

ELECTROLYTIC COLOURING OF POROUS ANODIC ALUMINUM FILMS

Ivan Kanazirski¹, Christian Girginov², Petya Nedyalkova³

^{1,3}University of Mining and Geology “St. Ivan Rilski”1700, Sofia, Bulgaria; E-mail: p.gencheva@mgu.bg

²University of Chemical Technology and Metallurgy1756, Sofia, Bulgaria

ABSTRACT. An overview of electrolytic coloring of porous anodic aluminum films is presented. The preliminary preparation of the surface, the frequency of the current, as well as the composition of the electrolyte are analysed. The different applications of the obtained coatings are presented.

Key words: electrolytic coloring, anodic aluminum films

ЕЛЕКТРОЛИТНО ЦВЕТЯВАНЕ НА ПОРЪОЗНИ АНОДНИ АЛУМИНИЕВИ ФИЛМИ

Ivan Kanazirski¹, Кристиан Гиргинов², Петя Недялкова³

^{1,3} Минно-геоложки университет „Св. Иван Рилски“, 1700 София

²Химикотехнологичен и металургичен университет, 1785 София

РЕЗЮМЕ. Представен е преглед на електролитното оцветяване на порести анодни алуминиеви филми. Анализират се съставът на сплавите, предварителната подготовка на повърхността, честотата на тока, както и съставът на електролита. Представени са различните приложения на получените покрития.

Ключови думи: електролитно оцветяване, анодни алуминиеви филми

Introduction

The porous anodic oxide films on aluminum can be used as matrices in which different substances, including metals, could be incorporated. Metal incorporation is usually performed by AC polarisation in aqueous solutions of metal salts (Wernick and Pinner, 1972).

In the late 19th century, at the very beginning of anodic oxidation studies, alternating current (AC) was used to grow alumina coatings. The advantage of this regime over direct current polarisation was accounted for the use of two identical electrodes and much simpler technological equipment. AC-anodising was, nevertheless, abandoned because of the severe condition to ensure equal surface and composition of the electrodes, as well as a superior quality of contacts.

The electrolytic coloring (“two-step”) process, also called Asada Process, was first in use in Europe and Asia during the 1960s and was introduced in the USA during the 1970s by ALCAN. The earliest claim to coloring anodised aluminum belongs to the Italian scientist Dr. V. Caboni. Dr. Caboni received an Italian patent in 1936 for impregnating aluminum oxide film with finely divided metal from aqueous solutions of the salts of copper, nickel, silver, or metals electropositive to aluminum. The final product of the two-step process is a conventional anodised (soft) oxide film, with coloring done in a subsequent step.

The coloring is produced by electrochemical action using a proprietary second step electrolyte, which contains the dissolved metal salts of tin, cobalt, nickel, or others. Alternating current (AC) power is applied to the process tank by means of a

counter-electrode. The applied AC power deposits metallic particles (pigment) of salt in the pores of the “first step” aluminum oxide film. The color is developed as a result of the optical effect produced by light scattering of metals which have been deposited in the pores of the oxide film. The electrolytically colored oxide film demonstrates very good weathering and corrosion resistance vs. the colored oxide film formed by immersion in organic dye or in an inorganic metal salt. The differences between immersion in organic/inorganic dye and electrolytic coloring are as follows:

1. In immersion, the absorption of dye/salts occurs on the top portion of the pores, while in two-step coloring, metallic colloids deposit at the base of the pores.

2. The organic dye may fade or discolor under sunlight, whereas electrolytic coloring has excellent light resistance to fading caused by light.

3. The organic/inorganic dye will be removed if the oxide film partially wears out vs. electrolytic coloring.

The most common metals incorporated are nickel Ni (Andersson et al., 1980; Lian-peng Tian et al., 2006; Girginov et al., 2012), copper Cu (Hsing-Hsiang et al., 2008; Girginov et al., 2012), tin Sn (Yongqing et al., 1999; Tsangarakis-Kaplanoglou et al., 2006), lead Pb (Yongqing, 2000), iron Fe, and silver Ag (Anicai, 1998).

Aluminum alloys

Aluminium alloys are alloys in which aluminium (Al) is the predominant metal. The typical alloying elements are copper, magnesium, manganese, silicon, tin, and zinc.

The 1xxx series alloys comprise aluminum of 99% or higher purity. This series has excellent corrosion resistance, excellent workability, as well as high thermal and electrical conductivity.

