Electrolytic coloring of anodic alumina in $CoSO_4$ solution Part two: Influence of the aluminum alloy type

Christian Girginov, Ivan Kanazirski, Tsvetan Dimitrov

Abstract: *Al_2O_3-matrices formed in H_2SO_4 are electrolytically colored in a $CoSO_4$ solution. The absorbance spectral characteristics are recorded in the wavelength range 380-750 nm. The obtained colored anodic films are in the light grey-grey-black hue. The influence of the coloring time, the type of Al alloy and the surface treatment on the spectral and color characteristics of the produced layers has been investigated. The interpretation of the color characteristics is based on different CIE (International Commission on Illumination) "color space" systems. In all cases the color intensity increases with coloring time. The type of alloy used affects the values of the color parameters characterizing the Al_2O_3-films. Samples with matt surface have higher light absorbance than the polished ones. The colored in a $CoSO_4$ solution oxide matrices show good reproducibility and decorative properties.*

Keywords: *anodic alumina films, electrolytic coloring, spectral characteristics, color characteristics.*

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 polarization [1] in aqueous solutions of metal salts. As a result of this electrochemical process composite coatings are formed, which exhibit good corrosion [2] and decorative properties. The most common incorporated metals are Ni [3, 4] Cu [5, 6], Sn [7], Pb [8], Fe [9], Ag [10]. Recently there has been a profound interest in Al_2O_3 matrices incorporated with cobalt [11, 12]. This interest is motivated by the interesting magnetic properties [13] of these systems. Aluminum matrices with incorporated cobalt can also have a successful application in the production of decorative anticorrosion coatings and solar selective layers. It is well known that for obtaining high quality and reproducible functional layers, the type of aluminum used [14], and the conditions of formation of the porous matrices are of great importance. In that sense, it was of interest to investigate the effect of the type of aluminum metal used, the pretreatment and coloring time, on the light absorbance in the visible region. This will provide information on the impact of these factors on the decorative color characteristics of these functional coatings.

EXPERIMENTAL

The experiments were carried out using samples of technical purity aluminum (99.5% Al) and two aluminum alloys A 8006 (97.90% Al, 0.25% Si, 1.44% Fe, 0.37% Mn) and A 8011 (98.55% Al, 0.66% Si, 0.70% Fe, 0.06% Mn), with a working area of 8 cm^2. They were put through a standard pretreatment procedure, which included: annealing at 400°C for 3 h, degreasing in CCl_4, electropolishing in a phosphoric acid-chromic acid electrolyte. Finally the specimens were rinsed out by double distilled water and dried out in air. Prior to each experiment the specimens were brightened in a solution CrO_3 (20 g dm^{-3}) and H_3PO_4 (15 ml dm^{-3} 85%) for 3 min at 85°C. Some of the specimens were mat in an aqueous solution of NaOH (2%) and $NaNO_3$ (3%), for 10 min at 80°C. Prior to the anodization the specimens were brightened in a solution containing CrO_3 (20 g dm^{-3}) and H_3PO_4 (15 ml dm^{-3} 85%), for 3 min, at 85°C. The matrix formation was carried out in 15 % aqueous H_2SO_4 at constant current density (15 mA cm^{-2}), and for 45 min at 20°C. A two-electrode cell with a platinum mesh counter electrode situated symmetrically around the working electrode was used for porous anodization. Under these conditions the anodic films have constant thickness (D = 20 μm) [15] and porosity (α = 0.15) [3]. The electrolytic coloring was carried out by AC (sinusoidal) polarization in an aqueous solution containing: $CoSO_4$ (10 g dm^{-3}), $(NH_4)_2SO_4$ (30 g dm^{-3}) and H_3BO_3 (50 g dm^{-3}) at 20°C. A home-made AC galvanostat was used ensuring current density 3.75 mA cm^{-2} (60 Hz). As a counter electrode graphite plates were applied.

The spectral characteristics of the colored specimens were recorded by precision spectrophotometer Shimadzu UV-3100 in the wavelength range 380-750 nm. The light absorbance (A) was calculated by reflectance (R) spectra: A = 100 – R. The color characteristics parameters were assessed by a reflectance tintometer (Lovibond RT 100).

RESULTS AND DISCUSSION

1. The effect of aluminum alloys on the light absorbance characteristics

Porous alumina was formed on three different aluminum alloys (Al 99.5%, A 8011 and A 8006). The films formed have the same thickness (D = 20 μm) and porosity (α = 0.15). The porous Al_2O_3-films are colored in $CoSO_4$ solution under constant current density (3.75 mA cm^{-2}), and temperature (20°C) with a frequency of 60 Hz. The coloring time was varied from 2 to 15 min. The obtained colored films exhibit light grey-grey-black shades. To investigate their decorative properties it is of interest to record their spectral absorbance characteristics within the visible range (380-750 nm). The experiments were carried out with samples, with two different surface pretreatments (electropolished and mat). Such spectral absorbance curves of the porous alumina formed on different aluminum alloys (Al 99.5%, A 8011 and A 8006), colored for 15 minutes (at 60 Hz) are presented in Figure 1.

