentration acids as nitric, sulfuric, hydrofluoric and others can be used. Instead, it is proposed to use cathode-anode processing operations and application of the zinc-nickel-boron nitride alloy in a universal, much more environmentally friendly electrolyte for simultaneous etching and deposition of coatings. A technology for applying a gradient zinc-nickel-boron nitride alloy with electrodeposition by rubbing has been developed. The process of copper plating of aluminum alloys from pyrophosphate electrolytes with electrodeposition by rubbing is studied. Such modes of coating as copper and zinc-nickel-boron nitride ones using anode tools with an area of 1 cm² and 3.75 cm² were established.

1. Introduction

Aluminum and its alloys are used in many industries because they have a number of advantages: low density, high corrosion resistance, increased electrical conductivity, good thermal conductivity and ductility. Alloys of aluminum with silicon – silumins have very good casting properties. It is, first of all, high fluidity. Duralumin, high-strength and granular (powder) alloys have a high specific strength. However, aluminum and aluminum alloys are not without drawbacks. Duralumin aluminum alloys have low corrosion resistance. Aluminum and its alloys are poorly soldered, have a high coefficient of friction, low hardness and wear resistance and not always sufficient decorative properties. To eliminate the shortcomings of aluminum and aluminum alloys and significantly improve their properties, electrolytic coatings can be used. Coatings allow combining the positive (valuable) properties of aluminum with the properties of the applied coatings. Aluminum and its alloys on the surface have a strongly bonded oxide film $\text{Al}_2\text{O}_3$. After complete removal, alumina is rapidly formed again. Therefore, despite the fact that various multi-operational technologies are used in electroplating for coating, it is not possible to achieve high-quality metallization of aluminum and its alloys, especially those working under harsh operating conditions. In this regard, the problem of creating high-quality, reliable, low-operational and inexpensive metallization of aluminum and its alloys is quite relevant [1]. One of the most common methods of metallization of these alloys is galvanic, based on the use of electrolysis. Electrolysis is also used in the electrodeposition by rubbing method. In contrast to the galvanic method, there is no galvanic bath in the method of electrodeposition by rubbing. A small volume of electrolyte
is held by a porous material attached to the anode tool. This method is more environmentally friendly, versatile, mobile and high-speed compared to the traditional galvanic method [2–4].

2. Experiment: materials and methodic

Samples were made of duralumin alloy D16 containing copper 3.8–4.9%, magnesium 1.2–1.8%, manganese 0.3–0.9% and silicon 0.5%, and from a cast aluminum alloy AL4 containing silicon 8–10%, manganese 0.25–0.5% and magnesium 0.17–0.3%. The samples were 40×60×1 mm in size.

For electrodeposition with rubbing, anode tools with a working area of 1 cm² and 3.75 cm² were used. The conductive part of the anode tools was made of 08H18N10T stainless steel containing carbon 0.8%, titanium about 1%, nickel 10% and chromium 18%. To hold the electrolyte and prevent a short circuit, the lower conductive part of the anode tools was wrapped with fabrics. First, a thin terry cloth with electrolyte absorption of 0.07 ml/cm² was used, and the second layer was made of a wear-resistant synthetic fabric consisting of polyester fibers (crimpl) with electrolyte absorption – 0.02 ml/cm².

To supply electrolytes, the dipping method and the jet method were used. The feed rate of the electrolyte by the jet method was 12–18 ml/cm² min. The speed of movement of the anode instruments was maintained from 15 to 20 m/min. The ratio of the cathode (coated) surface to the anode (area of the anode tool) was 2. Electrolytes were prepared using distilled water and chemically pure chemicals. To prepare the surface and for electrodeposition with rubbing an AC rectifier with current stabilization and protection against short circuit was used. The installation and anode instrument circuits are given in [5, 6]. The thickness of the coatings and the deposition rate were determined by the gravimetric method (by weight gain) on an analytical balance with an accuracy of 0.1 mg and using a high-precision micrometer. The adhesion strength of the coatings was checked by the following methods: applying a grid of scratches (grooves), brazing with a brass brush and heat treatment with heating to 190–200 °C, holding for 1 hour and cooling in air. In addition, the adhesion of the zinc-nickel-boron nitride coating was evaluated by the results of diffusion vacuum annealing with a heating temperature of 400 °C.