In the 2xxx series, copper is used as the principle alloying element and can be strengthened significantly through heat-treating. These alloys possess a good combination of high strength and toughness, but do not have the levels of atmospheric corrosion resistance as many other aluminum alloys. Therefore, these alloys are usually painted or clad for such exposures.

In the 3xxx series, manganese is the major alloying element in this series, often with smaller amounts of magnesium added. However, only a limited percentage of manganese can be effectively added to aluminum. 3003 is a popular general-purpose alloy because it has moderate strength and good workability and may be used in applications, such as heat exchangers and cooking utensils.

The 4xxx series alloys are combined with silicon which can be added in sufficient quantities to lower the melting point of aluminum without producing brittleness. Because of this, the 4xxx series produces excellent welding wire and brazing alloys where a lower melting point is required. Alloy 4043 is one of the most widely used filler alloys.

In the 5xxx series, magnesium is the primary alloying agent and it is one of the most effective and widely used alloying elements for aluminum. Alloys in this series possess moderate to high strength characteristics, as well as good weldability and resistance to corrosion in the marine environment.

The 6xxx series are versatile, heat treatable, highly formable, weldable, and have moderately high strength in addition to excellent corrosion resistance. Alloys in this series contain silicon and magnesium in order to form magnesium silicide within the alloy.

In the 7xxx series, zinc is the primary alloying agent, and when magnesium is added in a smaller amount, the result is a heat-treatable, very high strength alloy. Other elements, such as copper and chromium, may also be added in small quantities. The most commonly known alloys are the 7050 and the 7075.

According to the recommendations of the Aluminum Association, the preferred aluminum alloys for the “two-step” coloring are AA1XXX, AA3XXX, AA5XXX, and AA6XXX. The aluminum alloys of the 2XXX, 4XXX, and 7XXX series and casting are not recommended for electro coloring because of poor results.

Surface pre-treatment

Different methods of preliminary preparation of the surface of the working sample are applied.

For a start, degreasing in acetone, trichloroethylene or another organic solvent is necessary (Tsangaraki-Kaplanoglou et al., 2006).

The next step is alkaline cleaning (etching) for 1 min in 100 g/l NaOH or at 55 to 60°C for 3 to 5 minutes in a solution containing 100 g/l sodium hydroxide (Tsangaraki-Kaplanoglou et al. 2006), or 10 g/l sodium fluoride, 2 g/l sodium polyphosphate, and 2 g/l wetting agent or alkaline bath containing Na₂CO₃ (5 g/l), Na₃PO₄ (4.3 g/l), Na₂SiO₃ (0.5 g/l), and NaC₆H₁₁O₇ (10 g/l) (Arurault et al., 2004), and finally, immersing for 1 min in 1:1 v/v HNO₃ at room temperature.

Some researchers use electropolishing in a phosphoric-chromic acid electrolyte (210 cm³ H₂O, 40 g CrO₃, 450 g 85%

H₃PO₄, 150 g 96% H₂SO₄) at 80°C and by constant anodic current density of 0.2-0.3 A cm⁻² for 3 min (Girginov et al., 2013).

After rinsing in deionised water and drying in a stream of air at room temperature, the specimens are stored in a desiccator.

Anodic oxidation

Anodising is carried out in sulfuric acid solutions or in phosphoric acid solutions. The sulfuric acid solution contains 175 g/l H₂SO₄ and 1 g/l Al₂(SO₄)₃ x 18H₂O at 20°C (Tsangaraki-Kaplanoglou et al., 2006) or 180 g/l H₂SO₄ (M. Zemanová et al., 2009). Phosphoric acid is in a wider range of concentrations: 9%w/v according to Zemanová et al., (2009) to 2 M phosphoric acid as by Santiago and Fernandez (2014). Anodising is carried out with the constant current density of 1.5-2 A dm⁻².

Electrolytic colouring

Various electrolytes have been used for electrolytic colouring of porous anodic oxide films.

They contain base salt (NiSO₄, CuSO₄, SnSO₄, AgNO₃, FeSO₄, and others), as well as additives (H₃BO₃, (NH₄)₂SO₄, MgSO₄, H₂SO₄ and others). Their purpose is to maintain a constant pH value.

Our contribution

In a series of papers, we have presented electrodeposition of many metals (Girginov et al., 2012; Girginov et al., 2013; Girginov et al., 2018; Kozhuharov, et al., 2019).