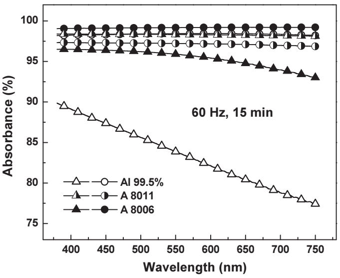

Fig. 1. Spectral absorbance curves of electrolytic colored films formed on different Al substrates for 15 minutes (60 Hz). The empty symbols denote the electropolished samples, while the filled – the mat ones.

The obtained results suggest that the increasing of coloring time leads to an increase of the spectral absorbance values (the samples exhibit a more intensive coloring). In all cases the mat pretreatment of the sample surface results in an increase of the absorbance capacity of the colored films.

2. The effect of aluminium substrate on the color characteristics

It is of practical interest to assess the color characteristics of the obtained functional decorative coatings, depending on the type of aluminum alloy. This assessment of the sample color characteristics can be performed using different color space approaches, developed within the CIE (International Commission on Illumination) system. The parameters characterizing the color of the obtained samples were determined on the basis of the most widely used (CIE)-color spaces [16]. The color characteristics of films, obtained by the longest coloring (15 minutes) AC polarization (60 Hz) were investigated. The samples obtained under these conditions have the highest absorbance ability in the visible region, and the most intensive coloring, respectively.

CIE (XYZ)-color space

This threedimensional color space contains all perceivable colors. In this color space system (1931) the tristimulus parameters (X, Y, Z) may be thought of as „derived” from the red, green and blue colors. The measured values (X, Y and Z) of the colored in $CoSO_4$ solution anodic films (polished and mat samples) are presented in Figure 2.

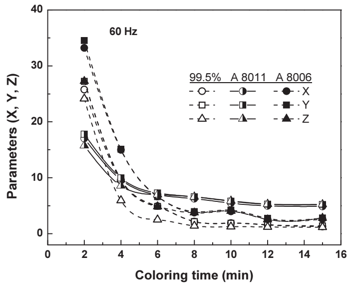

Fig. 2. The tristimulus values as a function of coloring time for the three types of metal substrate.

CIE (*xyY*)-color space

This twodimensional chromaticity system (1964) shows a special projection of the threedimensional (XYZ)-color space. The color can be divided into two parts: brightness and chromaticity. This space characterizes colors by a luminance parameter (Y) and two color coordinates (x and y) which specify the point on the chromaticity diagram. This system offers precision color measurement because the parameters are based on the spectral power distribution of the light. The measured color parameters (x and y) of the three alloys are presented in Figure 3.

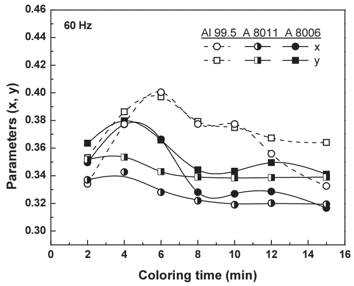

Fig. 3. Parameters (*x* and *y*) as a function coloring time for the used alloys.

CIE (L*a*b*)-color space

This space (1976) is commonly used for surface colors. The CIE (L*a*b*)-color scale is organized in a cubic form. The values of L* vary from bottom (L* = 0, black) to top (L* = 100, white). The parameters are as follows: a*>0 (red), a*<0 (green); b*>0 (yellow), b*<0 (blue). The axes of a* and b* are unlimited. These color parameters for electropolished and mat samples were measured and are shown in Figure 4.

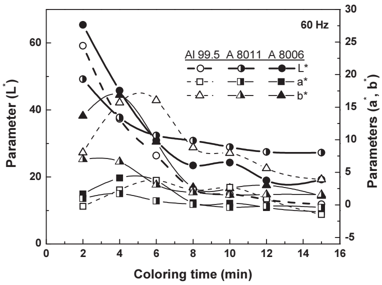

Fig. 4. Parameters (L*, a* and b*) vs. coloring time. Presented with empty symbols are the results for electropolished and with full – the mat samples.

The obtained results allow concluding that the films formed on the alloy A 8006 (97.90% Al, 0.25% Si, 1.44% Fe, 0.37% Mn) under equal other conditions have the most intense coloring. This finding is also confirmed by direct visual observation. The coloring intensity of A 8011 is greater than that of Al 99.5%. These results allow making an assumption that with increasing amount of alloying elements increases the absorbance ability of the colored in cobalt solutions anodic films.

CONCLUSION

The Al_2O_3-matrices, formed in H_2SO_4 and electrolytically colored in a $CoSO_4$ solution demonstrate good absorbance properties in the visible range wavelengths (380-750 nm). The obtained colored films exhibit light grey-grey-black shades. The color characteristics of these coatings are interpreted using different approaches (color space) developed within the International Commission on Illumination (CIE). The color characteristics of the samples are measured in three different color spaces. In all cases, an increase of the coloring time leads to an increase of the color intensity. It turns out that the spectral and color characteristics of the obtained functional layers based on porous Al_2O_3-films are also influenced by the type of alloy used. The absorbance ability of the colored in cobalt solutions films increases with the amount of alloying elements. The mat surfaces exhibit a higher light absorption than the polished samples. The formed (thickness 20 μm and porosity 0.15) and colored in $CoSO_4$ solution oxide matrices are promising functional layers with possible application as good decorative coatings.

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The paper is reviewed.