Discoloration of Anodized AA6063 Aluminum Alloy

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The effect of the anodizing process parameters and the influence of β′(Mg2Si) phase on the appearance of the anodized AA6063 aluminum alloy have been investigated. It was found that β′(Mg2Si) phase was preferentially oxidized at low anodizing voltages and the selective oxidation of β′(Mg2Si) phase resulted in the development of a rough alloy/film interface and the incorporation of silicon into the porous anodic film. The discoloration of the anodized alloy was attributed to the presence of Mg2Si phases. The total reflectance of the mechanically polished and anodized alloy was measured on a SPECORD 250 spectrophotometer within the wavelength range of 300–800 nm. A Philips XL30 field emission gun scanning electron microscope (FEG-SEM), equipped with energy-dispersive X-ray spectroscopy (EDS) on the surface of the anodized alloy was used to determine the effect of anodizing voltage on the appearance of the anodized alloy.

Experimental

An extruded plate of AA6063-T6 aluminum alloy (0.20–0.6 wt% Si; 0.45–0.9 wt% Mg; 0.35 wt% Fe; 0.10 wt% Cu; 0.10 wt% Mn; 0.10 wt% Cr; 0.10 wt% Zn; 0.10 wt% Ti; 0.15 wt% others; remainder aluminum) was used as the original material benchmark. The AA6063-T6 aluminum alloy specimens were then over-aged at 240 °C, 300 °C or 400 °C for 5 hours in a Gallenkamp Hotspot Furnace.

All specimens were mechanically ground with 800, 1200 and 4000 grit silicon carbide paper and polished sequentially using 6, 3 and 1 μm diamond paste with mecaprex polishing liquid as lubricant. For the determination of the precipitate distribution in the alloy, the mechanically polished specimens were first etched in 10 wt% NaOH solution at 60 °C for 60 s and then desmutted in 30 vol% HNO3 solution at room temperature for 30 s, followed by rinsing and drying in a cool air stream.

For anodizing, the mechanically polished specimens were degreased in acetone, rinsed in deionized water, and dried in a cool air stream. Following degreasing, the specimens were masked with lacquer to expose an area of 1 cm2. The lacquer was allowed to cure in air for at least 24 h. Alloys of different tempers were anodized individually in a 2 M sulfuric acid solution at 20 °C by linear polarization from the open circuit potential (OCP) to 3.5 V vs. saturated calomel electrode (SCE) at a sweep rate of 0.1 V/min. The linear polarization procedure enables separation of the contributions of the phenomena associated with anodizing of intermetallics from those associated with anodizing of the alloy matrix. Further specimens were potentiostatically anodized at 0.5, 1.5, 2.5 and 12 V (SCE) for constant charges of 1 C to determine the effect of anodizing voltage on the appearance and structure of the resultant anodic films.

A Solartron 1287 potentiostat was used for anodizing and data logging. A Nikon D90 digital camera was used to record the appearances of the anodized alloys of different tempers. All optical images were taken in dark time with a viewing angle of about 45°. The total reflectances of the mechanically polished and anodized alloys were measured on a SPECORD 250 spectrophotometer within the wavelength range of 300–800 nm. A Philips XL30 field emission gun scanning electron microscope (FEG-SEM), equipped with energy-dispersive X-ray spectroscopy (EDS) on the surface of the anodized alloy was used to determine the effect of anodizing voltage on the appearance of the anodized alloy.
dispersive X-ray (EDX) facilities, was used for characterization of the
alloy microstructure and the resultant anodic films. Cross sections
(nominal thickness 15 nm) of the anodic films attached to the alloy
substrates were generated by ultramicrotomy using a diamond knife.9
The ultramicrotomed sections were then examined in a JEOL 2000
FXII electron microscope, equipped with EDX facilities, operating at
an accelerating voltage of 120 kV. 3D volumetric reconstructions of
the selected anodic films were performed according to the literature.10

