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Kinetics of the electrolytic coloring process on anodized aluminum

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Abstract

The kinetics of tin electrodeposition during the electrolytic coloring of porous anodic oxide films on aluminum is studied as a function of the oxide properties, e.g., the thickness of the porous oxide layer, and the surface resistance offered by the barrier oxide layer. While the thickness of the porous oxide layer is controlled by the anodization time, the surface resistance is controlled by the anodization voltage, and the anodization bath temperature. Steady-state polarization measurements are employed to characterize the dependence of the coloring kinetics on the oxide properties. Measurements indicate that the kinetics of the electrolytic coloring process can be accelerated by: (i) reducing the surface resistance of the oxide film (primarily offered by the barrier oxide layer) by growing the oxide at a lower anodization voltage, and/or a higher bath temperature, or (ii) growing a thinner porous oxide layer by decreasing the anodization time. The electrochemical measurements are supported by gravimetric analysis of electrolytically colored alumina samples (using calibrated wavelength-dispersive X-ray fluorescence spectroscopy), and by optical spectrophotometry.

1. Introduction

Aluminum and its alloys are widely used in many engineering applications due to their high strength-to-weight ratio and good formability. Recently, aluminum has gained popularity as candidate construction material for car body components in the automobile industry. The light weight aluminum components can significantly increase automobile efficiencies without detrimental effects to the vehicle safety. Commercial applications, therefore, demand reliability and improved performance of the aluminum components, e.g., structural stability and durability, and corrosion resistance.

Surface durability, e.g., abrasion resistance and corrosion protection, of aluminum alloys can be achieved through its anodic oxidation, or anodization. Anodization of aluminum in H_2SO_4 electrolyte typically results in the growth of a porous oxide layer with a close-packed columnar hexagonal structure (Figure 1). At the base of the porous oxide structure is a compact, highly resistive barrier oxide layer that separates the aluminum substrate from the anodizing electrolyte. The structural features of the porous anodic oxide coatings have been the subject of detailed investigations – from experimental studies [1–4] to analytical and numerical modeling [5–7].

The as-grown anodic oxide films on aluminum are optically transparent. In several practical applications, therefore, the process of anodization is followed by electrochemically depositing metallic particles inside the oxide pores – the metallic particles (which deposit primarily at the base of the oxide pores near the barrier oxide layer) scatter low wavelength light thereby imparting a characteristic shade to the anodized surface. This technique of surface treatment, therefore, is referred to as *electrolytic coloring* [8]. As a popular example, electrolytic coloring using tin based electrolytes is used to impart bronze color to the anodized aluminum surface.

Several experimental studies on electrolytic coloring have been reported in the literature (e.g., Gohausen and Schoener [9], and Sato [10] for coloring using tin based electrolytes, Sato and Sakai [11] for nickel based electrolytes, and Serebrennikova et al. [12] for silver electrodeposition in anodic oxide pores). These studies have primarily focused on qualitatively analyzing the effect of the operating conditions (e.g., coloring voltage, and coloring bath temperature) on the AC coloring process, providing guidelines for optimal selection of the coloring process parameters. In other studies (e.g., Tsangaraki-Kaplanoglou [13]), researchers have investigated the influence of alloying elements in

