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OBTAINIG AND STUDY AN OPTICAL PROPERTIES OF BLACK COATINGS ON ALUMINUM ALLOYS

The article is devoted to the study of deposition processes of optically black coatings on aluminum parts. Such coatings are indispensable at analog optical systems designing for receiving and transmitting images. Unlike digital optical systems, analog ones are more resistant to radio interference. To transmit an image in such systems, reflection between two or more mirrors is used. The main characteristic of the mirror layer is the reflectivity, but it reflects not only the desired part of the radiation, but also the interfering radiation. To avoid image distortion, the internal and external non-reflective parts in such systems must have an optical black coating with high absorption of radiation in the visible part of the spectrum.

The article reveals the peculiarities of surface preparation of aluminum parts for obtaining optical black coatings. Since for military applications, devices based on aluminum alloys are increasingly used, combining strength and light weight, this is especially appreciated in field conditions.

It is known that aluminum and its alloys are characterized by a bright surface and the presence of a stable protective oxide film. Therefore, for the application of optical black coatings, it is proposed to use the process of anodizing aluminum with subsequent filling of the oxide film by adsorption or chemical methods or the use of intermediate metal coatings with an external optical black nickel coating.

The article provides a comprehensive analysis of the obtained black optical coatings on the aluminum surface. The main goal of the article is to compare the two obtained coatings with respect to the light absorption coefficient and corrosion resistance. The paper presents the results for various methods of preparation and application of coatings on the aluminum surface.

It was found that direct porous aluminum anodization followed by painting with an organic dye has poor resistance to UV-radiation and changes color after two weeks. It is shown that the coloring of the porous anodized layer by the electrochemical method shows better resistance to UV-radiation, but poor corrosion resistance.

A multilayer coating containing chemically and electrochemically applied nickel coatings with a top layer of black nickel coating has been found to have the best protective and optical properties. An electrolyte for the electrochemical deposition of a protective nickel coating is proposed, which, due to the content of fluorine ions, provides a non-porous coating and strong adhesion of the coating to the base. In addition, due to heat treatment, the adhesion and corrosion resistance of the multilayer coating increases.

Key words: *analogy optical systems, black optical coating, nickel coating, aluminum anodizing, UV-resistance, corrosion resistance.*

Formulation of the problem. In order to obtain a non-distorted image in analog optical systems, an important condition is the absence of parasitic reflection from the body parts of the optical system. For this, the parts must be covered by a coating that absorbs all visible radiation and thus reduces image distortion. Black nickel is the blackest coating of all that can be obtained by electroplating. Black chrome, black rhodium, black ruthenium – all these coatings are dark gray in color. The true black finish is black nickel only. Black nickel coating is used to give parts made of steel and non-ferrous metals special optical and decorative properties. Depending on the electrolyte composition and coating conditions, the coating on the product can be not only saturated black, but also dark brown, as well as blue-violet (with the use of an interference film). The thickness of the coating layer varies from 1 to 50 microns and depends on the metal to which it is applied, as well as on the requirements for the product. A rich and deep black color on the products is obtained if the current density is selected correctly. Black nickel plating is used both to give details a decorative look, in jewelry, and in various branches of the optical and machine industry.

For military applications, devices based on aluminum alloys are increasingly used, combining strength and low weight, which is especially appreciated in field conditions. However, aluminum and its alloys are characterized by a shiny surface and the presence of a stable protective oxide film. To apply optical black coatings, you can use aluminum anodization with the filling of the oxide film by adsorption or chemical methods or using intermediate metal coatings with the application of the top optical black nickel coating.

Analysis of recent research and publications. There are already many articles devoted to aluminum anodizing as protective and functional layer formation, in particular, with the creation of a black absorbent coating [1–5]. There are also many publications concerned to nickel and black nickel optical coatings on steel and non-ferrous bases. The direct application of galvanic coatings on the surface of aluminum and its alloys is complicated by the presence of a strong oxide layer on its surface, which prevents the production of coatings firmly attached to the base. Since the presented material is not sufficiently stable, the surface must be additionally protected before applying the black nickel optical coating.

As a coating, you can use galvanic metal coatings, as well as metallic and non-metallic coatings obtained by the method of vacuum spraying or thermal diffusion application. The simplest and most accessible is galvanic coatings.