3. Results and discussion

Considerable attention in this work was given to the development of surface preparation of aluminum alloys to increase the adhesion of the applied coatings, reduce the number of operations and low environmental hazards. Technological schemes were developed: “A” – without immersion preparation of surface, that is, with direct coating and scheme “B” with immersion preparation of surface. To reduce the number of operations of the technological process, the principle of combining operations was used, which can be implemented in the method of electrodeposition by rubbing. The first combination used in both schemes “A” and “B” is the simultaneous execution of machining and electrochemical degreasing. For this, an electrolyte suspension with micropowder of cubic boron nitride with a dispersion of the main fraction of 10 μm was used. Degreasing was performed using anode tools. Samples for all experiments were degreased in the following solution (g/l): sodium carbonate 40–50, trisodium phosphate 40–50, sodium metasilicate 3–5, syntanol (DS-10) 1–2, boron nitride up to 200. The electrolyte was heated to 60 – 70 °C and cathodic degreasing was performed at a current density of 5–10 A/dm² for 7 minutes. The quality of degreasing was controlled with the wetting of the sample surface with water.

For direct electrodeposition of the coating on aluminum alloys, a coating based on the zinc-nickel Zn – Ni electrolytic alloy was used. This alloy can be galvanized on aluminum, steel and other metals. The alloy is applied to provide reliable, anode “active protection” from corrosion of steel parts. With such protection, the coating is an anode in regards to steel and, dissolving, protects it from corrosion, therefore corrosion products are formed on the coating. Nevertheless, more and more often, protective coatings are required to ensure that active protection is accompanied by maintaining the surface almost unchanged during long-term operation. To some extent, this is characteristic of zinc-nickel alloy coating (12–15% Ni). Recent studies have focused on further improving the protective ability of these coatings and addressing some of the drawbacks of Zn – Ni coatings [7, 8]. It is known that when applying zinc coatings by selective rubbing onto a steel base of a large area, there is a significant etching of the zinc
coating at the edges. This occurs at a time when the electrode tool is far from the edge of the coating and this section has a low cathodic polarization [9]. The Zn–Ni alloy has advantages over zinc because of the less corrosion that occurs directly during rubbing. Considering the data of [10], we will compile table 1 of a comparative analysis of acid and alkaline electrolytes used for the galvanic deposition of Zn–Ni alloy, it will help us make the right choice of electrolyte for electrodeposition by rubbing.

### Table 1. Comparison of acidic and alkaline electrolytes used for Zn–Ni coating.

| Indicators                        | Acidic | Alkaline |
|----------------------------------|--------|----------|
| Current output                   | More   | Less     |
| Coating speed                    | Higher | Lower    |
| Scattering ability               | Lower  | Higher   |
| Coating ability – “starting characteristics” | Higher | Lower |
| Protective abilities             | High   | High     |

As can be seen from table 1, the main advantage of alkaline electrolytes is their high dissipation ability, this property is very important for traditional galvanic coating, it is secondary, not the most important for electrodeposition by rubbing. Moreover, the heightened “starting characteristics” of the electrolyte are especially important for the metallization of aluminum and other poorly coated metals. Acid electrolytes are more promising for direct coating of aluminum alloys with electrodeposition by rubbing. In scheme “A”, the technology of combining two operations in one universal electrolyte was used: electrochemical etching and almost immediately applied coating. We used this technology for metallization of molybdenum alloys and achieved good adhesion [11]. The same principle was used in another work [12] for coating aluminum alloys with the galvanic method. In this work, a Zn–Ni galvanic alloy of sulfate electrolyte was deposited on aluminum alloys, in which the cathodic treatment and then the anode treatment were first performed. The electrolyte, in addition to zinc sulfate and nickel sulfate, to increase electrical conductivity contains sodium sulfate and boric acid, as a buffer additive stabilizing the pH. The electrolyte also contains sodium fluoride. Sodium fluoride dissolves the oxide film on aluminum; aluminum binds to sodium fluoride into a fluoroaluminate complex. This contributes to obtaining a fine-grained structure of the coating and increases the adhesion of the coating to aluminum alloys. We suggest a technology for producing a gradient zinc-nickel-nitride boron coating due to changes in the concentration of electrodeposit metals and changes in the composition of electrolytes. To do this, we used the electrolytes shown in table 2. The purpose of obtaining such a gradient coating is to increase the adhesion of the applied coating and increase corrosion resistance. To solve this problem, a zinc-nickel-nitride boron coating Zn–Ni–BN was used with a gradual increase in the nickel content in the coating. The standard potential of aluminum is 1.66V, zinc – 0.76V, nickel – 0.25V. The potentials of coatings in real operating conditions will differ from standard ones, however, in real operating conditions, the zinc potential will be more negative compared to the potential of nickel. Accordingly, in the Zn–Ni–BN gradient coating, the potential will gradually change from more negative to more positive, this should increase the protective ability of such a coating. In the gradient Zn–Ni–BN coating, the coefficient of thermal linear expansion (CTLE) will change more smoothly. For aluminum, it is 1.7 times higher than that of nickel and slightly differs from the CTLE of zinc. Thus, in the gradient coating, the CTLE will also change more smoothly, and this should increase the adhesion of the coatings, especially when the temperature changes, for example, during soldering.
Table 2. The composition of the electrolytes to obtain a gradient coating Zn–Ni–BN.