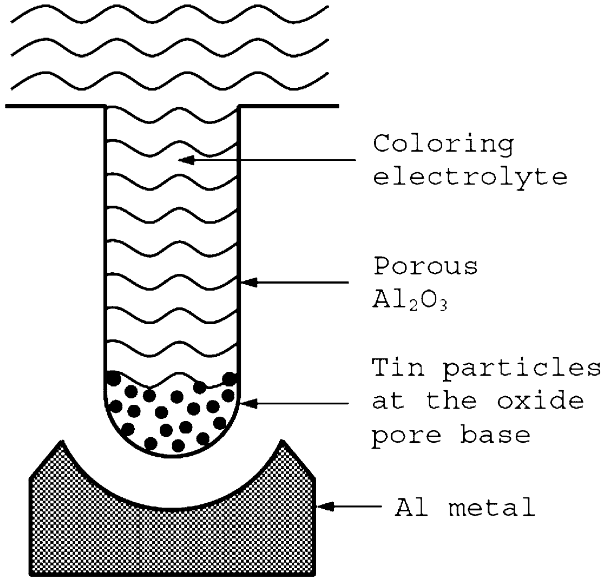

Fig. 1. Schematic representation of the electrolytic coloring process on anodized aluminum, during which tin particles are electrodeposited within the porous oxide structure, preferentially at the base of the oxide pores. The tin particles scatter low wavelength light, thereby imparting a bronze shade to the anodized aluminum surface.

aluminum on the anodization and electrolytic coloring characteristics particularly for tin based electrolytes.

In electrolytic coloring, metal deposition occurs on a resistive oxide surface that is prepared by anodization. Consequently, during coloring, one expects the metal deposition rate to be dependent on the properties of the oxide (e.g., the thickness of the barrier oxide layer, or its resistance), which are governed by the anodization process conditions under which it is grown (e.g., the anodization voltage, the bath temperature, and the oxide thickness). Moreover, non-uniformity of the current distribution during anodization (for the case of some complex geometries [5, 14]) can provide local variations in the oxide properties, e.g., thicker, more resistive oxide on the more accessible anode surfaces, and thinner, less resistive oxide on the less accessible anode surfaces. Such local variations can have a pronounced effect on the coloring current distribution rendering it more uniform or non-uniform depending upon the interplay between the ohmic and surface resistances during coloring. Analysis of such effects, however, requires first a quantitative characterization of the relationship between the coloring kinetics and the anodization process conditions, which, as of yet, has not been explored.

In the present work, we report steady-state polarization measurements aimed at characterizing the interdependence between the electrolytic coloring kinetics (particularly in tin-based electrolytes) and the properties of the underlying anodic oxide, e.g., the thickness of the porous oxide layer, and the resistance offered by the barrier oxide layer. In this work, the oxide properties are determined by controlling the voltage, the bath temperature, and the time during anodization. The electrochemical polarization measurements are correlated to gravimetric analysis of electrolytically colored samples (performed using calibrated wavelength-dispersive X-ray fluorescence spectroscopy) in order to determine the amount of metal deposited inside the oxide pores. Measurements indicate that the kinetics of the electrolytic coloring process strongly depends on the oxide properties. Metal deposition rate can be increased by: (i) reducing the surface resistance of the oxide film (primarily offered by the barrier oxide layer), by growing the oxide at a lower anodization voltage, and/or a higher bath temperature, or (ii) growing a thinner porous oxide layer by decreasing the anodization time.

2. Experimental procedure

2.1. *Aluminum anodization*

Porous anodic Al_2O_3 films were first prepared by anodizing 5 cm × 10 cm aluminum (alloy 6111) coupons potentiostatically at voltages of 12–16 V in a continuously stirred 15 wt.% H_2SO_4 electrolyte at bath temperatures of 20–35 °C. The anodization cell consisted of a single aluminum sheet cathode placed sufficiently far away from the anode ($\sim$15 cm). Voltage between the cathode and the anode sheets was applied using a SIFCO power supply, and the current was recorded. Continuous agitation was maintained in the anodization cell to ensure a uniform temperature throughout the bath. The configuration provided a uniform current distribution on the anode surface, as verified by oxide thickness measurements using a Fischerscope multi-measuring system. Oxide films with different thicknesses (7–25 μm) were grown by controlling the anodization time. The properties of the oxide (e.g., thickness of the barrier layer) were modulated by controlling the anodization conditions, i.e., anodization voltage (12–16 V), and the bath temperature (20–35 °C).