Results

Precipitation at different tempers.— Figure 1 shows secondary
electron micrographs of the etched AA6063-T6 alloy and the al-
loy after subsequent over-aging at 240, 300 and 400 °C for 5 hours.
Needle-shaped precipitates of 20–100 nm length, together with a sur-
face texture, are revealed on the etched AA6063-T6 alloy (Figure 1a).
According to previous work on Al-Mg-Si alloys, fine needle-shaped
precipitates of length about 20–50 nm are β’(Mg2Si) phase11–13 and
needle-shaped or rod-shaped precipitates of length about 50–700 nm
are β′(Mg2Si) phase.12,14,15 Therefore, the precipitates shown in
Figure 1a are β’(Mg2Si) phase or fine β′(Mg2Si) phase. Further, the
rod-shaped precipitates of 200–600 nm length in the 240 °C-aged al-
loy (Figure 1b) are β′(Mg2Si) phase and the rod-shaped precipitates
of 500–800 nm length in the 300 °C-aged alloy are further coars-
ened β′(Mg2Si) phase (Figure 1c). When the temperature was in-
creased to 400 °C, which is higher than the solvus temperature of
β′(Mg2Si) phase,16,17 all the needle-shaped and rod-shaped precipi-
tates dissolved into the solid solution and a surface texture appeared
again on the etched surface. It is noticed that the surface texture dis-
appeared when the precipitates in the alloy matrix were considerably
coarsened, suggesting that the surface texture mainly resulted from
alloying elements in the solid solution of the alloy. The mechanism
for the formation of the surface texture during alkaline etching has
been reported elsewhere.18

Anodizing of the alloys of different tempers.— Previous work8,19
has indicated that intermetallics of different compositions in alu-
mminum alloys are oxidized at specific voltages or voltage ranges.
The characteristic voltages/voltage ranges could be determined from
the current density-voltage responses of the alloys which were linearly
polarized from the OCP to higher voltages. Figure 2 shows the current
density-voltage responses during anodizing of AA6063-T6, 240 °C-, 300 °C- and 400 °C-aged alloys from the OCP to 3.5 V (SCE). Inter-
estingly, a significant current surge, which started immediately after
∼0 V (SCE), peaked at ∼1.5 V (SCE) and ended at ∼3.0 V (SCE),
was observed for the alloys aged at 240 and 300 °C. Such current surge
was absent for the alloy of T6 temper and the alloy aged at 400 °C,
suggesting a correlation between the current surge and the presence
of β′(Mg2Si) phase. It is believed that the preferential oxidation of
β′(Mg2Si) phase precipitates within the specific range of polarization
voltages resulted in the current surge. As revealed in Figure 1, the
300 °C-aged alloy had relatively coarser (probably also larger volume
fraction) β′(Mg2Si) phase precipitates compared with the 240 °C-aged
alloy. Consequently, the current peak for the 300 °C-aged alloy was
greater than that for the 240 °C-aged alloy.

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In order to investigate possible correlation between the appearance, the morphologies of the anodic films and the oxidation of the $\beta'(\text{Mg}_2\text{Si})$ phase, the 240°C-aged alloy was selected for anodizing at 0.5, 1.5, 2.5 and 12 V (SCE) respectively. The previous voltages correspond to different stages of the current surge in Figure 2. Figure 3 compares appearances of the 240°C-aged alloy after anodizing at different voltages for 1 coulomb of charge passed. The alloy anodized at 0.5, 1.5 and 2.5 V (SCE) display discolored appearances, contrasting with the normal appearance of the alloy anodized at 12 V (SCE).