| Components, g/l | Electrolyte 1 | Electrolyte 2 | Electrolyte 3 |
|-----------------|---------------|---------------|---------------|
| Zinc sulfate    | 240–300       | 160–200       | 40–50         |
| Zinc chloride   | 40–50         | 176–220       | 232–290       |
| Nickel sulfate  | 80–100        | 16–200        | 20–30         |
| Nickel chloride | 80–100        | 176–220       | 232–290       |
| Sodium sulfate  | 40–100        | 6–12          | 30–50         |
| Glycine         | 20–30         | 30–50         | 20–30         |
| Sodium acetate  | 20–30         | 30–50         | 20–30         |
| Boric acid      | 20–30         | 30–50         | 20–30         |
| Sodium fluoride | 15–20         | 30–50         | 20–30         |
| Preparation OS-20 | 0.1–0.5  | 0.1–0.5       | 0.1–0.5       |
| Gelatin         | 0.1–0.3       | 0.1–0.3       | 0.1–0.3       |
| Saccharin       | 0.5–1.5       |               |               |
| Boron nitride   | 5–10          | 5–10          | 5–10          |
| pH              | 1.9–2.0       | 2.5–3.0       | 3.5–4.0       |

Electrolytes 1–3 contain cubic boron nitride (elbor) MRTU 2-036-1-68 brand LM 1/0. The grain size of the main fraction (95%) is 1 μm and smaller, i.e., the main fraction contains boron nitride nanopowder BN. Cubic BN is second only to diamond in hardness. In addition, BN when electrically rubbing coatings on aluminum alloys activates the surface, which is especially important when applying coatings on aluminum alloys. Also, during electrodeposition by rubbing, BN can smooth out microprotrusions, which contributes to the production of smoother, semi-shiny coatings. It is known that nanopowders can adsorb cations of molecules dissociated in the electrolyte, which improve their delivery to the cathode. Hitting the nanoparticles with the deposition surface, they locally destroy the double electric layer (DEL), energetically activate the deposition zone, while at the same time bringing ions adsorbed on the surface of the nanoparticles to a distance less than the thickness of the DEL. Nanopowders, as a rule, increase the adhesion of coatings and reduce their porosity [13]. Electrolytes 1–3 contain the preparation OS-20 which is a mixture of polyethylene glycol esters of synthetic primary higher fatty alcohols. OS-20 is a surfactant and helps to increase the sedimentation stability of nanosuspension. OS-20 eliminates pitting, improves the wettability of the surface of aluminum alloys with electrolyte. Electrolytes 2 and 3 contain gelatin. Gelatin and OS-20 contribute to the production of fine crystalline and shiny coatings. Presumably, they form colloidal ion complexes with metal ions and increase cathodic polarization. Gelatin can be adsorbed on microprotrusions and block their growth; accordingly, it is a shiner. However, it must be borne in mind that gelatin, especially at relatively high concentrations in electrolytes, reduces the ductility of the coatings. Therefore, the gelatin content in electrolytes does not exceed 0.3 g/l.

