INTERFERENCE-COLORED FINISHES
FOR AUTOMOTIVE ALUMINUM ALLOYS

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The purpose of this research was to develop and understand interference-coloring technology for anodized aluminum alloys. The deposited metal salt in the porous anodic coat can cause optical interference effects and produce colors ranging from blue, green, yellow, red, and various shades. The processes for producing these colors are still mainly in the R&D stage because they are complicated and can only be consistently produced through a sophisticated programmable rectifier and under well-controlled experimental conditions. In this paper, the interference colors as function of metal deposition height are clearly demonstrated through Transmission Electron Microscopy (TEM) study.

INTRODUCTION

Aluminum and its alloys are widely used in many engineering applications due to its high strength to weight ratio and good formability. One of the best ways to protect the aluminum surface is anodization, which is an electrochemical process, where the surface of the aluminum metal is converted to aluminum oxide at the anode during application of electrical current in an acidic solution. As the electricity is applied to the parts, two coating layers are produced on the aluminum surfaces, an inner barrier layer and an outer porous layer. The compact barrier layer is very thin (~ 20 nanometers) with protective dielectric properties. The porous layer is much thicker (as much as 50 microns), which forms an excellent corrosion-protection coating. These films are nearly transparent and therefore the aluminum can retain its metallic appearance.

There are many ways to color the aluminum oxide surface; the most important coloring method for exterior applications of aluminum parts is electrolytic coloring of the anodic oxide by electro-deposition of metal inside the pores. The colored anodic film not only has rich metallic luster but also has better colorfast properties. It is also very hard; with excellent abrasion, wear, and corrosion resistance. Although it has a manufacturing advantage of producing multiple colors with a single electrolytic tank, it only offers limited colors, from light bronze to medium bronze to black. However, due to its environmental friendliness and simplicity, color anodizing has been widely used for architectural applications.

The concept of the interference coloring, first introduced in the late 1970s, is similar to the electrolytic coloring method, but can produce many colors ranging from blue, green, yellow to red. In recent years, tremendous progress has been made to make the interference coloring the most technically advanced coloring method (1,2,11). In general, after anodization, the interference coloring is achieved by modifying the pore structure at the base of the pores in a conditioning tank. The metal salt is then deposited into the pores to produce various interference colors. Interference coloring usually requires sophisticated and precise programming in applied current and voltage. In this report, the interference colors as function of metal deposition heights are clearly demonstrated through Transmission Electron Microscopy (TEM) study.

Anodizing is an electrochemical process in which the aluminum part is made to be the positive electrode (anode) in a suitable electrolyte (e.g., sulfuric acid); a sufficiently high voltage is applied to establish the desired polarization to deposit oxygen at the surface [4-5]. The formation of oxide takes place by the migration of Al^{3+} ions from the metal towards the electrolyte interface, and the O^{2-} ions in the opposite direction. The anodic half-cell reaction for the oxide formation is shown as follows:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \uparrow$$

In the sulfuric acid anodizing process, the oxide formed is slowly dissolved by the electrolyte. Thus, a porous oxide coating is produced (see Fig. 1). The net coating growth rate and its porosity depends on the equilibrium set up between the film growth and dissolution [6-7].

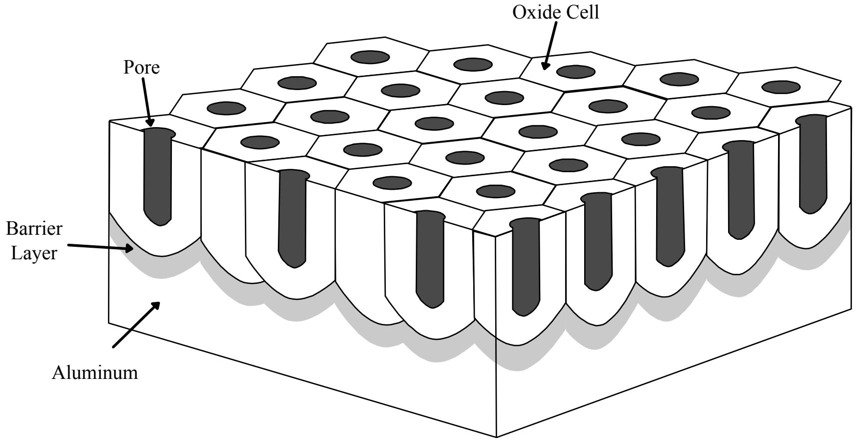

Figure 1. Schematic illustration of anodic oxide structure;
typical oxide thickness, 10 to 30 µm; pore diameter, 20 nm.