The total reflectances of the four samples were measured in the wavelength range of 300–800 nm, as shown in Figure 4, with the total reflectance of the mechanically polished surface used as a benchmark of the original surface prior to anodizing. The total reflectance of the filmed surfaces fluctuated within the wavelength range of visible light, contrasting with the relatively constant total reflectance of the mechanically polished surface within the same wavelength range, suggesting that the fluctuation of the total reflectance of the filmed surfaces resulted from anodizing of the alloy. Additionally, it is clearly revealed in Figure 4 that the profiles of the total reflectance curves are different for the four samples, suggesting that the alloys anodized under different conditions have different responses to the visible light and, therefore, show different colored appearances. As discussed later, the different responses mainly arise from the different compositions of the resultant films and the alloy/film interface profiles. The integrated total reflectance (the integrated area, between the total reflectance curve and the wavelength axes, divided by wavelength range) of the alloy surfaces is 23, 28, 49 and 79% for anodizing at 0.5, 1.5, 2.5 and 12 V (SCE) respectively. The last value, which corresponds to the normal appearance, is close to that of the mirror-finished surface (83%), suggesting a correlation between the discoloration and the total reflectance. Figure 5 shows secondary electron micrographs of the 240°C-aged alloy after anodizing at 0.5, 1.5, 2.5 and 12 V (SCE),
revealing dark spots of several hundred nanometers dimensions in the anodic films formed at 0.5, 1.5 and 2.5 V (SCE), with the population density of the dark spots in the anodic films decreasing in the order of 0.5 > 1.5 > 2.5 V (SCE). No dark spots were revealed on the alloy surface after anodizing at 12 V (SCE) (Figure 5d). Evidently the higher the population density of the dark spots on the anodized alloy surface, the lower the integrated total reflectance of the surface. This suggests that the discolored appearance is related to the dark spots. Since the anodic films with dark spots were formed within the voltage range at which the preferential oxidation of β′(Mg2Si) phase could occur, as revealed in Figure 2, it is thus suggested that the preferential oxidation of β′(Mg2Si) phase has led to the formation of the dark spots on the anodized alloy and consequently the discolored appearance.

Following comparison of the 240 °C-aged alloy anodized at different voltages, alloys of different tempers anodized at 1.5 V (SCE) were compared. Figure 6 shows the appearances of the AA6063-T6, 240 °C-, 300 °C- and 400 °C-aged alloys after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed. Discolored appearances on the 240 °C- and 300 °C-aged alloys were displayed while the normal appearance was evident for the AA6063-T6 and 400 °C-aged alloys. This agrees with the findings that there were high population densities of β′(Mg2Si) phase in the 240 °C- and 300 °C-aged alloys and relatively little β′(Mg2Si) phase in the AA6063-T6 and 400 °C-aged alloys. The total reflectances of AA6063-T6, 240 °C-, 300 °C- and 400 °C-aged alloys after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed are displayed in Figure 7, revealing significantly reduced integrated total reflectance for the 240 °C-aged (28%) and 300 °C-aged (32%) alloys compared with the AA6063-T6 (66%) and 400 °C-aged (75%) alloys, consistent with the appearances of the alloys. The comparatively lower integrated total reflectance of the AA6063-T6 (66%) than that of the 400 °C-aged (75%) and mirror-finished (83%) alloys was due to the presence of β′(Mg2Si) phase although of reduced size and population density in the AA6063-T6 alloy (Figure 1a) compared with the 240 °C-aged and 300 °C-aged alloys. The reduced integrated total reflectance of the anodized AA6063-T6 alloy should also affect the appearance of the alloy. However, such influence is probably too trivial to be detected by the naked eye. Figure 8 shows secondary electron micrographs of the AA6063-T6, 240 °C-aged, 300 °C-aged and 400 °C-aged alloys after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed, clearly revealing dark spots on the 240 °C-aged (Figure 8b, repeat of Figure 5b) and 300 °C-aged (Figure 8c) alloys and dark spots of largely reduced population density on the AA6063-T6 (Figure 8a) and 400 °C-aged (Figure 8d) alloys. On the 300 °C-aged alloy (Figure 8c) dark spots had shape and population density comparable with those of the coarse β′(Mg2Si) phase in the alloy substrate (Figure 1c), confirming that the dark spots resulted from preferential oxidation of β′(Mg2Si) phase. Figure 9 displays a scanning electron micrograph of the alloy side of the alloy/film interface, revealed by selectively removing the anodic film formed on the 240 °C-aged alloy by anodizing at 1.5 V (SCE) for 1 coulomb of charge passed, showing rod-shaped cavities with a distribution similar to that of the rod-shaped β′(Mg2Si) precipitates in the alloy (Figure 1b). It is noted that the spherical cavities represent the cross sectional views of the rod-shaped cavities. Therefore, it is evident that the dark spots observed on the anodized alloy were associated with the cavities. The cavities, as proved later, were associated with faster oxidation of β′(Mg2Si) precipitates compared to the alloy matrix. Figure 10 compares the appearances of the 240 °C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed and the same anodized alloy after film stripping and re-anodizing at 12 V for 1 coulomb of charge passed. Since anodizing of the alloy after mirror finishing at 12 V for 1 coulomb of charge passed did not result in discolored appearance (Figure 3b), the discolored cavity of the alloy (Figure 10b) is ascribed to the rod-shaped cavities revealed in Figure 9.