Saccharin also contributes to the production of shiny coatings and reduces internal stresses, primarily nickel, so it is part of electrolyte 3. Electrolyte 2 contains aminoacetic acid (glycine) and sodium acetate, these substances have good buffering properties. Glycine with nickel can form a complex $\left[ \text{Ni}(\text{GLy}) \right]^+$, which in an acidic environment is a cation and acquires a positive charge. This complex compound has a negative logarithm of instability constants (ion equilibrium constants) $\lg K = 5.7$. This complex is concentrated near a negatively charged cathode and it has a positive effect on the quality of the deposited coatings. In the electrolyte, complexes could appear: $\left[ \text{Ni}(\text{GLy})_2 \right] c \lg K = 10.54$ and $\left[ \text{Ni}(\text{GLy})_3 \right] c \lg K = 14.26$ [14]. The complex compounds of glycine based on zinc $\left[ \text{Zn}(\text{GLy}) \right]_2$ are formed at a pH above 6, and at a pH above 4.5 the complex $\left[ \text{Zn}(\text{GLy}) \right]_3$ is formed, it has $\lg K = 5.3$ and acts as a cation. In [15], data are presented on the low resistance of zinc glycine complexes and, accordingly, the electrodeposition of zinc from such solutions occurred with a slight overvoltage. During the deposition of nickel and zinc from complex cations, there is an increase in the concentration of glycine in the
cathode layer and, accordingly, conditions are created for the formation of stronger nickel complexes \([\text{Ni}(\text{GLy})_2]\) и \([\text{Ni}(\text{GLy})_3]\). Complex compounds of nickel with glycine are stronger than complex compounds of zinc and, accordingly, glycine contributes to the enrichment of the alloy with nickel, bringing the polarization curves of nickel deposition to the polarization curves of zinc deposition. The content of nickel and zinc was defined with analytical method. The content of boron nitride was calculated by subtracting the total content of zinc and nickel (percentages are given by weight) from 100%. The results are presented in table 3.

Table 3. The effect of electrolytes on the composition of the coatings.

| Composition       | Electrolyte 1 | Electrolyte 2 | Electrolyte 3 |
|-------------------|---------------|---------------|---------------|
| Nickel            | 4.3           | 11.4          | 23.1          |
| Zinc              | 89.5          | 82.9          | 72.0          |
| Boron nitride     | 6.2           | 5.7           | 4.9           |

Thus, when using electrolytes from 1 to 3, the nickel concentration in the coatings increases due to an increase from 0.3 to 3 in the ratio of nickel to zinc in the electrolyte, and also due to an increase in the glycine concentration from 0 to 50 g/l in the electrolyte. In this case, the potential of the first coating layers is closest to the potential of aluminum, and as the coating thickness increases, the potential becomes more electropositive. Moreover, if during the application of electrolytic coatings on steel, we try not to exceed the nickel content above 12–16% in order to maintain the anode, active corrosion protection mechanism, in the galvanic pair “aluminum alloy – coating electrolytic Zn – Ni alloy of any composition”, the coatings will be cathodic. Since Zn – Ni alloys with increased nickel content become more chemically and corrosion resistant, there is a need for a gradual increase of nickel in the coating, i.e. in creating a gradient coating with an increased concentration of nickel. However, too high nickel content of the coating can create high internal stresses in the coating. To eliminate lamination and to make transitions in nickel concentration in the coating more smooth, diffusion (homogeneous) annealing in a vacuum furnace can be used.

Thus, the technological scheme “A” will consist of the following operations: combined operation of simultaneous degreasing and grinding, performed by rubbing electrodeposition; rinsing in deionized water; cathodic treatment by rubbing electrodeposition in electrolyte 1 with a current density of 10 A/dm² for 20 seconds; anodic treatment by rubbing electrodeposition in electrolyte 1 with a current density of 10A/dm² for 20 seconds; electrodeposition by rubbing of Zn – Ni – BN alloy in electrolyte 1 with a cathode current density \((D_c)\) of 30 A/dm² for 4 min; electrodeposition by rubbing of \(Zn – Ni – BN\) alloy in electrolyte 2 with \(D_c = 30A/dm^2\) for 4 min; electrodeposition by rubbing of \(Zn – Ni – BN\) alloy in electrolyte 3 with \(D_c = 30A/dm^2\) for 4 min; rinsing in deionized water; drying; diffusion vacuum annealing with an isothermal holding temperature of 400°C for 3 hours and cooling together with the furnace; quality control.

