Effects of Alloy Types on the Gloss of Anodized Aluminum

Yar-Ming Wang, Hong-Hsiang (Harry) Kuo, Sheila Kia Materials & Processes Lab, General Motors R&D, Warren, MI 48090, USA

The effects of alloying elements, microstructures, and coating thickness on the surface gloss of anodized aluminum panels were investigated. Three automotive aluminum alloys (AA5083, AA5657, and AA6111) were tested. The oxide film growth rates for the three alloys are all in the 0.46 to 0.49 mm/min range. The gloss of anodized AA5657 is the highest, followed by AA6111 and AA5083. For AA5657 and AA6111 alloys, the magnesium contents are about the same, but AA6111 alloy has much higher manganese, silicon, and copper contents, contributing to the higher roughness and lower gloss. For AA5083 alloy, the grain size changes during forming do not affect the gloss changes during anodizing.

For more information, contact:

Dr. Yar-Ming Wang GM R&D Center MC 480-106-224 30500 Mound Road Warren, MI 48090-9055 Phone – (586) 986 0762 Fax – (586) 986 8697 E-mail: yar-ming.wang@gm.com

INTRODUCTION

Anodizing is an electrochemical process in which the aluminum part is made the positive electrode (anode) in a suitable electrolyte (e.g., sulfuric acid); sufficiently high voltage is applied to establish the desired polarization to deposit oxygen at the surface. The aluminum surface reacts with the oxygen to produce adherent, oxide coatings:

$$2Al + 5H_2O \rightarrow Al_2O_3 + O_2\uparrow + 5H_2\uparrow$$

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



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

Anodizing technology for aluminum that goes back to 1940's, is extensively used in architecture applications – especially in Europe [1]. For automotive applications, the gloss requirements are more demanding than the architecture applications, and it is important to determine the surface gloss of the finished part and to determine how the final gloss is affected by different factors. In this investigation, we studied the effects of alloying elements, microstructures, and coating thickness on the gloss of anodized aluminum for three automotive alloys (AA5657, AA5083, and AA6111).

EXPERIMENTAL PROCEDURE

MATERIALS

Three types of alloys were tested in this work. The chemical composition of these alloys is given in Table I [2]. The AA5657 is an automotive trim alloy. The AA6111 is an alloy commonly used for exterior aluminum body parts [3]. The AA5083 is from the family of alloys used in unexposed automotive applications.

					-	-			
Alloy	Mg	Mn	Si	Cu	Fe	Zn	Cr	Ti	Al
5083	4.60	0.79	0.10	0.02	0.18	0.01	0.11	0.01	bal.
5657	0.59	< 0.01	< 0.1	0.03	0.03	< 0.01	< 0.01	0.02	bal.
6111	0.66	0.20	0.60	0.85	0.23	0.01	0.01	0.03	bal.

Table I: Alloy Composition (Weight%)

The AA5083 alloy was tested as received and in the fully annealed condition. The AA5657 alloy was tested in as-received condition (one-side bright-rolled). The alloy AA6111, which is a heat-treatable alloy, was tested as received and after heat treatment at 177°C for 30 minutes.

The metal surfaces for alloys 6111 and 5083 were manually polished with a polishing wheel prior to anodizing (alloy 5657 was received as bright-rolled). Polishing was done using a Dewalt random-orbital sander (Model# DW421). Initial sanding was done using 3M Hookit Gold sanding pads at 400 grit (#00957) followed by 3M Hookit Finishing films at 600, 800, and 1500 grit (#00955, 00954, and 00951, respectively). The amount of sanding varied with the initial condition of the aluminum samples.

ANODIZING PROCESS

The anodizing process diagram is described in Figure 2. The aluminum surface is first cleaned in an alkaline cleaning tank, followed by dipping in the de-smut tank to remove black surface film (smut), then anodized for varying length of time (depending on the coating thickness desired) to grow a porous oxide layer. The film is then sealed in a two-step sealing process that basically hydrates the oxide, causing it to expand and fill up the pore spaces. Rinsing operations are incorporated between process steps to minimize the cross-contamination of the process solutions.



Figure 2. Anodizing process diagram.

GLOSS MEASUREMENT

The gloss of the sample surface was measured using a portable Micro-TRI Gloss meter (BYK-Gardner GmbH). The unit was placed directly on the sample and the gloss measurement was taken at both 60° and 85° illumination angles. The illumination angle is the angle between the axis perpendicular to the sample surface and directed light. The directed light reflected from the surface is measured photoelectrically and described by the reflectometer value R. This is a relative measurement based on the gloss value of 100 for a highly polished black glass plate with a refractive index of 1.567.