2.2. *Electrolytic coloring*

The anodized aluminum samples were electrolytically colored using a tin based electrolyte (18 g l^{-1} tin sulfate + 20 g l^{-1} sulfuric acid at 20 °C). Coloring was performed potentiostatically in a two-electrode cell (consisting of the anodized aluminum sample as the cathode, and a stainless steel anode) similar in design to that employed during anodization. For measuring the electrolytic coloring polarization curve, a voltage was applied between the cathode and the anode, and the corresponding coloring current was recorded at steady-state, which took at least 60 s to reach. The voltage was increased in a step-wise manner, and the corresponding current was measured to generate the polarization curve in the voltage range of 8–24 V. Coloring at voltages above 24 V resulted in spalling and destruction of the film, possibly due to excessive hydrogen evolution and local changes in pH. For gravimetric analysis, electrolytically colored aluminum samples were prepared using potentiostatic coloring for different coloring time periods ($t = 30$–270 s). The amount of tin deposited was indirectly measured using wavelength-dispersive X-ray fluorescence spectroscopy technique specifically designed and calibrated for analyzing the tin content [15]. For characterizing the color shade produced by the deposited tin, the sample surface was analyzed using a Minolta CM 3700d spectrophotometer.

3. Results and discussion

In this section, the effects of the oxide properties on the kinetics of DC electrolytic coloring are analyzed. The oxide properties are modulated indirectly by means of controlling the anodization process conditions, e.g., the anodization voltage (in the range 12–16 V), the anodization bath temperature (in the range 20–35 °C), and the anodization time (in the range 15–40 min.). The effect of each process parameter is characterized independently, as described in detail below.

3.1. *Effect of the anodization voltage*

Figure 2 shows the effect of the anodization voltage at which the oxide films were grown on the kinetics of the electrolytic coloring reaction. The oxide films were first formed by potentiostatic anodization (at 12, 14, and 16 V) in a 15 wt.% H_2SO_4 bath at 20 °C. The anodization time was varied, thereby providing films with a constant thickness of the porous oxide layer (10 ± 0.5 μm). Figure 2 indicates that, for a given porous oxide thickness, the films formed at a lower anodization voltage exhibit accelerated coloring kinetics as compared to films formed at a higher anodization voltage. The anodization voltage determines the thickness of the barrier oxide layer formed during the anodizing step, e.g., a higher anodization voltage favors formation of the oxide film over its field assisted dissolution [1, 8] resulting, at steady-state, in a relatively thicker barrier oxide layer. On the other hand, a lower anodization voltage limits the barrier film growth, while maintaining a relatively high dissolution rate, thereby providing a thinner barrier film thickness under steady state conditions. An estimate of the barrier layer thickness as a function of the anodization voltage can be obtained from the unit barrier thickness values reported by Keller et al. [1] for anodization in H_2SO_4 electrolyte, i.e., 15.2 nm barrier oxide for anodization at 16 V, as compared to 11.4 nm for anodization at 12 V. Since surface resistance during coloring is governed by the barrier oxide thickness, the thinner barrier oxide (grown at 12 V) provides a lower surface resistance resulting in a higher coloring rate (e.g., 40 mA cm^{-2} at a coloring voltage of 12 V) as compared to the inhibited coloring kinetics (e.g., 6 mA cm^{-2} at the same coloring voltage of 12 V) observed for oxides grown at a higher anodization voltage (16 V). It is important to note that the term "coloring rate" corresponds to the net current density during electrolytic coloring (as reported in the Figure 2). The actual metal deposition current density, however, is just a small fraction of the net current density. Majority of the current passed is consumed in side reactions such as hydrogen evolution. In the present study, for the range of anodization voltages (16–20 V dc) and coloring parameters (120 s at 20 V dc) used, we observed current efficiencies in the range of about 5–10%, implying that about 90–95% of the current passed was consumed in hydrogen evolution. These efficiencies are similar to those observed by Tsangaraki-Kaplanoglou et al. [13], who also observed that the current efficiency is a function of the coloring voltage and time.

