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Electrolytic coloring of porous aluminum oxide films in $CoSO_4$ solution

Ch. A. Girginov[1]*, I. A. Kanazirski[2], V. G. Ilcheva[1]

[1]*University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria*

[2]*University of Mining and Geology "St. Ivan Rilski" 1700 Sofia, Bulgaria*

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Anodic oxide matrices have been formed in a 15 % H_2SO_4 solution on three types of aluminum electrodes: Al (99.5%) and two alloys (8006 and 8011). The obtained Al_2O_3-films (thickness 20 µm, porosity 0.15) have been colored in a $CoSO_4$ solution using AC-polarization with different duration (2-15 min) and at frequencies in the range (20-100 Hz). A comparative study has been conducted on the spectral characteristics (in the UV-VIS-NIR region) of the colored films with two different surface pretreatments: electropolished and chemically mat. It has been found, that in all cases the increase of coloring time (the quantity of cobalt incorporated in the pores respectively) leads to an increased absorbance capability of the coatings. The optimal process frequency is determined to be 60 Hz. Furthermore, the pretreatment of the metal surface has no significant influence on the quantity of cobalt incorporated in the Al_2O_3-matrices. The obtained results show that the colored in $CoSO_4$ porous anodic films on aluminum and its alloys exhibit good absorbance characteristics in the visible, as well as in the UV and NIR regions. This makes them suitable to serve as decorative (black) coatings and also have a potential application as solar collector elements.

Key words: alumina films, cobalt electrodeposition, aluminum alloys, spectral characteristics.

INTRODUCTION

In the pores of anodic oxide films on aluminum various metals can be electrochemically incorporated. This is done by AC polarization [1] in different aqueous solutions of salts of these metals. The most common application of the porous Al_2O_3 colored in electrolytes containing metal ions is to form decorative and corrosion resistant coatings on aluminum and its alloys. The colored porous alumina films have found increasing implementation as light-absorbing coatings to produce conversion layers as part of solar collectors. Recently there has been a profound interest in Al_2O_3 matrices incorporated with cobalt [2-5]. This interest is motivated by the attractive magnetic properties [4] these systems exhibit. The colored with cobalt Al_2O_3 films also demonstrate good color decorative properties [6]. Through incorporation of cobalt it is possible to successfully prepare black films [7] for short times (5 min) of electrolytic coloring. A strict pre-treatment procedure of the aluminum surfaces and control of the coloring conditions of the porous arrays is required in order to obtain high quality and reproducible functional layers [8]. It is a matter of interest to investigate the light reflectance of anodic Al_2O_3 colored in cobalt-containing solutions depending on the forming conditions, the type of the aluminum alloy and the metal surface pretreatment. The determination of the amount of cobalt incorporated within the pores is of practical interest as well.

EXPERIMENTAL

The electrodes (8 cm^2) were cut from aluminum sheets (99.5%) and two aluminum alloys: 8006 (97.90% Al, 0.25% Si, 1.44% Fe, 0.37% Mn) and 8011 (98.55% Al, 0.66% Si, 0.70% Fe, 0.06% Mn). They were put through a standard pretreatment procedure: annealing, degreasing, electropolishing, rinsing and finally drying. Some of the specimens were mat in an aqueous solution (2% NaOH and 3% $NaNO_3$). The film formation was carried out in 15 % H_2SO_4 at constant current density (15 mA cm^{-2}), for 45 min, at 20°C. The formed under these conditions anodic films have a thickness of 20 µm [9] and porosity of about 0.15 [10]. A two-electrode cell with a platinum mesh serving as counter electrode was used for anodization. The cobalt deposition 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 delivering and keeping a constant current density of 3.75 mA cm^{-2}, in the frequency range 20 - 100 Hz. Graphite rods were used as counter electrodes. The light reflectance

* To whom all correspondence should be sent:
E-mail: christian.girginov@gmail.com

spectra (*R*) in the UV-VIS-NIR region (200-2500 nm) have been measured using a Shimadzu UV-3100 spectrophotometer with $BaSO_4$ sphere. The amount of cobalt deposited within the pores was estimated by means of ICP-OES (Prodigy, Teledyne Leeman Labs). For this purpose the coloured films were dissolved in a mixture of concentrated nitric acid and water (1:1), at 20°C for 3-4 min.

RESULTTS AND DISCUSSION

1. Spectral characteristics

1.1. Effect of AC polarization frequency on the light absorbance

The influence of the AC polarization frequency on the light absorbance of the colored porous matrices in the UV-VIS-NIR wavelength range (200-2500 nm) has been investigated. The colored oxide films are in the light grey, grey, black hue. 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. The spectral characteristics were determined as a function of wavelength for five AC frequencies (20-100 Hz). Fig. 1 presents results obtained for polished and mat aluminum (99.5%) samples colored at three frequencies.

