Electrolytic coloring of anodic alumina in $CoSO_4$ solution Part one: Influence of pre-treatment and the AC polarization frequency

Christian Girginov, Ivan Kanazirski, Tsvetan Dimitrov

Abstract *Porous Al_2O_3-films have been formed in H_2SO_4 and subsequently electrolytically colored in a Co containing solution. The influence of the AC polarization frequency (sinusoidal) on the light absorbance and color characteristics of the colored porous matrices (thickness 20 μm) in the visible wavelength range 380-750 nm has been investigated. The evaluation of the color characteristics of the samples was carried out on the basis of different approaches (color space) developed within the system CIE (International Commission on Illumination). The color parameters were determined as a function of frequency and coloring duration. The influence of the aluminum surface pre-treatment on the light absorbance and color characteristics has been studied. The most significant light absorbance is found at a frequency of 60 hertz. In all cases, the mat surface provides greater light absorbance. The colored oxide films are in the light grey, grey, black hue. The formed and colored in $CoSO_4$ solution oxide matrices are promising functional layers with a possible application as very good decorative coatings.*

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

INTRODUCTION

It is well known, that in the pores of anodic oxide films on aluminium various metals can be electrochemically incorporated. This can be accomplished by AC polarization [1] in aqueous solutions of salts of these metals. Most frequently these are Ni [2, 3], Cu [4, 5], Sn [6, 7], Pb [8], Fe [9], Ag [10], Co [11, 12] salts. The formed by this manner composite coatings can be used as solar selective layers [3, 5]. One of the possible applications of the electrolytic coloring of anodic alumina films in metal ions containing solutions is the production of decorative anticorrosive coatings [13]. For the obtaining of high quality and reproducible functional layers the pre-treatment of the aluminum surfaces as well as the coloring conditions of the porous arrays are of crucial importance [14]. The formation of such functional coatings is oftentimes carried out via cobalt ions electrodeposition within the porous Al_2O_3 matrices. Cobalt has become very attractive for its special magnetic properties [11]. Less attention has been paid to the application of cobalt doped porous Al_2O_3 films in their capacity as decorative coatings. It is of interest to investigate the effect of AC polarization frequency, the coloring time, and surface pretreatment on the light characteristics in the visible range. Thus information about their decorative color characteristics can be obtained.

EXPERIMENTAL

The experiments were carried out using samples of technical purity aluminum (99.5% Al), with a working area of about 8 cm^2. The working electrodes were consecutively annealed, degreased, electropolished, washed and dried [3]. The porous films were formed galvanostatically (15 mA cm^{-2}) at constant temperature (20°C) in a 15% aqueous solution of H_2SO_4. A conventional two-electrode cell with a platinum mesh serving as a counter-electrode was used. The films formed in these conditions exhibit a thickness D = 20 μm [15] and porosity α = 0.15 [3]. Some of the specimens were mat in an aqueous solution of 2% NaOH and 3% $NaNO_3$, for 10 min at 80°C. Prior to each experiment the specimens were brightened in a solution containing 20 g dm^{-3} CrO_3 and 15 ml dm^{-3} 85% H_3PO_4 for 3 min at 85°C. The electrolytic coloring was carried out by AC (sinusoidal) polarization in an electrolyte consisting of: $CoSO_4$ (10 g dm^{-3}), $(NH_4)_2SO_4$ (30 g dm^{-3}) and H_3BO_3 (50 g dm^{-3}) at 20°C. A custom AC galvanostat was used as a power source for constant current density (3.75 mA cm^{-2}), in the frequency range 20 - 100 Hz. Graphite rods were used as counter electrodes. The light absorbance (A) was calculated by reflectance (R) spectra: A = 100 – R, at normal incidence in VIS region (380-750 nm) using a Shimadzu UV-3100 with $BaSO_4$ sphere.

The color parameters (within the CIE system) were assessed using a tintometer (Lovibond RT 100).

RESULTS AND DISCUSSION

1. The effect of frequency of AC polarization on the light absorbance and color characteristics

It is of practical interest to determine the light absorbance and color characteristics of the obtained functional coatings, depending on the AC polarization frequency. For this purpose the characteristics of the films obtained during the longest (15 minutes) coloring have been plotted. These specimens have the largest absorbance ability in the visible region, and the most intense color, respectively. The results for the light absorbance of polished and mat samples are presented in Figure 1.