The coating thickness was determined with the gravimetric method using formula 1.

\[
h = \frac{(m_2 - m_1) \times 10000}{(\rho_1 n_1 + \rho_2 n_2 + \rho_3 n_3) \times S},
\]

where: \(h\) is the coating thickness, microns; \(m_2\) is the mass of the coated sample, g; \(m_1\) is the mass of the sample without coating, g; \(\rho_1\) is the density of zinc in g/cm³; \(n_1\) is the fraction of zinc in the coating in fractions of a unit; \(\rho_2\) is the density of nickel in g/cm³; \(n_2\) is the fraction of nickel in the coating in fractions of a unit; \(S\) is the area of the covered area in cm²; \(\rho_3\) is the density of boron nitride in g/cm³; \(n_3\) is the fraction of boron nitride in the coating in fractions of a unit.

For electrodeposition with rubbing, an anode tool with an area of 3.75 cm² with jetting of electrolyte was used. When using the electronic rubbing modes specified in the technological scheme “A”, smooth, semi-shiny coatings without visible defects were obtained. When measured with a high-precision
micrometer, the thickness varied from 36 to 49.5 μm in different parts of the coated sample. The total average coating thickness calculated by formula 1, obtained under these conditions according to scheme “A”, was 47.6 μm. The average coating rate was 4 μm/min.

To implement the technological scheme “B” immersion solutions were prepared; their compositions are given in table 4. The immersion treatment of aluminum alloys was performed by dipping. Processing time in electrolytes 4 and 5 of a duralumin alloy is 8–20 seconds, of cast aluminum alloy is 10–30 seconds. After this, the samples were washed in water, especially thorough washing should be performed after treatment in electrolyte 4 due to the presence of sodium hydroxide in its composition, however, solution 4 is cheaper than solution 5. Differences in the adhesion of copper coatings obtained when immersion solutions are used in surface preparation 4 and 5 were not found.

Table 4. Compositions for applying immersion coatings Zn and Zn – Ni on aluminum alloys: duralumin D16 and casting AL4.

| Components, g/l | Electrolyte 4 | Electrolyte 5 |
|----------------|--------------|--------------|
| Zinc Sulfate   | 20–30        |              |
| Hydrofluoride Zinc | 20–40       |              |
| Hydrobromide Nickel | 200–220    |              |
| Sodium hydroxide | 100–150     |              |
| Ammonium hydrogen fluoride | 30–40     |              |
| Potassium nitrate tartrate | 8–10       |              |
| Ferric chloride | 1–3         |              |
| Sodium nitrite  | 0.5–1        |              |

In technological scheme B, the process of electrodeposition by rubbing of copper coatings was used. Alkaline copper plating electrolytes were applied, since one of the main disadvantages of the main acid copper plating electrolytes is the inability to obtain a sufficiently high, necessary adhesion of the copper coating on aluminum alloys due to the contact release of copper. Contact copper release is not completely suppressed even in the presence of special additives introduced into acidic electrolytes. Many alkaline copper plating electrolytes do not have this disadvantage. Pyrophosphate electrolytes are the simplest in composition, stable and harmless in comparison with other alkaline electrolytes of copper plating. For electrodeposition by rubbing pyrophosphate electrolytes 6 and 7 were used, their compositions are given in table 5.

Table 5. Compositions of pyrophosphate copper plating electrolytes for electrodeposition by rubbing.

| Components, g/l | Electrolyte 6 | Electrolyte 7 |
|----------------|--------------|--------------|
| Copper sulfate | 32–40        | 96–120       |
| Potassium pyrophosphate | 300–350     | 300–350     |
| Citric acid    | 15–20        |              |
| Sodium selenic acid | 0–0.3      | 0–0.3        |
| Additive CPEO in ml/l |          | 15–25        |
| pH             | 8.3–8.7      | 8.3–8.7      |

Pyrophosphate copper electrolyte 6 (table 5) is intended for preliminary copper plating of aluminum alloys. In this electrolyte, it is possible to apply both shiny coatings in the presence of sodium selenic acid concentration of 0.1–0.3 g/l, and matte in the absence of this salt. Copper electrolyte 7 can be used for faster main copper plating. It contains CPEO additive which is a condensation product of oxalic acid and ethylene glycol. The use of the CPEO additive in galvanic electrolytes decreased the porosity of the
copper coating, increased the penetrability of complex-shaped products while expanding the range of the working current density [16]. The additive has also been shown to be effective in electrodeposition by rubbing. To determine the modes of electrodeposition by rubbing, the maximum permissible cathodic current density was established for pyrophosphate electrolytes, these data are presented in table 6.