The results show that with increasing frequency the absorbance capacity of the films decreases. For the experiments an operating frequency of 60 Hz was chosen, which is relatively close to the industrial power frequency (50 Hz).

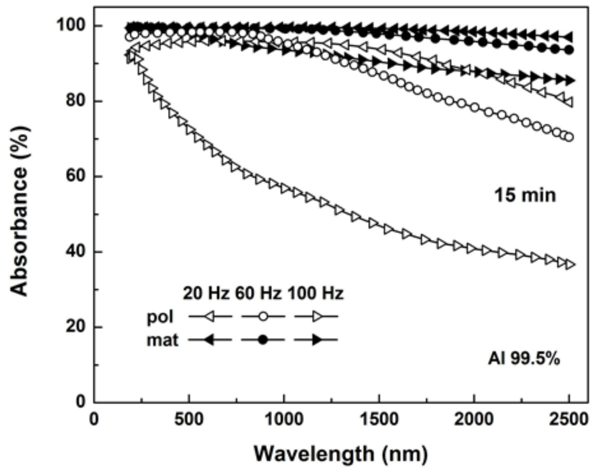

Fig. 1. UV-VIS-NIR absorbance spectra of samples colored in $CoSO_4$ for 15 min at three frequencies. The empty symbols denote electropolished, while the filled ones – mat samples.

1.2. Effect of coloring time on the light absorbance

The Al_2O_3-matrices (thickness 20 μm, porosity 0.15), formed in H_2SO_4 and electrochemically colored in a $CoSO_4$ solution demonstrate good light absorption properties in the wavelengths range 200-2500 nm. The formed and colored under these conditions oxide matrices are promising functional layers with possible application in solar selective absorbers. Moreover, their color characteristics present them as very good decorative coatings. The increase of coloring time leads to higher spectral absorbance (Fig. 2), and to an increase of the color intensity, respectively.

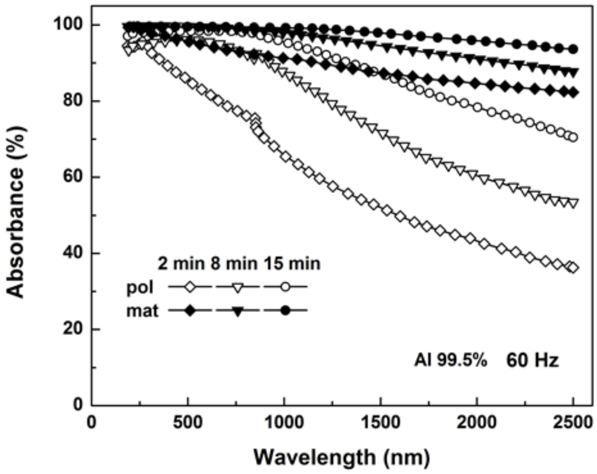

Fig. 2. Absorbance spectra of samples, colored with different duration, here also the empty symbols denote polished, and filled ones – mat electrodes

1.3. Effect of surface pretreatment on the light characteristics

The influence of the aluminum surface pre-treatment on the light reflectance has been studied. In all cases, the preliminary matting of the aluminum surface leads to an increase of the light absorbance, which is clearly evident from the data presented in Fig. 1 and Fig. 2.

1.4. Effect of alloy type on spectral characteristics

It was of practical interest to study the influence of the aluminum sample type. Comparative studies of three types of aluminum samples (99.5%) and two aluminum alloys: 8006 and 8011 have been conducted. The results (Fig. 3) show that in all cases, Al (99.5%) exhibits higher reflectance than the aluminum alloys. This result indicates that the presence of alloying elements increases the light absorbance capacity of the colored anodic films.

2. Amount of cobalt deposited into the pores

2.1. Effect of AC polarization duration

The amount of cobalt incorporated within the pores was determined by the ICP-OES method. This amount per unit area as a function of coloring time has been estimated (Fig. 4), it can be seen that it is proportional to the coloring time.

This result is logical and similar dependencies have been obtained by other authors for different metals [10] incorporated within the pore volume.

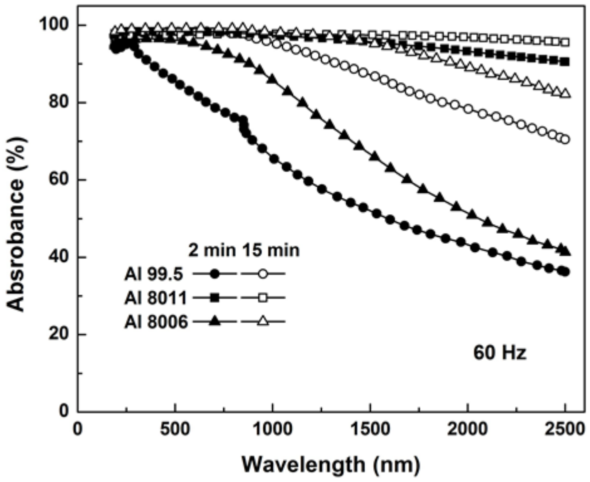

Fig. 3. Reflectance spectra of three types of aluminum samples at two coloring durations (2 and 15 minutes).