In the case of using aluminum or its alloys as a base, the process of applying galvanic coatings is characterized by several features. They are due to the presence of a strong and easily recoverable oxide film on the surface of aluminum (due to the high activity of the metal to oxygen), which prevents good adhesion of the deposited metal to the base. In addition, contact release of copper, zinc, silver, nickel, tin, chromium and other more positive metals can occur on this metal, which can also impair adhesion of sediments to the base. Aluminum is significantly different from deposited metals in terms of thermal expansion coefficient, hydrogen overvoltage, and so on. Due to highlighted reasons at applying galvanic coatings to aluminum and its alloys, special preparation of the surface of the base is necessary, which would reduce the effect of the above factors. There are various methods of preparing the surface of aluminum before applying galvanic coatings: chemical, electrochemical and mechanical.

Three methods are used to apply galvanic coatings to aluminum and its alloys:

– contact (or zincate) method, in which the oxide film is removed before coating and replaced with a thin layer of contact deposited metal (most often zinc, cadmium, nickel and others);

– electrochemical method, by means of which the thickness of the oxide film is increased by anodizing in special solutions to obtain a highly porous layer, which ensures the strength of adhesion with the galvanic coating applied afterwards.

– galvanic method, by means of which galvanic coatings of electrolytes containing activators are applied to the surface of aluminum or its alloys. With this method, it is not necessary to apply special methods of pre-treatment of the surface of the parts.

Contact method.

This method is used most often due to its simplicity, cheapness and versatility. Most of the coatings that are deposited on aluminum and its alloys are applied to an interlayer of contact-deposited zinc, which is why this method is often called "zinc".

Zinc deposition can be carried out from acidic or alkaline solutions, but in practice, alkaline solutions are more often used.

When processing in an alkaline zincate solution, the oxide film dissolves:

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O, \qquad (1.1)$$

and contact zinc deposition:

$$2H_2O + 2Al + 3ZnO_2^{2-} = 2AlO^{2-} + 3Zn + 4OH^- . \quad (1.2)$$

Good adhesion of galvanic coatings to the zinc layer is achieved with thin and dense layers of zinc. The thickness of the zinc coating depends mainly on the concentration of caustic sodium in the solution: the higher it is, the thinner the deposit. To increase the density of the zinc layer, modifiers can be introduced into the zinc solution: ferrous salt (10...20 g/l), $FeCl_3$ (1...2 g/l) or $NaNO_2$ (1 g/l). The growth of the film in zincate solutions continues in the first 15 seconds, therefore the duration of treatment is not of great importance. For pure aluminum and its alloys with manganese, it is 10 s, for alloys with silicon – 5...10 s, for alloys with copper – 5 s.

Double treatment in a zincate solution is often practiced. To do this, the zinc film obtained during the first treatment is removed by etching in a 30–50% solution of nitric acid, and after thorough washing, it is treated again in a zincate solution. After the second application, the obtained layer of zinc is again removed in a solution of nitric acid. The mechanism of film adhesion improvement with two-time processing is not yet completely clear, but such processing gives good results. It is possible to galvanically deposit a layer of other metals (Cu, Zn, Cd, Cr, Ag, Ni) on contact zinc (one-time treatment). Ordinary electrolytes are recommended for applying galvanic coatings on the zinc layer.

Electrochemical method.

Phosphoric acid electrolytes have become the most widely used for pre-anodizing aluminum alloys before applying galvanic coatings. The thickness and quality of the oxide film depend on the voltage on the electrolyzer, temperature, duration of treatment and acid concentration. The necessary degree of porosity is provided by concentrated solutions of phosphoric acid.

It is recommended to process only A1 alloys in this way. Unsatisfactory adhesion of galvanic coatings to the base is observed on pure or technical aluminum after anodization in H_3PO_4.

When the galvanic coating is deposited on the oxidized surface of aluminum, nuclei are formed at individual points of the cathode. Then the sediment forms "islands" on the surface to be covered, which gradually grow into a continuous coating. The first layers of metal when deposited on the oxide layer have a dark, even black color, regardless of whether copper, nickel or silver is deposited, and only as the coating builds up, it takes on a normal appearance. The most common processes of electrodeposition of metals on the oxide layer are nickel plating (sulphuric acid or sulfamate electrolyte) and copper plating (pyrophosphate electrolyte).