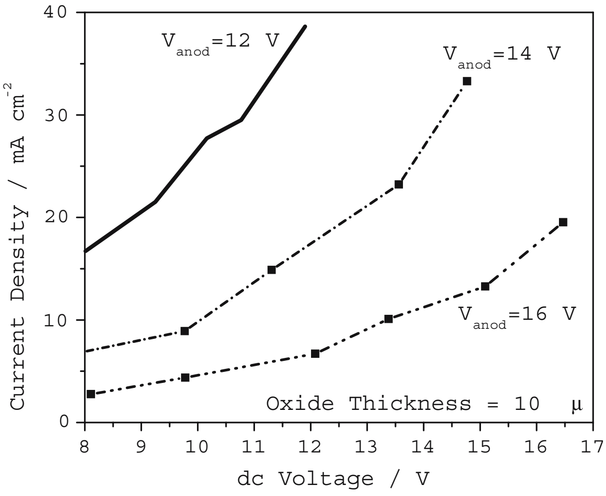

Fig. 2. Kinetics of the DC electrolytic coloring process on anodized aluminum as a function of the voltage at which the anodic oxide is grown. The coloring current was recorded under steady state conditions, which took at least 60 s to reach. Anodization was performed potentiostatically (at 12, 14, and 16 V, respectively) in a 15 wt.% H_2SO_4 bath at 20 °C. The anodization time was varied, thereby providing films with a constant thickness of the porous oxide layer (10 ± 0.5 μm).

In electrolytic coloring, the true area available for electrochemical reaction is different than the geometric area of the sample immersed in the coloring electrolyte. This is evident from Figure 1, which indicates that the hexagonal columnar structure of the oxide film provides an electrochemical surface area at the pore bottom that is lower than the total geometric surface area of the electrode. Since the current densities reported in this study are based on the geometric surface area (since it can be measured accurately), they are sensitive to variations in the true electrochemical surface area available for coloring. The true surface area is directly proportional to the pore density (n) and the square of the pore base diameter (D^2). Thus, an estimate of the true surface area at the pore base per unit geometric area can be obtained from the value of the parameter nD^2. Patermarakis et al. [2, 3] have analyzed the variation of this parameter as a function of the bath temperature and the anodization current density. Their analysis indicates that in the range of anodization voltages under consideration in this study (12–16 V), the current densities (10–20 mA cm^{-2}) only marginally affect these structural features, i.e., only about 20% variation in the true surface area. Therefore, the increased area at the pore base provided at higher anodization current densities cannot completely account for the order of magnitude variation in the coloring rate observed in Figure 2. This indirectly points towards the role of varying barrier oxide properties (with varying anodization voltage) in modulating the electrolytic coloring kinetics.

3.2. *Effect of the anodization temperature*

Figure 3 shows the dependence of the kinetics of electrolytic coloring of porous Al_2O_3 films (formed potentiostatically at 16 V in a 15 wt.% H_2SO_4 electrolyte) on the anodization bath temperature. Three bath temperatures were investigated: 20, 28, and 35 °C. The anodization time was controlled to provide a constant porous layer thickness (10 ± 0.5 μm). Figure 3 indicates that, for a given porous oxide thickness, the films formed at a higher anodization temperature exhibit accelerated coloring kinetics as compared to films formed at a lower anodization temperature. The anodization temperature determines the thickness of the barrier oxide layer formed during the anodizing step, e.g., a higher anodization temperature favors dissolution of the formed oxide resulting in thinner barrier oxide layer. On the other hand, a lower anodization temperature prevents rapid oxide dissolution, thereby providing thicker barrier films under steady state conditions. An estimate of the barrier layer thickness as a function of the anodization temperature can be obtained from the unit barrier thickness values reported by Keller et al. [1] for anodization in sulfuric acid, i.e., 15.2 nm for anodization at 20 °C, as compared to about 13 nm for anodization at 35 °C. Since surface resistance during coloring is governed by the barrier layer thickness, the thinner barrier oxide (grown at 35 °C) provides a lower surface resistance resulting in a higher coloring rate (e.g., 10 mA cm^{-2} at a coloring voltage of 12 V) as compared to the inhibited coloring kinetics (e.g., 6 mA cm^{-2} at the same coloring voltage of 12 V) observed for oxides grown at a lower anodization temperature.