Table 6. The effect of the area of the anode tools ($S_a$) and the composition of the electrolytes on the maximum allowable cathodic current densities (A/cm$^2$) when dipping the anode tools into the electrolyte in the numerator and when jetting the electrolyte in the denominator.

| $S_{a}, \text{ cm}^2$ | Electrolyte 6 | Electrolyte 7 |
|----------------------|--------------|---------------|
| 1                    | 8/16         | 20/38         |
| 3.75                 | 3.2/7        | 9/19          |

As can be seen from table 6, in electrolyte 7, the maximum allowable current densities for electrodeposition by rubbing are much higher than in electrolyte 6. This is due to the higher concentration of copper ions in electrolyte 7, compared with the copper content in electrolyte 6. The maximum allowable cathodic current density is also influenced by the area of the anode tools, the smaller the anode tool, the higher the maximum allowable cathodic current densities can be applied. This is due to improved diffusion of copper ions. So, for example, when using an anode tool with an area of 0.02 cm$^2$, even in electrolyte 6 the maximum permissible cathodic current density of 200 A/dm$^2$ was reached. The feed rate of the electrolyte in the jet method is an order of magnitude higher than the feed rate of the electrolyte in the dipping method; it allowed increasing the permissible cathodic current densities. For depositing a copper coating with a total thickness of at least 24 μm, you can use the modes with jet feeding of electrolytes presented in table 7.

Table 7. Modes (cathodic current density $D_c$, A/dm$^2$ and time) for applying a copper coating with a thickness of $25 \pm 1 \mu m$ for electrodeposition by rubbing with anode tools with an area of $1 \text{cm}^2$ and $3.75 \text{ cm}^2$.

| Modes | $S = 1 \text{ cm}^2$ | $S = 3.75 \text{ cm}^2$ |
|-------|----------------------|------------------------|
|       | Electrolyte 6 | Electrolyte 7 | Electrolyte 6 | Electrolyte 7 |
| $D_c$, A/dm$^2$ | 16    | 38    | 7     | 19     |
| Time, min | 1.5   | 4     | 2.5   | 8      |

As can be seen from table 7, the total time for electrodeposition by rubbing when using an anode tool with an area of $1 \text{ cm}^2$ is almost two times less than for an anode tool with an area of $3.75 \text{ cm}^2$. This is due to the use of higher $D_c$ due to better diffusion when using smaller anode tools. However, the area of the resulting coating for the anode tool $S = 3.75 \text{ cm}^2$ is 3.7 times larger than for the anode tool with $S = 1 \text{ cm}^2$.

Thus, the technological scheme “B” consists of the following operations:
- combined operation of simultaneous degreasing and grinding, performed by electrodeposition by rubbing;
- washing in deionized water;
- immersion treatment;
- rinsing in deionized water;
- electrodeposition by rubbing in the electrolyte of preliminary copper plating 6;
- electrodeposition by rubbing in electrolyte 7 of the main copper plating;
- washing in deionized water;
drying;
quality control.

Quality control included external inspection, determination of coating thickness and adhesion test. Copper coatings were electrodeposited without visible defects from dull to semi-shiny and shiny, depending on the content of shine-forming additives in the electrolyte. The results of checking the adhesion of zinc-nickel and copper coatings obtained using the preparation scheme A and B are presented in table 8.

| Schemes      | The method of measuring adhesion |
|--------------|----------------------------------|
| Scheme A     | +/+                              |
| Scheme B     | +/-                              |

Table 8 shows the methods for measuring adhesion: 1 – by brushing with a brass brush, 2 – by scratching (making grooves), 3 – the method of heat treatment (heating). The coating control standard does not recommend a heating method to test the adhesion of copper coatings on aluminum alloys, so this method was used only for zinc-based alloys.