Additionally, ultramicrotomed cross sections of selected anodic films, attached to the alloy matrix, have been examined to show how preferential oxidation of β′(Mg2Si) precipitates modified the morphology and/or composition of the resultant anodic films. Figure 11 shows the transmission electron micrograph of the cross section of the anodic film formed on the 240 °C-aged alloy after anodizing at 12 V (SCE) for 1 coulomb of charge passed, revealing a typical porous anodic film of 513 nm thickness and a relatively flat alloy/film interface. Using this film as the benchmark for the anodic film of normal appearance, the correlation between the film morphology and the discoloration of the anodized alloy could be manifested. Figure 12 illustrates the transmission electron micrograph of the cross section of the anodic film formed on AA6063-T6 alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed, revealing a porous anodic film of 350–380 nm thickness with an irregularly shaped alloy/film interface. Since the alloy substrate was mirror-finished prior to anodizing, the irregularly shaped alloy/film interface arose from the formation of the anodic film. A dashed-line parallel to the film surface was drawn at the alloy/film interface region, to reveal the local protrusion of the anodic film into the alloy substrate at the sites indicated by the arrows. The
Figure 8. Scanning electron micrographs of the (a) AA6063-T6; (b) 240 °C-aged; (c) 300 °C-aged and (d) 400 °C-aged alloys after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed.

Figure 9. Scanning electron micrograph of the alloy side of the alloy/film interface, revealed by selectively removing the anodic film formed on the 240 °C-aged alloy by anodizing at 1.5 V (SCE) for 1 coulomb of charge passed.

Figure 10. Optical micrographs of the 240 °C-aged alloy: (a) after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed; and (b) after subsequent film stripping and re-anodizing at 12 V for 1 coulomb of charge passed. (Color online)

Figure 11. Transmission electron micrograph of the cross section of the anodic film formed on the 240 °C-aged alloy after anodizing at 12 V (SCE) for 1 coulomb of charge passed.

Figure 12. Transmission electron micrograph of the cross section of the anodic film formed on AA6063-T6 alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed.
The cross section of the anodic film formed on the 240°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed is shown in Figure 13, revealing the anodic film with thickness varying from ~270 nm to ~490 nm, i.e. significantly different from that revealed in Figure 12. Assuming the dashed-line represents the alloy/film interface at the places with the thinnest film, it is clearly indicated that the anodic film had preferentially grown at the locations as indicated by the arrows. Taking into account the size of β'(Mg2Si) precipitates, 200–600 nm length, and the expected preferential oxidation of β'(Mg2Si) precipitates at the selected voltage (Figure 2), it is suggested that the sites of local film growth were related to preferential oxidation of β'(Mg2Si) precipitates.