The characteristics of the anodic film is highly dependent upon factors such as electrolyte type, concentration and temperature as well as anodizing voltage, current density and time. Anodizing starts with the formation of a barrier (i.e., non-porous) film. Although this film is barely soluble in the electrolyte, with increasing anodizing time the oxide film will grow inward and the outer surface will be slowly dissolved in the electrolyte at the same time. The precise balances of these two actions are needed during anodization in order to produce a desired porous film. This porous film can be electrolytically colored and the method is similar to the electroplating process in principle because metal is deposited in the pores of the anodic oxide film. The bath voltage necessary for metal deposition in electroplating is of the order of a few volts. During electrolytic coloring, however, a higher voltage of about 10 to 20 V is used. This difference is because of the existence of the barrier layer. It is difficult to pass current through the barrier layer, and high voltages are necessary for depositing metal. When the size of the pores in anodic film is properly controlled for electrolytic coloring, the resultant film can be colored through an interference coloring effect.

The objective of this paper is to document the effect of the height of metal deposition in the aluminum oxides layers during interference coloring, which in turn has profound impact on the development of a viable coloring technology for engineering applications of very stringent requirements.

CONCEPT OF INTERFERENCE COLORING

Interference coloring method is different from the conventional two-step electrolytic coloring process. The color effect is due to the interference of visible wavelengths rather than light scattering. An intermediate conditioning (pore modification) stage is added prior to conventional electrolytic coloring. When this process is carefully controlled, it gives a greater color range than traditional electrolytic coloring method. Colors of red, orange, yellow, bronze, brown, green, blue and violet can be produced, depending on the time of the intermediate stage, and coloring voltage and time.

The ultramicrotomy coupled with transmission electron microscopy study [8] show that the intermediate conditioning stage results in the growth of new enlarged pores at the base of the pre-existing film. The metal deposited during coloring is at the base of these enlarged pores. Both Alcan [9,10] and Sheasby et al. [11] suggested that the interference effect arises from light reflecting from deposit surfaces and the underlying aluminum substrate. In order to accomplish a good interference effect, the deposit surface area at the bottom of the pore must be larger than that formed after conventional anodizing. This pore widening treatment not only provides a large reflecting surface but also ensures more uniform metal deposits to establish a good separation between two reflection surfaces to set up an interference color.

EXPERIMENTAL

The Interference Coloring process in general consists of two steps [12].

1. *Conditioning Process*: This step is to alter the pore size and determine the final sample color. It involves an application of combined AC and DC currents in a conditioning bath of 20% sulfuric acid with 0.5 g/L aluminum at 70°F. An infinite combination of AC/DC steps can be used to obtain various colors. Typically, four sequential steps are successfully applied during conditioning, i.e. (1) DC current, (2) AC current, (3) DC current and (4) DC current.

2. *Coloring Process*: This step deposits tin into the pores to set up interference colors. It involves immersing the sample in a coloring bath with 20 g/L sulfuric acid, 8 g/L tin at 70°F and then applying AC current with a ramp time of 10 seconds to a target voltage of 12.5 volts and holding it for 60 seconds.

   The samples are then sealed for 15 minutes in CS2 cold seal (Clariant Corp.) and 15 minutes in hot water seal for corrosion and color protection.

GMR&D has designed and built a comprehensive lab capable of interference-color anodizing, which involves modification of the pore structure at the base of the pores in a conditioning tank after anodization. The tin metal is then deposited into these pores to produce various interference colors. We have consistently produced interference-colored test panels using various aluminum alloys (i.e., AA5657, AA5083, AA6111, AA6063, see Table 1 for compositions). Typical AA5657 interference-colored samples for TEM studies were prepared by alkaline cleaning and anodizing in 160 g/L sulfuric acid electrolyte at 20°C bath temperature with applied current density of 15 A/ft^2 for 35 minutes. This would produce around 15 µm thickness anodic film. After anodizing, the interference coloring was produced according to our coloring procedures. One batch of specimens remained unsealed, and the second batch of specimens was sealed by first dipping the sample in CS-2 cold-seal solution for 15 min, followed by dipping in boiling water for 15 min. Another series of AA6063 panels were color-anodized by a supplier and were used for the TEM study below.