As can be seen from the results obtained, when using technological scheme A, all samples passed the adhesion test. When using scheme B, coatings on a cast aluminum alloy did not pass the adhesion tests by the grooves method. This is due to the fact that the cast aluminum alloy contains more silicon compared to the duralumin alloy. For metallization of cast aluminum alloys, if necessary, to have a top layer of copper, technological scheme A was used and a Zn – Ni – BN coating was applied, and then a copper coating of pyrophosphate electrolytes was applied. This option was tested, and it gave a good adhesion result. As can be seen from table 5, the adhesion of the coatings is higher to the duralumin alloy. Samples of D16 duralumin alloy coated with both a gradient zinc-nickel-boron nitride alloy using technological scheme A and copper using scheme B passed all adhesion tests.

4. Conclusion
In comparison with standard technological schemes two more environmentally friendly technological schemes for the metallization of aluminum alloys by the method of electrodeposition by rubbing with a reduced number of operations have been developed. Scheme B using immersion coatings made it possible to apply high-quality shiny copper coatings to duralumin alloys with high adhesion. In scheme A (direct coating of aluminum alloys) through the use of combined operations of simultaneous grinding and degreasing, etching and deposition of zinc-nickel-boron nitride alloy in one universal electrolyte reduced the number of operations. Technological scheme A allows obtaining high-quality, semi-shiny coatings with high adhesion strength to duralumin and cast aluminum alloys. The applied coating is a gradient zinc-nickel-boron nitride alloy with an increased nickel content as the coating thickness increases from 4.3% to 23.1%.

References
[1] Skopintsev V D, Margolin L N and Farafonov V V 2019 Galvanotekhnika i obrabotka poverkhnost Electroplating and surface treatment vol 27 2 9–22
[2] Semenychev V V 2017 Galvanotekhnika i obrabotka poverkhnosti Electroplating and surface treatment vol 25 1 23–27
[3] Demin S A and Vinogradov S S 2018 Works of VIAM 9 43–50 DOI: 10.18577/2307-6046-2018-0-9-43-50
[4] Naletov B P and Tyurikov E V 2009 *Aviation materials and technologies* 2(11) 25–29
[5] Moskovits M 1993 Galvanotekhnika i obrabotka poverkhnosti *Electroplating and surface treatment* vol 2 3 40–45
[6] Tikhonov A A and Sokolova A Yu 2010 *Bulletin of the Novgorod state University Yaroslav The Wise* 60 102–105
[7] Shekhanov R F, Gridchin S N and Balmasov A V 2019 Galvanotekhnika i obrabotka poverkhnosti. *Electroplating and surface treatment* vol 27 4–8
[8] Kuznetsova I O, Saveljev A V, Nyrkov N P and Shuvalov D A 2019 Vestnik nauki *Bulletin of Science* vol 3 6(15) 382–8
[9] Ivshin Ya V and Kadrikov R A 2014 Galvanotekhnika i obrabotka poverkhnosti *Electroplating and surface treatment* vol 22 3 40–4
[10] Ralf Kraus 2013 Galvanotekhnika i obrabotka poverkhnosti *Electroplating and surface treatment* vol 21 4 24–9
[11] Tikhonov A A, Arendateleva S I and Perepelitsa T I 2019 *IOP Conf. Series: Materials Science and Engineering* 656 012050
[12] Novikov A N and Bakaeva N V 2004 *Patent RU2237757*
[13] Ilyin In A, Semenychev In B, Naletov B P, Salakhova R K and Tyurikov E V 2010 Patent RF 2 389 828 *Bul. 14*
[14] Dolgih O V, Sotskaya N V and Shamaeva E S 2006 Kondensirovannyye sredy i mezhfaznyye gransitny Condensed media and interfaces vol 8 4 275–282
[15] Berezin N B, Berezina T N, Mezhevich Zh V and Chevela V V 2006 Vestnik Kazanskogo universiteta *Kazan University Herald* vol 16 5 267–8
[16] Kolchugin A V, Opolovnikov V R, Priyatkin G M and Vasiliev V V 1997 *Patent RU 2094543*