COATING THICKNESS MEASUREMENT

The oxide coating thickness was measured by a Fischerscope MMS unit (Fischer Technology, Inc.). This device uses eddy current method to measure coating thickness. When a conductive material (aluminum) is subjected to an AC magnetic field from the probe, eddy-currents occur in the material in proportion to the frequency and resistivity. The induced eddy currents generate an opposing magnetic field, which alters the circuit reactance and the output voltage of the probe. Non-conductive coating such as anodized coating introduces a gap (lift-off) between the probe and aluminum. This gap produces a loss in eddy current penetration, which is compared to a measurement directly on the base material to determine coating thickness.

SURFACE ROUGHNESS MEASUREMENT

Three–dimensional surface roughness was measured on the oxide/air and the metal/oxide interfaces by a non-contact Wyko Optical Profiler by Veeco Corporation. Due to the transparent nature of the aluminum oxide, double interference fringes occur at both the oxide/air surface and the metal/oxide interfaces, causing measurement problems. For an accurate oxide surface roughness measurement, we vacuum-deposited a thin Au-Pd layer onto the oxide/air surface to eliminate the interference fringe from the metal/oxide interface. To measure the metal surface roughness after anodizing, the oxide film was stripped off in a phosphoric/chromic stripping solution. A Ra value, which is a measure of the surface profile arithmetic average deviation from the centerline, was used to quantify the surface roughness.

METALLOGRAPHY

All alloys were examined metallographically to determine the grain structure. For AA5083, the samples were first aged at 150°C for 24 hours to precipitate Al_3Mg_2 at the grain boundaries; this promotes preferential attack at the grain boundaries in the etching process to reveal grains [4]. For other alloys, no aging steps were required to reveal grain structures. Alloy samples were mounted on their edge and examined by optical microscopy. The etchants and the etching conditions for various alloys are listed in Table II.

Table II: Etchants and Etching Conditions for Various Alloys

Alloy	Etchants (vol%)	Temperature (°C)	Time (minutes)	
5083	0.5 HF	Room temp	2	
5657	$10 H_3 PO_4$	50	4	
6111	0.5 HF	Room temp.	2	

RESULTS AND DISCUSSION

OXIDE FILM GROWTH

The effect of anodizing time on oxide film growth for the three alloys were examined in this study, and the results are shown in Figure 3. The oxide film thickness increases linearly with anodizing time. Table III lists the oxide growth rates for the three alloys, as given by the slope of the fitted straight lines to the data (Figure 3). It is observed that the growth rates for the alloys tested are all in the range of 0.46 to 0.49 μ m/min. For AA5083, annealing increases the growth rate by 6%, and for AA6111, heat treatment increases the growth rate by 4%. More samples should be tested to verify the statistical significance of these results. The coating thickness is governed by the current density (15 A/ft² in our study) and the time of anodizing. On the amp-min basis, the growth rates are calculated to be in the range of 30.7 to 33.0 amp-min/ft²/µm.



Figure 3. Oxide coating growth for three alloys.

Alloy	Treatment	Growth Rate (µm/min)	Growth Rate (amp-min/ft ² /µm)
5083	Cold-worked	0.464	32.3
5083	Annealed	0.489	30.7
5657	As-received (AR)	0.483	31.1
6111	As-received (AR)	0.455	33.0
6111	After heat-treatment (HT)	0.483	31.1

Table III: Coating Growth as a Function of Alloy Types and Heat Treatment

MICROSTRUCTURES

Figure 4 shows the microstructure typical of the cold-worked AA5083 material. It consists of fine equiaxed grains with an average diameter of ~ 5 μ m. After annealing, the average grain size is increased to ~ 10 μ m (Figure 5). Figure 6 shows the microstructure of the AA5657 material. It shows a cold-worked structure with elongated grains in the rolling direction. The microstructures of the AA6111 in asreceived and in heat-treated conditions are shown in Figures 7 & 8, respectively. Both have the same average grain size of ~ 20 μ m, and the heat treatment, due to its relatively low temperature and short duration (177°C for 30 minutes) [5], does not seem to affect the grain size.



Figure 4. Optical micrograph of AA5083 in cold-worked state.



Figure 5. Optical micrograph of AA5083 after superplastic forming.



Figure 6. Optical micrograph of AA5657.