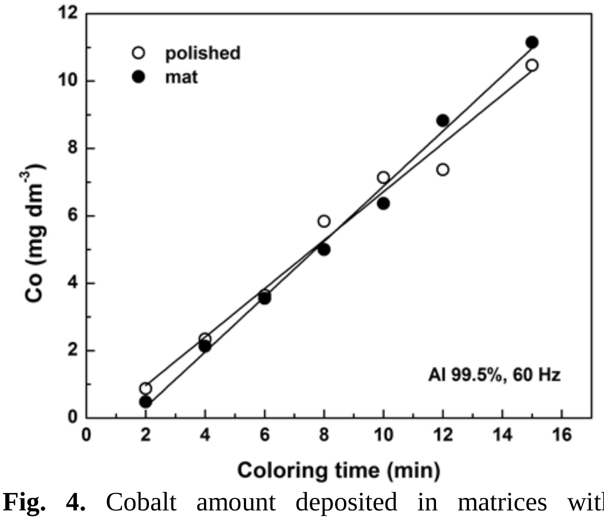

Fig. 4. Cobalt amount deposited in matrices with different coloring duration. Empty symbols are for polished electrodes, and filled ones – mat samples.

2.2. Effect of AC polarization frequency

The amount of cobalt incorporated into the porous matrices has been assessed according to the AC-polarization frequency. It turns out that this quantity is significantly affected by the frequency of the coloring current. An example of this influence for films formed on aluminum (99.5%) is presented in Fig. 5.

The data presented in Fig. 5 demonstrate a linear $m_{Co}(f)$-dependence. Furthermore the surface pretreatment (polishing, matting) has no significant influence.

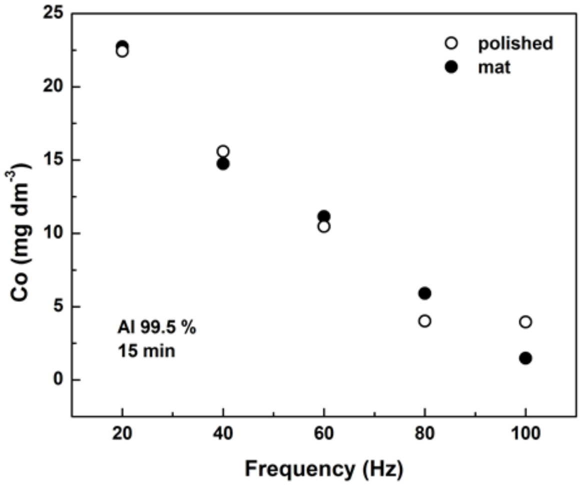

Fig. 5. Amount of Co deposited in matrices (15 minutes) vs. coloring current frequencies. The empty symbols denote polished, and filled ones – mat electrodes.

2.3. Effect of alloy type

The actual application of colored oxide films involves the use of different types of technical purity aluminum and aluminum alloys. In this respect investigating the influence of the type of anodized aluminum on the amount of deposited cobalt may be crucial for the application of these coatings. For this purpose three different types of aluminum have been used in the study: 99.5% Al sheets and two (8006 and 8011) aluminum alloys (Fig. 6).

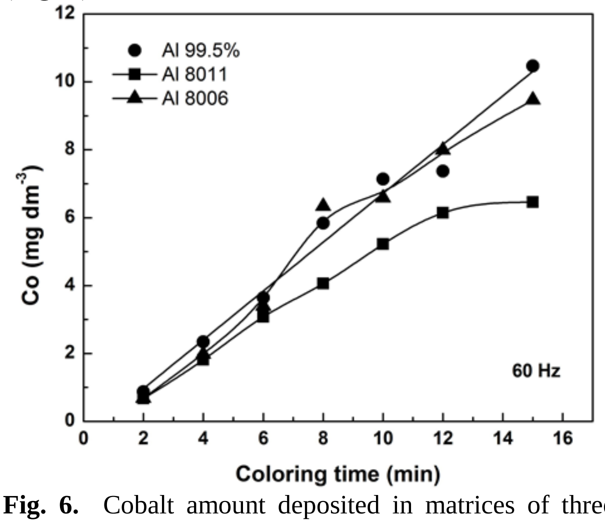

Fig. 6. Cobalt amount deposited in matrices of three types aluminum samples, colored at 60 Hz.