Galvanic method.

With this method, galvanic coatings are applied to parts made of aluminum and its alloys after the usual surface preparation (mechanical, chemical) from electrolytes with special additives – activators (F^-, $S_2O_8^{2-}$, $P_2O_7^{4-}$, NO_2^-).

When using aluminum alloys, one of the methods of leveling the effect of the oxide film and creating a continuous layer of metal coating is the deposition of contact nickel from a chloride-phosphate solution.

A powder nickel is deposited on top of the formed nickel contact film, which does not reduce adhesion, but increases the roughness of subsequent layers of galvanic coatings. With this method of protecting the surface of aluminum, there are no strict requirements for the preliminary preparation of aluminum parts. After applying the contact film, electrolytic coatings of metals and alloys are applied, as for the nickel sublayer. Heat treatment significantly improves the adhesion of the coating to the base. Methods of coating aluminum with preliminary anodic oxidation of the surface are used quite rarely and mainly for decorative coatings that are not subjected to mechanical and thermal loads after that.

Direct coating on aluminum is the simplest. At the same time, there are no operations for preliminary modification of the surface. Preliminary preparation of parts includes degreasing in an alkaline composition and etching in nitric acid.

The most attractive from the point of manufacturability, soldering ability, heat resistance and corrosion resistance is to obtain a nickel coating from an electrolyte with the following composition, g/l: $NiSO_4 \cdot 7H_2O$ – 150…250, H_3BO_3 – 23…30, NaF – 1..3, NaCl – 1…3, $K_2S_2O_8$ – 1…3.

The temperature of electrodeposition is 50...60°C, cathodic current density – 1.0...2.0 A/dm^2, pH 4.0...4.4.

The parts are hung without current, and it is desirable to withstand 1-min. and then turn on the current.

To increase the covering capacity (details of a complex profile), it is suggested to add sodium sulfate 40–60 g/l or lithium sulfate 16–25 g/l to the electrolyte. The latter supplement is more effective. After applying such a coating, it is recommended to carry out heat treatment at 180–300°C for 0.5–2 hours [4, 5].

At the temperature of the electrolyte below 45 ^{0}C, there is a sharp deterioration of the adhesion strength. At elevated temperatures, persulfate self-decomposes, and nickel oxidizes to the trivalent state with the formation of a black precipitate of hydroxide. When using low current densities, parts may not be covered, and when high current densities are used, the coating may swell. Therefore, during the operation of such an electrolyte, it is necessary to control the pH and concentration of persulfate. If the technology involves heat treatment, then coatings capable of delaying hydrogen diffusion must be applied after this operation, otherwise heat treatment does not improve adhesion.

Any types of galvanic coatings can be used as surface coatings after applying a protective sublayer after preliminary activation of the applied and heat-treated nickel sublayer.

Task statement. The work aims to develop the influence of aluminum surface pretreatment and coating application regimes on the optical and corrosion properties of obtained black absorbent coating.

Presentation of the main material

Materials and methods of research. All chemical was used of p.a. grades. As a base for all investigations the 6061 aluminum alloy was used. Research was conducted on aluminum alloy parts to create a black surface for parts of the military optical system.

For this, the parts were subjected to preliminary treatment, which included degreasing, etching, application of chemical nickel coating, application of galvanic nickel coating, heat treatment and application of black optical nickel coating.

When producing samples with a single-layer coating, a layer of nickel was applied directly to the prepared surface of aluminum samples. Preliminary preparation included degreasing with an alkaline solution and etching in a dilute hydrochloric acid solution to etch the oxide film.

For degreasing, the ready-made degreasing composition Ecasit BTU 40 of the company Metalchemie Ukraine was used. The concentration of the composition for degreasing is 50 g/l, the degreasing temperature is 50–60°C, and the operation time is 5–10 minutes. Since the composition of degreasing includes alkaline components and surfactants, to clean the surface of the part, warm washing in water at a temperature of 50–60°C for 1–2 minutes was carried out, followed by cold washing for 1–2 minutes. Water purified by reverse osmosis was used to prepare electrolyte solutions and wash parts between operations.