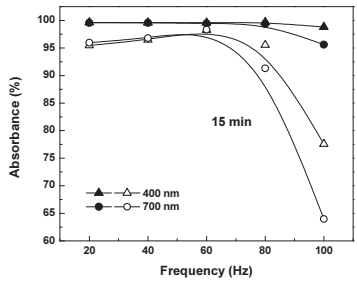

Fig. 1. Spectral absorbance curves vs. frequency of electrolytic colored films in $CoSO_4$ containing electrolyte (for 15 mins) for two deferent wavelengths. The empty symbols denote the electropolished samples, while the filled – the mat ones.

The evaluation of the color characteristics of the samples can be accomplished using different approaches (color space) developed within the system CIE (International Commission on Illumination). The colors of the obtained coatings were assessed using the most common CIE–color spaces [16].

CIE (XYZ)-color space (1931)

In this concept the tristimulus values are called X, Y and Z, which may be thought of as „derived" parameters from the red, green and blue colors. The threedimensional CIE (XYZ)-color space is the basis for all color management systems. This color space contains all perceivable colors. The measured tristimulus values of the colored anodic films (polished and mat specimens) are presented in Figure 2.

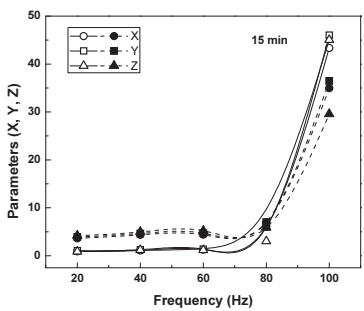

Fig. 2. The tristimulus values as a function of frequency of AC polarization. Here also the empty symbols present the electropolished, and the filled ones – the mat samples.

CIE (*xyY*)-color space (1964)

In this model of color can be divided into two parts: brightness and chromaticity. The CIE(XYZ)-color space was deliberately designed so that the *Y* parameter was a measure of the brightness (luminance) of a color. The chromaticity of a color was then specified by the two derived parameters (*x* and *y*), which are functions of (X, Y and Z). The measured color parameters of the obtained samples (polished and mat) are presented in Figure 3.

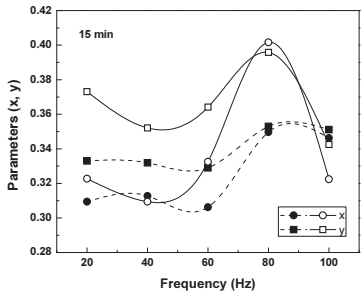

Fig. 3. Parameters (*x* and *y*) as a function of frequency of AC polarization. With empty symbols are plotted the results for electropolished, and with filled symbols these for the mat samples.

CIE (L*a*b*)-color space (1976)

The intention (L*a*b*) is to produce a color space that is more perceptually linear than other color spaces. Perceptually linear means that a change of the same amount in a color value should produce a change of about the same visual importance. This space is commonly used for surface colors. The CIE (L*a*b*)-color scale is organized in a cube form. The values of L* vary from top (L*= 100, white) to bottom (L*= 0, black). 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. The color parameters for polished and mat samples are shown in Figure 4.

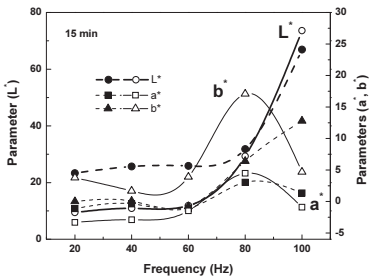

Fig. 4. Parameters (L*, a* and b*) vs. frequency. With empty symbols are given the results for electropolished and with full – the mat samples.

The obtained data allow to be concluded that the most intense color is achieved when the polarization of the oxide arrays is performed with a frequency of 60 hertz. This result is also confirmed by direct visual observation of the colored specimens.

2. The effect of coloring time on the light absorbance and color characteristics

The porous Al_2O_3-films are colored in $CoSO_4$ solution under constant current density (3.75 mA cm^{-2}) and various duration (2-15 min) at 20°C.

The colored films are in light grey, grey, black tones. Therefore, it is of interest to record their spectral absorbance characteristics within the visible range (380-750 nm). Samples with two different pretreatments have been investigated (electropolished and mat). The spectral absorbance curves of the porous alumina films colored with three different durations vs. wavelength of the colored matrices are presented in Figure 5.

