ELECTROLYTIC COLOURING OF ANODIC ALUMINA FILMS IN METAL IONS CONTAINING SOLUTION
PART TWO: ELECTROLYTIC COLOURING IN CuSO₄ CONTAINING SOLUTION

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ABSTRACT

The Al₂O₃ matrices (20 μm) are formed in H₂SO₄ and are subsequently electrolytically coloured in a CuSO₄ solution. Good absorption properties in the wavelength range 200-2500 nm are ascertained. The approach of s.c. “color space” proves to be a convenient one for interpretation of the colour characteristics of these coatings in the visible range as this approach aims determination of lots of colour parameters. It is also found that the copper amount deposited into the pores is proportional to the colouring time. Moreover, the calculated integral absorbance of solar light, within wavelengths range under investigation, is very high, which defines them as prospective coatings in the field of solar energy conversion.

Keywords: anodic alumina films, electrolytic colouring, colour characteristics, spectral characteristics.

INTRODUCTION

It is well known that the porous anodic oxide films on aluminium can be electrochemically coloured by AC polarization [1] in aqueous solutions of salts of various metals – Ni [2], Cu [3], Sn [4, 5], Pb [6], Fe [7], Ag [8]. By this manner composite coatings used both as decorative and solar selective layers could be formed.

The formation of such functional coatings is oftentimes accomplished by deposition of copper within the porous matrices [3]. It is a matter of interest to investigate the effect of colouring time and copper amount on light (visible and solar) absorbance of anodic Al₂O₃ coloured in copper-containing solutions in order to gain information about their decorative color characteristics.

EXPERIMENTAL

The experiments were carried out using samples of technical purity aluminum (99.5%), with a working area of about 8 cm². Their preliminary treatment included: annealing, degreasing, electropolishing, washing and drying (see part I). The porous films were formed galvanostatically with a current density of 15 mA cm⁻² at 20°C in a 15% aqueous solution of H₂SO₄. A conventional two-electrode cell with platinum mesh serving as a counter-electrode was used. The films formed in these conditions exhibit a thickness D = 20 μm [9] and porosity α = 0.15.

The electrolytic colouring was carried out by AC polarization in an electrolyte consisting of: CuSO₄ (10 g dm⁻³), (NH₄)₂SO₄ (30 g dm⁻³) and H₃BO₃ (50 g dm⁻³) at 20°C. A custom AC galvanostat was used providing a constant current density (3.75 mA cm⁻², 60 Hz). Graphite rods were used as counter electrodes.

The spectral characteristics of the coloured films were recorded by a spectrophotometer JASCO Corp. (V-570) in the wavelengths range 340-1500 nm. Shimadzu UV-3100 with BaSO₄ sphere was used to plot reflectance...
spectra at normal incidence in the UV-VIS-NIR region (200-2500 nm) for calculation of the solar absorbance. The colour characteristics were assessed by a reflectance tintometer (Lovibond RT 100).

The coloured films were dissolved in a mixture of concentrated nitric acid and water (1:1), at room temperature. The quantity of copper electrochemically deposited was determined using the ICP-OES method (Prodigy, Teledyne Leeman Labs).

**RESULTS AND DISCUSSION**

**The effect of colouring time on the light absorption characteristics**

The porous Al₂O₃-films are coloured at 20°C under constant current density (3.75 mA cm⁻²), current frequency (60 Hz) and various duration (3-20 min).

The coloured films exhibit the same beige-brown-black shades as the shades demonstrated by nickel pigmented films. One of the possible applications of the coloured films is in production of decorative anticorrosion coatings. Therefore, it is of interest to take their spectral characteristics within the visible range.

The spectral curves of the porous alumina films coloured with different durations are initially registered as reflectance R(λ) vs. wavelength. Thereafter, the light absorbance is calculated as the difference: A(λ) = 100 - R(λ). The A(λ)-dependencies of the coloured matrices are presented in Fig. 1.

The increase of colouring time leads to more significant light absorption as it has also been found for the nickel-pigmented specimens.

**The effect of colouring time on the colour characteristics**

It is of practical interest to determine the color characteristics of the obtained functional coatings, depending on colouring time.

This can be accomplished using different approaches (color space) developed within the system CIE (International Commission on Illumination) color assessment:

**CIE (XYZ)-colour space**

In this model the tristimulus values are called X, Y and Z, which may be thought of as „derived” parameters from the red, green and blue colours.

The measured tristimulus values of the coloured anodic films are presented in Fig. 2.

**CIE (xyY)-colour space**

In this concept the colour 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 colour. The chromaticity of a colour was then specified by the two derived parameters (x and y), which are functions of all three tristimulus values (x, y and Y). The measured colour parameters of the obtained samples are presented in Fig. 3.

![Fig. 1. Light absorbance curves of electrolytic coloured films at various durations in CuSO₄-containing electrolyte.](image1)

![Fig. 2. The tristimulus values as a function of colouring time.](image2)
CIE (L* a* b*) color space

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.

The colour parameters for this approach are shown in Fig. 4. The reference values for these parameters are as follows: L* = 94.02, a* = 0.30 and b* = 2.79. Thus the sample-reference differences (ΔL*, Δa* and Δb*) could be calculated.

Solar light absorbance

The coatings produced could be used as functional solar light-absorbers. For this reason it was of interest to investigate the light absorbance (A) within a wider wavelengths range (200 – 2500 nm). The solar absorbance (A) is defined as a fraction of the radiation, incident on the surface of the sample that is absorbed. The integrated absorbance was calculated using the formula [10]:

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A = \frac{\int_{350}^{2200} I_{sol}(\lambda) [1 - R(\lambda)] d\lambda}{\int_{350}^{2200} I_{sol}(\lambda) d\lambda}
\]

where \( I_{sol}(\lambda) \) and \( R(\lambda) \) are the intensity of solar radiation and the total reflectance of the sample at given wavelength \( (\lambda) \), respectively. The calculations are performed using data about the spectral dispersion of the solar energy (AM2) that is characteristic for the present geographic location. The integration was done numerically using Gauss quadrature method with 32 points.

The reflectance of 20 min coloured anodic film (thickness 20 μm, porosity 0.15) is presented in Fig. 5. For comparison, the reflectance of a polished aluminium sample and an uncoloured Al₂O₃-matrix are also presented.

The integral absorbance calculated (A = 84.7 %) within wavelengths range under investigation (350 – 2200 nm) depicts that the anodic films coloured in CuSO₄ containing electrolyte could find application as elements of solar selective absorbers.

Copper amount deposited into the pores

The amount of copper incorporated within the pores is estimated by means of ICP-OES. The quantity of Cu per unit area as a function of colouring time is presented in Fig. 6. It can be seen that the amount of deposited copper within the pores is proportional to the colouring time. This result is logical and similar dependencies have been obtained by other authors [11, 12] for other metals incorporated within the pore volume.

CONCLUSIONS

The Al₂O₃-matrices (20 μm), formed in H₂SO₄ and electrolytically coloured in a CuSO₄ solution demonstrate good absorption properties in the wavelengths range 200-2500 nm. The colour characteristics of these coatings in the visible area are interpreted using different approaches (colour space) developed within the International Commission on Illumination. It also turned out that the integral absorbance of solar light within wavelengths range under investigation is very high (A = 84.7 %). The amount of copper
deposited per electrode area is determined as well. It is found that this amount is proportional to the colouring time. The formed and coloured under these conditions oxide matrices are promising functional layers with possible application in solar selective absorbers. Moreover, their colour characteristics present them as very good decorative coatings.

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REFERENCES