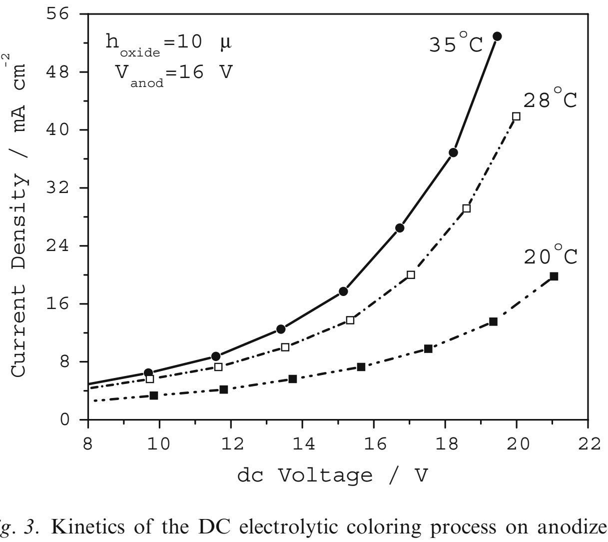

Fig. 3. Kinetics of the DC electrolytic coloring process on anodized aluminum as a function of the anodization bath temperature. The coloring current was recorded under steady state conditions, which took at least 60 s to reach. Anodization was performed potentiostatically at 16 V in a 15 wt.% H_2SO_4 bath at 20, 28, and 35 °C. The anodization time was varied, thereby providing films with a constant thickness of the porous oxide layer (10 ± 0.5 μm).

As discussed in the previous section, the current densities reported in Figure 3 are based on the geometric surface area of the aluminum specimen. The true electrochemical area available for the electrolytic coloring process, however, is different than the geometric area and is a function of the anodization temperature. An estimate of the relative change in the true surface area as a function of the temperature can be obtained based on variations in the parameter nD^2 (defined above as the product of the pore density of the oxide and the square of the pore based diameter) reported elsewhere [2, 3]. In the range of anodization temperatures used in this study (20–38 °C), the true electrochemical surface area at the pore bottom can change by a factor of about 1.4. The variations in the true coloring area can, therefore, significantly affect the coloring rate measurements at low coloring voltages; however, at high coloring voltages, the measured coloring currents are observed to change by a factor of 3 or more (e.g., from 12 mA cm^{-2} at 18 V for oxide films formed at 20 °C to about 36 mA cm^{-2} for films formed at 38 °C), i.e., by a factor much larger than 1.4 attributable to changes in the pore base area.

3.3. *Effect of the porous oxide thickness*

In the previous two sections, the dependence of the coloring kinetics on the anodization conditions was established for films with a constant porous layer thickness. In this section, we analyze the effect of the porous layer thickness on the coloring kinetics (Figure 4), keeping the anodization voltage and the bath temperature constant. Figure 4 indicates that an increase in the thickness of the anodic oxide causes a decrease in the coloring current density (at a given coloring voltage). However, the influence of oxide thickness on the coloring kinetics is relatively weak as compared to the effect of the anodization voltage and the bath temperature on the coloring rate. While the oxide thickness typically causes a change in the coloring current density from about 3 mA cm^{-2} (for a 25 μm thick oxide, at 12 V coloring voltage) to about 5 mA cm^{-2} (for a 7 μm thick oxide, at 12 V coloring voltage), i.e., change in the coloring rate by a factor of about 1.6, the anodization voltage and temperature affect the coloring kinetics significantly, sometimes causing an order of magnitude change in the current