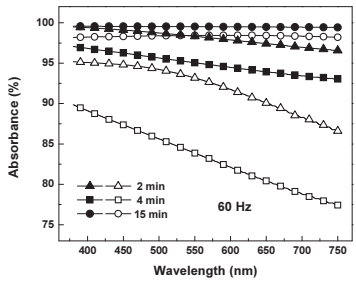

Fig. 5. Spectral absorbance curves of electrolytic colored films at deferent durations in $CoSO_4$-containing electrolyte. The empty symbols denote the electropolished and the filled ones – the mat samples.

The increase of coloring time leads to a rise of the spectral absorbance, and to an increase of the color intensity, respectively. In all cases the preliminary matting of the aluminum surface leads to an increase of the light absorbance.

The influence of the duration of AC polarization on the color characteristics has been studied (at 60 Hz) for polished and mat samples of technical purity aluminum (99.5%). To characterize the properties of the obtained decorative coatings the above mentioned CIE-color spaces have been employed.

CIE (XYZ)-color space

The tristimulus values (X, Y and Z) for polished and mat samples vs. coloring time (AC sinusoidal polarization in an electrolyte, containing $CoSO_4$ are presented in Figure 6.

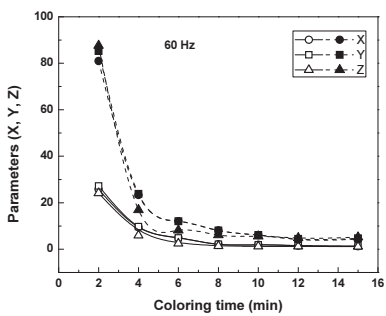

Fig. 6. Parameters (X, Y and Z) vs. coloring time. The empty symbols refer to the electropolished and the filled - to mat samples.

CIE (*xyY*)-color space

The chromaticity of the colors (parameters *x* and *y*), for samples colored with different durations is presented in Figure 7.

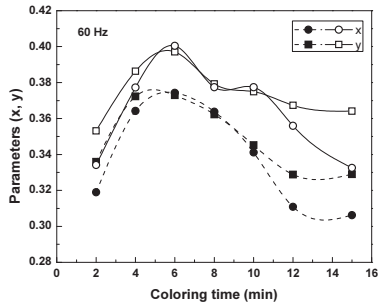

Fig. 7. Parameters (*x* and *y*) as a function of coloring time. The empty symbols denote the electropolished samples, while the filled – the mat ones.

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

The parameters (L*a*b*) in this three dimensional space for the investigated specimens are plotted vs. coloring time in Figure 8.

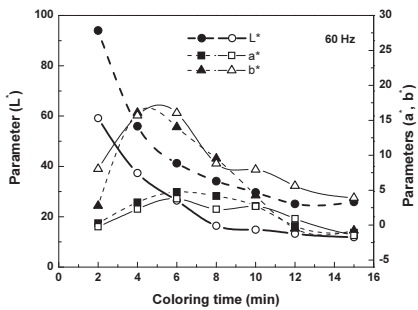

Fig. 8. Parameters (L*, a* and b*) vs. coloring time. With empty symbols are plotted the results for electropolished, and with filled symbols these for the mat samples.

The reference values for these parameters are as follows: L*=94.02, a*=0.32 and b*=2.75. Thus the sample-reference differences (ΔL*, Δa* and Δb*) could be calculated.

CONCLUSION

The Al_2O_3-matrices (20 μm), formed in H_2SO_4 and electrolytically colored in a $CoSO_4$ solution demonstrate good decorative properties in the wavelengths range 380-750 nm. The colored oxide films are in light grey, grey, black hue. The most intense coloring at equal other conditions is achieved in AC (sinusoidal) polarization at a frequency of 60 hertz. In all cases with increasing coloring duration the obtained coatings increase their spectral absorbance. The surface treatment (polishing, matting) influences the characteristics of the colored porous Al_2O_3-films. The mat surface provides greater light

absorbance. The color characteristics of these coatings in the visible area are interpreted using different color space developed within the International Commission on Illumination. The formed and colored in $CoSO_4$ solution oxide matrices are promising functional layers with possible application as very good decorative coatings.

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The paper is reviewed.