Table 1. Alloy Composition (Weight %)

Alloy	Mg	Mn	Si	Cu	Fe	Zn	Cr	Ti	Al
5083	4.50	0.60	<0.40	<0.10	<0.40	<0.25	0.10	<0.15	94.80
5657	0.59	<0.01	<0.10	0.03	0.03	<0.01	<0.01	0.02	99.20
6063	0.45	<0.10	0.40	<0.10	<0.35	<0.10	<0.10	<0.1	98.90
6111	0.80	0.20	0.60	0.70	0.25	<0.10	0.05	0.06	97.30

Sample preparation procedures for TEM study was described elsewhere [3].

RESULTS AND DISCUSSION

The TEM micrographs of the AA6063 panels reveal a porous film tied to the aluminum substrate by a barrier layer. Tin deposits are located mainly at the bottom of the pores and are usually at a uniform height. Interference coloring is produced by the constructive or destructive interference of the light reflected from two reflective surfaces (upper surface of the tin deposits and the aluminum/aluminum oxide interface) [4]. The distance between the two reflective surfaces (i.e., thickness t) determines the color and is given by the thin-film interference equation:

$$t = k\lambda/(2n),$$

where λ is the wavelength in the air,
n is index of refraction (1.7 for Al_2O_3),
k is the number of waves contained in the path length 2t.

Table 2 shows an excellent agreement between the measured and calculated thickness using the aforementioned equation. As the thickness of the tin deposit increases, the wavelength increases, and the color changes progressively from purple to red. Figure 2 shows the comparison of tin deposit thickness versus observed color. Although the pore enlargement is not evident in this case, it is remarkable that the observed colors correspond to the calculated colors very nicely.

Table 2. Wavelength of various colors versus measured and calculated tin deposit height of interference-colored AA6063 Alloy

Color	Wavelength (nm)	Calculated Height (nm)	Measured Height (nm)	Color Observed
Red	760-630			
Orange	630-590	180	210	Orange
Yellow	590-560	164	153	Yellow-green
Green	560-490	144	125	Green
Blue	490-440	129	100	Light blue
Indigo	440-420			
Violet	420-380	110	95	Purple

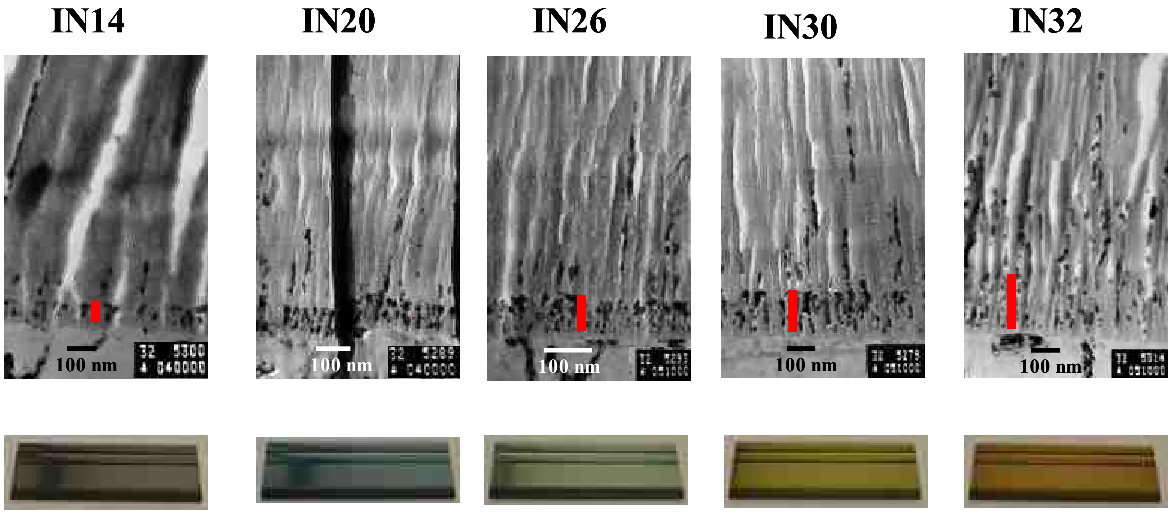

Figure 2. Interference color specimens - Comparison of tin deposit thickness versus observed color.

CONCLUSIONS

Transmission Electron Micrographs confirm that the measured heights of the tin deposition of the interference-colored panels match very well with the theoretical values calculated from the thin-film interference equation. TEM technique could be a very useful quality control tool for interference coloring process. The pore widening modification at the bottom of the film claimed in the literature was not evident from TEM pictures. High resolution TEM needs to be used to resolve this issue.

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