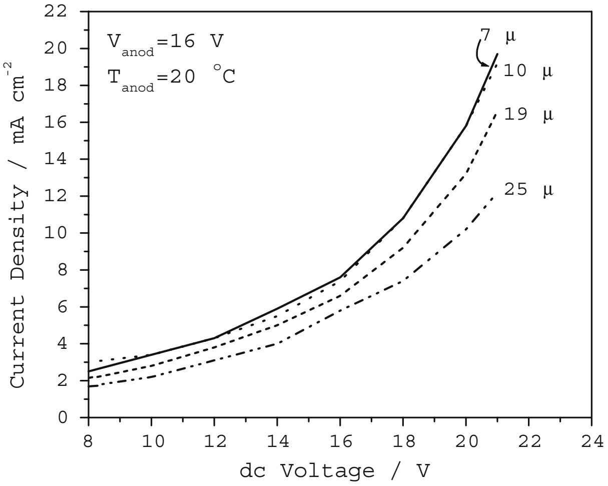

Fig. 4. Kinetics of the DC electrolytic coloring process on anodized aluminum as a function of the thickness of the porous oxide layer. The coloring current was recorded under steady state conditions, which took at least 60 s to reach. The anodic oxides were grown at a constant voltage (16 V) in a 15 wt.% H_2SO_4 bath at 20 °C. The anodization time was varied, thereby providing films with a constant barrier layer thickness, but different thicknesses of the porous oxide layer (7–25 μm).

density at a given coloring voltage. The rationale for the dependence of the coloring kinetics on the oxide thickness is, as of yet, unclear; however, we speculate that this effect may be the result of several competing processes, e.g., increased mass transport resistance for diffusion of the tin ions within the longer oxide pores, or local variations in the sulfuric acid concentration and temperature at the pore base that impact the true pore base diameter, thereby altering the true electrochemical area available for the coloring reaction. It has also been shown [12] that the rate of tin deposition during AC electrolytic coloring, particularly for the case of alloy 6111, depends somewhat on the composition and morphology of the film, which change as a function of the anodization film thickness and time. For example, thicker porous oxide films exhibit a higher volume fraction of silicon or silicon–iron bearing phases, which can promote tin deposition at locations farther away from the pore base [12]. This process by itself, however, would lead to an increase in the tin deposition rate with an increase in the porous oxide thickness – contradictory to the experimental results shown in Figure 4.

To further verify the dependence of the coloring rate on the thickness of the porous oxide, we have performed gravimetric analysis (using calibrated wavelength-dispersive X-ray fluorescence spectroscopy) on electrolytically colored specimens to determine the amount of tin deposited within the oxide pores. Figure 5 indicates that the amount of tin deposited per unit geometric area of the anodized aluminum sample, at a constant coloring voltage of 20 V for 120 s, increases with decreasing thickness of the porous oxide. As an example, an increase in the oxide thickness from 8 μm to 25 μm (provided by an increase in the anodization time from about 15–45 min.) causes a decrease in the amount of deposited tin from about 125 μg cm^{-2} to about 42 μg cm^{-2}. Since the shade of the color obtained is directly proportional to the amount of the deposited tin, coupons with a higher oxide thickness appeared faint brown in color as opposed to the dark bronze color imparted to anodized aluminum coupons with a thinner oxide layer. To confirm our observations from visual inspection, we performed optical spectrophotometry on the colored aluminum samples to determine the lightness value (L) of the color shade – a lightness value close to zero indicating a dark black color, and a lightness value close to 100 corresponding to a transparent film. The optical spectrophotometry indicated that, while coupons with a thick oxide layer provided a lightness value (L) of about 51 characteristic of the faint bronze shade, coupons with a thin oxide layer provided a lightness value of about 36 representative of the high tin content within the oxide pores.