After degreasing, the oxide film was etched in hydrochloric acid with a concentration of 5% wt. for 20–50 seconds and rinsing in cold water for 1–2 minutes.

To create a protective film tightly bonded to the surface of the aluminum alloy, chemical nickel plating was used in a solution with the following composition, g/l: $NiSO_4 \cdot 7H_2O$ – 25…50, H_3PO_4 – 230…300.

The temperature of the chemical nickel sub-layer deposition was 80–85°C, the deposition time 3–5 minutes.

After that, a protective nickel coating was applied to the parts from an electrolyte with the following composition, g/l: $NiSO_4 \cdot 7H_2O$ – 150…250, H_3BO_3 – 23…30, NaF – 1..3, NaCl – 1…3, $K_2S_2O_8$ – 1…3.

The temperature of the electrolyte was 50...60°C, the cathode current density was 1.0...2.0 A/dm_2, pH 4.0...4.4. The parts were suspended without current and kept for 2 min., and then the calculated current was turned on.

To strengthen the adhesion of the nickel sublayer to the base, after applying the main protective nickel coating, the obtained samples were heat treated in a drying cabinet at a temperature of 220°C for 2 hours.

After that, a black nickel plating was applied to the areas that should have a black non-reflective surface.

Electrolyte with the following composition, g/l, was used for black nickel plating: $NiSO_4 \cdot 7H_2O$ – 150…250, $ZnCl_2$ – 15-25, additive Black Nickel 30 ml, additive Netzmittel N3 10 ml.

The black nickel coating was deposited on the surface of the nickel coating previously activated in a hydrochloric acid solution at a current density of 0.2 A/dm^2.

To compare the corrosion resistance and optical properties of black coatings, a black coating was also obtained on an anodized aluminum alloy.

Surfaclean 990 Metalchemie Ukraine degreaser was used to degrease the aluminum alloy before anodizing. The concentration is 50 g/l, the degreasing temperature is 60 ^{0}C, and the duration of the operation is 5–10 minutes.

After that, the parts were rinsed in warm (60°C) and then in cold deionized water for 1–2 minutes.

The etching was carried out with Activator DO45 (50 g/l) at a temperature of 25°C for 3–5 minutes. After that, it was rinsed in deionized water at room temperature for 1–2 minutes, and anodization was carried out in a sulfuric acid solution of 200 g/l at an anodic current density of 1 A/dm^2 for 30 minutes.

After rinsing in deionized water for 1–2 minutes, electrochemical coloring was carried out in a solution of the following composition, g/l: $CuSO_4 \cdot 5H_2O$ – 35, $MgSO_4 \cdot 7H_2O$ – 20, H_2SO_4 – 5. Electrochemical coloring was carried out on alternating current at a voltage of 10 V for 3–5 min, after which 15 min at a voltage of 15 V.

After rinsing in deionized water for 2 min, the pores of the oxide film on the aluminum alloy were closed in hot (95°C) deionized water for 30 min.

For comparison, part of the anodized samples was coloring by adsorption dyeing in a solution of aniline black dye (5 g/l) at a temperature of 80 ^{0}C for 15 min, followed by closing the pores in hot water, as in the case of electrochemical coloring of the anodic film.

An experimental stand was developed to experimentally determine the degree of blackness. The basis of the design is a sample in the form of a strip of material 10*100 mm installed in a horizontal position on tripod 4 (Fig. 1). A coating with a known degree of blackness (1) was applied to one half of the sample (soot was used), and a coating whose degree of blackness was to be determined was applied to the other half.

A heating element is installed from below, which is connected to the power source 3. The power source allows setting different values of current and voltage on the heater, thus providing different values of temperatures on the surface of the sample in the desired range.

The temperature of the test sample is measured by thermocouples 5 and a thermal imager 9. The thermocouples are connected to the cold junction block and then through the switch 7 to the voltmeter 8. The thermal imager is installed at some distance from the sample, and the radiation temperatures of surfaces 1 and 2 are measured.