The obtained results show a linear increase of the amount of incorporated cobalt with coloring time. For the 8011 alloy there is a tendency for a slower growth of incorporated cobalt. This may be due to the presence of more alloying elements in larger quantities than Al 99.5%. In general, the spectral characteristics of colored samples demonstrate high light absorbance capacity.

3. Absorbance of the colored coatings

As it has already been mentioned, the colored porous matrices could find application as decorative coatings and selective solar absorbers. In this sense it was of interest to determine the absorbance values (*A*) of the colored coatings in two spectral regions:

i) visible range (380 - 740 nm)
ii) far infrared-visible-near UV (200 – 2500 nm).

It is necessary to take on account the incident solar energy on the ground [11]. For this purpose, data about the spectral dispersion of the solar energy (AM2) that is characteristic for present geographic location are used. The solar absorbance (*A*) is defined as a fraction of the radiation, incident on the surface of the material that is absorbed. It is a function of both the intensity of solar radiation $I_{sol}(\lambda)$, and the total reflectance of the sample $R(\lambda)$, and is given by [12]:

$$A = \frac{\int_{\lambda_1}^{\lambda_2} I_{sol}(\lambda)\left[1 - R(\lambda)\right] d\lambda}{\int_{\lambda_1}^{\lambda_2} I_{sol}(\lambda) d\lambda}$$

The integration is done numerically using *Gauss* quadrature method with 32 points. The values of the integral absorbance (*A*) within these two spectral regions for some of the samples are given in Table 1.

Table 1. Absorbance of the colored coatings

Samples	Aluminum	Frequency (Hz)	Absorbance (380-740 nm) (%)	Absorbance (200-2500 nm) (%)
1	99.5%	20	95.45	93.81
2	99.5%	60	95.33	92.95
3	8006	20	94.37	93.59
4	8006	60	93.84	91.49
5	8011	20	91.95	89.97
6	8011	60	92.83	91.22

The obtained results indicate, that the colored in $CoSO_4$ solution porous Al_2O_3-matrices exhibit high light absorbance in the visible, as well as in the far infrared-visible-near UV regions. This makes them suitable as decorative (black coatings) and perspective for application as a part of solar energy collectors.

CONCLUSION

The Al_2O_3-matrices (thickness 20 μm, porosity 0.15), formed in H_2SO_4 and electrochemically colored in a $CoSO_4$ solution demonstrate good light selective properties in the wavelengths range 200-2500 nm. The most intense coloring at equal other conditions is achieved in AC (sinusoidal) polarization at a frequency of 60 Hz. In all cases with increasing coloring duration the obtained coatings increase their spectral absorbance. It is found that the amount of cobalt deposited per electrode area is proportional to the coloring time. The surface treatment (polishing, matting) influences the characteristics of the colored porous Al_2O_3-films. The mat surface provides greater light absorbance. The formed and colored in $CoSO_4$ solution oxide matrices are promising functional layers with possible application as light-absorbing coatings in solar collectors.

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ЕЛЕКТРОХИМИЧНО ОЦВЕТЯВАНЕ НА ПОРЕСТИ ОКСИДНИ ФИЛМИ ВЪРХУ АЛУМИНИЙ В РАЗТВОРИ НА $CoSO_4$

К. А. Гиргинов[1], И. А. Каназирски[2], В. Г. Илчева[1]

[1]*Химикотехнологичен и Металургичен Университет, 1756 София, България*

[2]*Минно-геоложки Университет "Св. ИванРилски", 1700 София, България*

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(Резюме)

В разтвор на H_2SO_4 (15 %) са формирани анодни оксидни матрици върху три вида алуминиеви образци: Al (99.5%) и две сплави (8006 и 8011). Получените Al_2O_3-филми (дебелина 20 µm, порестост 0.15) са оцветявани в разтвор на $CoSO_4$ при променливо-токова поляризация с различна продължителнаст (2-15 мин) и при различна честота (20 - 100 Hz). Проведено е сравнително изследване на спектралните характеристики (в UV-VIS-NIR област) на оцветените филми върху електроди с две различни предварителни обработки на повърхността: електрополирани и химично матирани. Установено е, че във всички случаи с увеличаване на продължителността на оцветяване (респективно на внедреното количество кобалт в порите) абсорбционната способност на покритията нараства. Оптималната честота на процеса на електрохимично оцветяване е 60 Hz. Предварителната обработка не оказва значимо влияние върху количеството метал отложен в Al_2O_3-матрица. Получените резултати показват, че оцветените в $CoSO_4$ порести анодни филми върху алуминий и негови сплави проявяват добри абсорбционни характеристики както във видимата, така и в UV-VIS-NIR области. Това ги прави подходящи като декоративни (черни покрития) и с перспектива за приложения като елементи в слънчевите колектори.