Figure 7. Optical micrograph of AA6111, as-received.



Figure 8. Optical micrograph of heat-treated AA6111.

GLOSS OF ANODIZED ALLOYS DURING ANODIZATION

Alloy AA5083

The surface roughness (Ra) and 85° -gloss of AA5083 after annealing are shown in Figure 9 as a function of coating thickness for both metal/oxide interface and oxide/air interface. The metal surface roughness starts with a Ra value of 150 nm before anodizing. As the coating thickness increases from 0 to 5 µm, the Ra value increases linearly to 380 nm. From 5 to 15 µm coating thickness, the metal surface roughness values show a much gradual increase from 380 to 490 nm. After 15 µm coating thickness, the metal surface roughness stays relatively constant at approximately 500 nm. The oxide/air surface roughness increases from 150 to 300 nm as the coating thickness grows from 0 to 5 µm. For coating thickness greater than 5 µm, the oxide roughness remains relatively constant at 280 nm.

As shown in Figure 9, the variation in the surface roughness of the oxide surface with oxide thickness follows almost the same pattern as that for the metal surface, with most of the changes happening over the first 5 μ m of the film growth. The surface gloss decreases very sharply over the first 1 μ m film growth, dropping from 135 (before anodizing) to about 100 (25% drop in gloss). From 1 to 25 μ m coating thickness, the gloss decreases more gradually from about 100 to 76.



Figure 9. Variations of surface roughness and gloss with coating thickness for AA5083.

The relationships between gloss and surface roughness are depicted in Figures 10 & 11, for metal surface and oxide surface, respectively. On the basis of the calculated regression coefficients (see Figures 10-11), it is deduced that the gloss during anodization correlates strongly with the metal surface roughness, and to a lesser degree with the oxide surface roughness. Since aluminum oxide is transparent, one would expect the metal/oxide interface to be the prevailing reflecting surface and its surface characteristics (roughness, texture, etc.) have greater effect on the gloss of the anodized part.



Figure 10. Variations of gloss with metal/oxide interface roughness.



Figure 11. Variations of gloss with oxide/air interface roughness.

Alloy AA6111

The surface roughness (metal/oxide interface, and oxide/air interface) and 85° -gloss of heat-treated AA6111 are shown in Figure 12 as a function of coating thickness. The metal surface roughness starts with a Ra value of 55 nm (before anodizing). As the coating thickness increases from 0 to 10 µm, the Ra values increase linearly to 340 nm. From 10 to 27 µm coating thickness, the metal surface roughness values remain relatively constant. The oxide roughness shows an increase from 55 to 170 nm as the coating thickness grows from 0 to almost 5 µm. For coating thickness greater than 5 µm, the oxide roughness varies gradually from 170 to 250 nm.

As shown in Figure 12, most of the gloss decrease occurs over the first 3 μ m film growth, dropping from 130 before anodizing to about 95 (25% drop in gloss). From 3 to 27 μ m coating thickness, the gloss remains more or less the same.



Figure 12. Variation of surface roughness and gloss with coating thickness for AA6111(HT).

Alloy AA5657

The surface roughness (metal/oxide interface, and oxide/air interface) and 85°-gloss of AA5657 are shown in Figure 13 as a function of coating thickness. The metal surface roughness starts with a Ra value of 53 nm (before anodizing). As the coating thickness increases from 0 to 5 μ m, the Ra value increases slightly to 65 nm. From 5 to 10 μ m coating thickness, the metal surface roughness values actually decrease to 49 nm. The metal surface roughness shows a gradual increase from 49 to 80 nm as the coating thickness grows from 10 to 23 μ m. The oxide surface roughness reaches a maximum at a coating thickness of almost 5 μ m; it then decreases with increasing coating thickness, remaining almost constant after about 15 μ m.

As shown in Figure 13, most of the gloss decrease occurs over the first 10 μ m film growth, dropping from 150 (before anodizing) to about 116 (23% drop in gloss). From 10 to 23 μ m coating thickness, the gloss remains more or less the same.



Figure 13. Variations of surface roughness and gloss with coating thickness for AA5657.

EFFECT OF ALLOY GRAIN SIZE

Aluminum alloys of fine grain size often give superior finishes in comparison with alloys of coarser crystal structure. The effect of grain size on gloss during anodization is shown in Figure 14 for AA5083 cold-worked (AR) and after annealing (AN). The grain size of the AN material is two times larger than the CW material (see Figures 4-5). However, Figure 14 clearly indicates that the surface roughness or the gloss changes during anodization shows little correlation with grain size. Finer grain size and wider size ranges will be investigated in future studies.