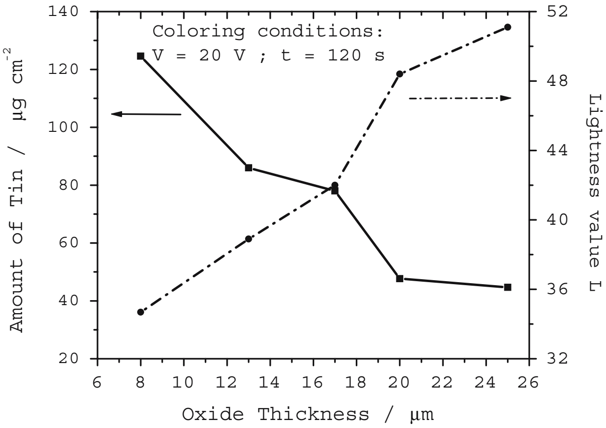

Fig. 5. Gravimetry (using calibrated X-ray fluorescence spectroscopy) and colorimetry of electrolytically colored aluminum samples. The aluminum samples were first anodized at 16 V in a H_2SO_4 electrolyte, for different anodization time periods (15–45 min), resulting in different oxide layer thicknesses (8–25 μm). The anodized aluminum films were then colored in a tin-based coloring electrolyte at 20 V for 120 s.

The dependence of the color shade on the thickness of the underlying oxide, and the overvoltage at which it is formed (Figure 2) can be used to obtain graded coloring of aluminum substrates: by controlling the oxide thickness distribution (simply by using insulating shields near the anode, or through well characterized electrochemical cell design), one can obtain a surface with varying thickness of the barrier and porous oxide layers. This surface when subjected to electrolytic coloring can then provide preferential coloring of the areas with thinner barrier and porous oxide, as compared to those where the thick oxide film offers a large surface resistance for the electrolytic coloring reaction. This distribution of the coloring current can be used to obtain graded coloring of the aluminum substrate. While the required color contrast can be obtained through controlling the anodic oxide thickness distribution, the average lightness value of the electrolytically colored aluminum

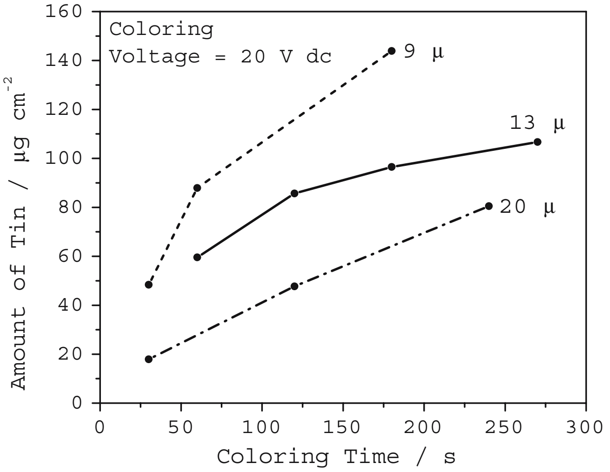

Fig. 6. Gravimetric analysis (using calibrated X-ray fluorescence spectroscopy) of electrolytically colored anodized aluminum. The aluminum samples were first anodized at 16 V in H_2SO_4 electrolyte, for different anodization time periods, resulting in different oxide layer thicknesses (9–20 μm). The anodized aluminum films were then colored in a tin-based coloring electrolyte at 20 V, for different coloring time periods (t = 30–270 s).

surface can be controlled by varying the coloring time. As shown in Figure 6, the amount of tin deposited within the oxide pores (at a given coloring voltage, in this case 20 V) is an approximately linear function of the coloring time. However, especially at low porous oxide thickness, the tin deposition rate decreases at long times (e.g., $t > 180$ s), probably as a result of the complete filling of the oxide pores with metallic tin, a condition that imparts a characteristic dark black color to these films. It is recommended that coloring of such oxide films with completely filled pores be discontinued to avoid surface defects and spalling.

4. Conclusions

The process of tin-based electrolytic coloring of porous anodic oxide films on aluminum is analyzed. Electrochemical polarization measurements of the kinetics of tin electrodeposition within the oxide pores, coupled with gravimetry and colorimetry of the colored aluminum surface, are used to characterize the dependence of the tin electrodeposition rate on the properties of the underlying substrate, i.e., the anodized aluminum. Measurements indicate that the kinetics of the electrolytic coloring process can be accelerated by: (i) reducing the surface resistance of the oxide film (primarily offered by the barrier oxide layer) by growing the oxide at a lower anodization voltage, and/or a higher bath temperature, or (ii) growing a thinner porous oxide layer by decreasing the anodization time.

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