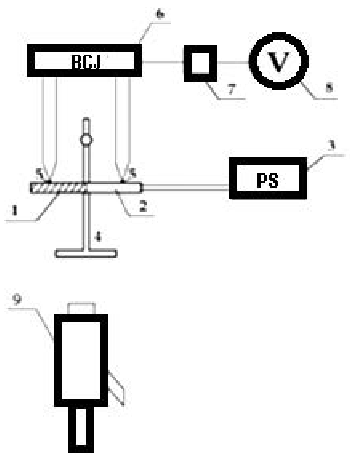

Fig. 1. Scheme of the installation for determining the blackness of samples: 1 – surface with a known degree of blackness, 2 – investigated surface, 3 – power source (PS), 4 – tripod, 5 – thermocouples, 6 – block of cold junctions (BCJ), 7 – switch, 8 – millivoltmeter, 9 – thermal imager

Research results indicate that the degree of blackness of nickel-plated samples is 0.94–0.95, and the degree of blackness of anodized aluminum samples is 0.89–0.92.

The corrosion resistance of the obtained samples was checked in a heat and moisture chamber at a temperature of 30 ^{0}C and a humidity of 90% for 7 days. The nickel-coated samples did not undergo significant changes, while the anodized aluminum samples showed white spots due to aluminum corrosion.

Conclusions. The possibility of obtaining an optical black coatings on aluminum alloys by the methods of applying a black nickel coating and aluminum anodizing with electrochemical coloring of the film has been established.

High degrees of blackness of the obtained films and high corrosion resistance of optical nickel coatings on aluminum alloy parts was established.

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Дробязко А.А., Лінючева О.В., Бик М.В. ОТРИМАННЯ ТА ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ОПТИЧНИХ ЧОРНИХ ПОКРИТТІВ НА АЛЮМІНІЄВИХ СПЛАВАХ

Стаття присвячена вивченню процесів осадження оптично чорних покриттів на алюмінієвих деталях. Такі покриття є незамінними при створенні аналогових оптичних систем одержання та передачі зображення. На відміну від цифрових оптичних систем, аналогові є більш стійкими до радіоперешкод. Для передачі зображення у таких системах використовується відображення між двома і більше дзеркалами. Основною характеристикою дзеркального шару є відбивна здатність, але він відбиває не тільки бажану частину випромінювання, але й заважаюче випромінювання. Щоб уникнути спотворення зображення, внутрішня і зовнішня невідбиваючі частини у таких системах повинні мати оптичне чорне покриття з високим поглинанням випромінювання у видимій частині спектру.

У статті розкрито особливості підготовки поверхні алюмінієвих деталей для одержання оптичних чорних покриттів. Так як для військових застосувань все частіше використовуються пристрої на основі алюмінієвих сплавів, що поєднують міцність і малу вагу, що особливо цінується в польових умовах.

Відомо, що алюміній і його сплави характеризуються світлою поверхнею і наявністю стійкої захисної оксидної плівки. Тому для нанесення оптичних чорних покриттів запропоновано використовувати процес анодування алюмінію із подальшим наповненням оксидної плівки адсорбційними або хімічними методами або використання проміжних металевих покриттів із зовнішнім оптичним чорним нікелевим покриттям.

У статті проведено комплексний аналіз отриманих чорних оптичних покриттів на поверхні алюмінію. Основною метою статті є порівняння двох одержаних покриттів щодо коефіцієнту світлопоглинання та стійкості до корозії. В роботі наведено результати для різних методів підготовки та нанесення покриттів на поверхню алюмінію.

З'ясовано, що пряме пористе анодування алюмінію з подальшим фарбуванням органічним барвником має погану стійкість до ультрафіолетового випромінювання і змінює колір через два тижні. Показано, що забарвлення пористого анодованого шару електрохімічним методом демонструє кращу стійкість до УФ-випромінювання, але погану стійкість до корозії.

Встановлено, що найкращі захисні та оптичні властивості має багатошарове покриття, що містить хімічно та електрохімічно нанесені нікелеві покриття, із верхнім шаром чорного нікелевого покриття. Запропоновано електроліт для електрохімічного осадження захисного нікелевого покриття, який завдяки вмісту іонів фтору забезпечує безпористе покриття і міцне зчеплення покриття з основою. Крім того, за рахунок термообробки підвищується адгезія і стійкість до корозії багатошарового покриття.

Ключові слова: *аналогові оптичні системи, чорне оптичне покриття, нікелеве покриття, анодування алюмінію, стійкість до ультрафіолету, корозійна стійкість.*