Figure 14. Metal surface roughness and gloss values as a function of coating thickness for AA5083.

EFFECT OF ALLOYING ELEMENTS

The effect of alloying elements on metal surface roughness during anodization is shown in Figure 15. Among the alloys, AA5083 and AA5657 show the highest and lowest metal surface roughness, respectively. At a given anodizing current density, aluminum alloys with magnesium content greater than 1% tend to produce coatings of lower gloss values [6]. The AA5083 has a high magnesium content (4.60%, see Table I); during anodization, both aluminum and magnesium are oxidized at the metal/oxide interface [1]. The differential oxidation rates of aluminum and magnesium will result in roughening of the metal surface. For a low magnesium content alloy (AA5657 at 0.59%, see Table I), the surface roughness does not increase much; however, for a high magnesium content alloy (AA5083), the surface roughness increases substantially during anodization. For AA5657 and AA6111 alloys, the magnesium contents are about the same, but AA6111 alloy has higher manganese, silicon, and copper contents. These elements tend to remain on the metal surface during anodization; the interfacial enrichments of the alloy elements further promote differential oxidation of the metal surface, thus contribute to the increase in roughness [7-8].



Figure 15. Variations of metal surface roughness with coating thickness for different alloys.

Figure 16 shows the gloss versus coating thickness for the three alloys. AA5657 shows the highest gloss; AA6111 has a slightly higher gloss than AA5083 alloy. For AA 5657, the gloss exhibits a linear decrease as the coating thickness increases from 0 to 10 μ m. With coating thickness greater than 10 μ m, no further gloss loss is observed. For AA6111 and AA5083 alloys, the critical coating thickness is around 1-3 μ m.



Figure 16. Variations of gloss with coating thickness for different alloys.

CONCLUSIONS

In this investigation, we selected three automotive aluminum alloys (AA5083, AA5657, and AA6111) to study the effects of alloying elements, microstructures, and coating thickness on the gloss of anodized aluminum. Under similar anodizing conditions, the gloss of anodized AA5657 is the highest, followed by AA6111 and AA5083. For all the alloys, there is a decrease in gloss of the panels with increasing oxide thickness. The decrease in gloss correlates strongly with the increase in metal surface roughness during anodization, and to a lesser degree, with the increase in the oxide surface roughness. For a low magnesium content alloy (AA5657), the surface roughness does not increase much with oxide growth. However, for a high magnesium content alloy (AA5083), the surface roughness increases substantially during anodization due to differential oxidation rates of aluminum and magnesium. For AA5657 and AA6111 alloys, the magnesium contents are about the same, but AA6111 alloy has much higher manganese, silicon, and copper contents, contributing to the higher roughness and lower gloss. Of all the factors investigated, alloy composition and coating thickness are the two most important parameters affecting the gloss of finished parts.

ACKNOWLEDGEMENTS

We would like to thank Dusanka Radovic and Robert Kubic for optical micrographs of the alloy microstructures, and Bob Paluch and Joe Simmer for test cell design. Also, we greatly appreciate the effort by Mike Zseng and Jessica Taylor of MEDA for preparing the test samples.

REFERENCES

- 1. S. Wernick, R. Pinner, P.G. Sheasby, The Surface Treatment And Finishing Of Aluminum And Its Alloys, ASM International, Finishing Publication Ltd., Vol. 1&2, 5th edition, 1987
- 2. MatWeb http://www.matweb.com/searchindex.htm
- 3. R. Verma, A.K. Ghosh, S. Kim, and C. Kim, Materials Science & Engineering A, 191, P. 143-150, (1995)
- 4. K. Kannan, J.S. Vetrano, and C.H. Hamilton, Met. and Mat. Trans. A, 27A, p.2947, (1996)
- 5. J. Bryant, Met. and Mat. Trans. A, 30A, p.1999, (1999)
- 6. C.M. Jackson and R.W. Thomas, Transactions of the Institute of Metal Finishing, 57, p. 105-109 (1979)
- 7. X. Zhou, G.E. Thompson, P. Skeldon, G.C. Wood, K. Shimizu, and H. Habazaki, Corrosion Science, 41, p.1599, (1999)
- 8. H. Habazaki, K. Shimizu, P. Skeldon, G.E. Thompson, G.C. Wood, and X. Zhou, Corrosion Science, 39, p.731, (1997)