The Al₂O₃-matrices with a thickness (D) of 20 µm and porosity (a) of 0.15%, formed in sulfuric acid, serve as a good basis for obtaining coloured functional coatings. As a result of the conducted studies, it was found that NiSO₄, CuSO₄, and (NiSO₄ + CuSO₄)–containing electrolytes ensure the obtaining of qualitative coatings with excellent reproducibility. The quantity of incorporated metal within the pores is proportional to colouring time for each electrolyte. Electrolytic colouring in CuSO₄ incorporated more copper than nickel (in NiSO₄) for all colouring times. In the visible spectrum, the light absorbance increased with colouring time and after 10 minutes reached a maximum value (absorbtion A 96%) for three investigated electrolytes. Absorption had a maximum at 60 Hz frequency in the range of 20-100 Hz. The coatings obtained in this study possess good decorative properties (beige-brown-black shades) in the visible region. Also, the high degree of light absorbance in the studied range (340-1500 nm) gives them a good perspective for use in solar collectors.

The Al₂O₃-matrices, formed in H₂SO₄ and electrolytically coloured in a CoSO₄ solution, demonstrate good absorbance properties in the visible range wavelengths (380- 750 nm). The obtained colored films exhibit light grey - greyish-black shades. The colour characteristics of these coatings are interpreted using different approaches (colour space) developed within the International Commission on Illumination (CIE). The colour characteristics of the samples are measured in three different colour spaces. In all cases, an increase of the colouring time leads to an increase of the colour intensity. It turns out that the spectral and colour characteristics of the obtained functional layers based on porous Al₂O₃ films are also influenced by the type of alloy used. The absorbance ability of the solutions films coloured in cobalt increases with the amount of alloying elements. The mat surfaces exhibit a higher light absorption than the polished samples. The oxide matrices formed

(thickness 20 μm and porosity 0.15 %) and coloured in CoSO_4 solution are promising functional layers with possible application as good decorative coatings.

The next research shows the results of experiments performed on the AC electrochemical Ag-incorporation in the AAO matrices on the technically pure AA1050 aluminum alloy.

The research activities were a part of systematical characterisation of the impact of the anodisation of AA1050 alloy samples, combined with AC-electrochemical silver incorporation. The surface of the modified sample was submitted to determination of the obtained colour, hydrophobicity, and mechanical strength. The characterisation of the surface properties was completed by definition of the surface morphology, composition, and performance in a conventional model corrosive medium. The main inferences done for the obtained results are formulated below:

- The preliminary treatment procedures resulted in silver-like shining surfaces, whereas the anodisation and AC-assisted silver incorporation led to pale gray and mahogany brown colours, as a result of the formation of a porous surface and the subsequent partial pore filling with Ag_2O . These colour modifications were quantified according to the CIE ($L^*a^*b^*$) system.

- These colour alterations were accompanied by changes in the surface hydrophobicity after the respective treatments. The respective contact angle measurements have revealed that both the AAO and Al-O-Ag layers are definitely hydrophilic, due probably to entrapped water in the film pores.

- The nano-indentation tests have shown that the anodisation leads to significant hardness increment, whereas the silver incorporation does not lead to remarkable alterations of mechanical properties.

- The SEM topological observations have not shown the typical highly ordered pores distribution but rather randomly distributed pits, formed probably on locations of intermetallic inclusions. The related EDX map analyses have revealed an increase of the oxygen content and an insignificant amount of incorporated silver. Besides, it has been established that the anodisation proceeds with involvement of sulfur from the electrolyte.

- The XPS analyses have shown that the surface of the native oxide layer of AA1050 is composed of Al_2O_3 and partly from $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$, whereas the AAO and Al-O-Ag films are composed of alumina only. Any traces of Ag have not been registered on the surface layer.

- The EIS spectra, acquired after 168 hours of exposure to the model corrosive medium, were submitted to data fitting to suitable model equivalent circuits. The spectra fitting has revealed the apparent capacitive character of the AAO layers, due to the dielectric properties of the dense AAO underlayer. The Ag-doped spectra samples required the addition of a diffusion element for the description of the diffusion limitations inside the Ag_2O layer capillaries inside the pores of the AAO layer.

- The respective PDS curves have shown a sharp rise of the polarisation resistance by about three orders of magnitude after anodisation, followed by negligible decrease after silver incorporation. The respective corrosion potential values also follow a trend of sharp shift in positive direction for the AAO layers, with a less considerable shift in the same direction for the Al-O-Ag films, (Girginov et al., 2012; Girginov et al., 2013; Girginov et al., 2018; Kozhuharov, et al., 2019).

Conclusion

The formed and colored aluminium oxide matrices are promising functional layers with possible application as very good decorative coatings. They have an application as light-absorbing coatings in solar collectors.

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