The cross section of the anodic film formed on the 300°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charges is shown in Figure 14. Similar to Figure 13, the thinnest regions of the anodic film had a thickness of about 270 nm. Further, at some locations, anodic film was evident in the alloy up to 800 nm from the film surface and was not connected with the bulk film on the cross section, as indicated by the arrows. However, based on this conventional 2D TEM image, it is difficult to determine the oxidation path for the isolated film regions. 3D volumetric reconstruction of the sample was conducted, with selective transparency applied to the alloy matrix and colors applied to anodic oxides of different compositions. (Color online)

Figure 13. Transmission electron micrograph of the cross section of the anodic film formed on the 240°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed.

Figure 14. Transmission electron micrograph of the cross section of the anodic film formed on the 300°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed.

Since high angle annular dark field (HAADF) microscopy was strongly dependent on the average atomic number of the element encountered by the incident electron beam and it is less affected by defocus and sample thickness variation compared with traditional transmission electron microscopy, the technique was used to further characterize the anodic film. Figure 16 shows a HAADF image of the cross section of the anodic film formed on the 300°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed, revealing dark lines (indicated by arrows) in the middle of the regions of the anodic film associated with oxidation of β'(Mg2Si) precipitates. The dark lines correspond to voids in the anodic film. Scrutiny of the typical film regions (inset in Figure 16) revealed that pores in the anodic film surrounding the dark lines had developed in the directions normal to the dark lines, suggesting that film had grown from the dark lines (this is discussed further later). Figure 17 displays the EDX spectra taken from the bulk anodic film and the film immediately adjacent to the dark line, as indicated by A and B in the inset of Figure 16, revealing much stronger signal of silicon at location B compared with location A. The enrichment of silicon in the anodic film adjacent to the dark lines is related to the oxidation of β'(Mg2Si) precipitates since only β'(Mg2Si) precipitates could provide the increased silicon content. The relatively low level of magnesium detected in the anodic film in the regions is probably because magnesium species migrated faster than aluminum and silicon species during anodizing and were ejected into the electrolyte under the electric field.

**Discussion**

*Oxidation of Mg2Si precipitates.*— The decomposition of Mg2Si during anodic oxidation has been a controversial issue for long time. Keller and co-workers reported that silicon from solid solution was ejected into the electrolyte under the electric field.
converted to SiO$_2$ in the anodic film rather than the elemental form.$^{21}$ Cote et al. stated that on anodic oxidation of an aluminum alloy, the magnesium in Mg$_2$Si migrated away, leaving the silicon not appreciably oxidized.$^{22}$ Forsyth anodized 6061 and 7010 aluminum alloys in sulfuric acid electrolyte under typical conditions and successfully located the decomposed Mg$_2$Si in the resultant anodic film using aniline dye Malachite Green.$^{23}$ Based on the transparent form of the anodized due to its relatively high activity. As for silicon in Mg$_2$Si, it may be oxidized to silica or exists in elemental form. Based on the morphology of the anodic films formed at different potentials (Figures 11–16), it is believed that silica or elemental silicon was present in the resultant anodic films, depending on the anodizing voltage.

At relatively high voltage, e.g. 12 V (SCE), $\beta'(\text{Mg}_2\text{Si})$ was oxidized together with aluminum matrix, probably with an anodizing rate greater than the matrix.$^{24}$ In this case, magnesium and silicon in $\beta'(\text{Mg}_2\text{Si})$ were oxidized to MgO and SiO$_2$ respectively. Taking the Pilling-Bedworth ratios (P-B ratios) of Mg and Si as 0.81 and 2.15, respectively,$^{25}$ the weighted average P-B ratio of $\beta'(\text{Mg}_2\text{Si})$ is 1.26, which is close to that of aluminum (1.28). Therefore, similar expansion ratio can be expected for $\beta'(\text{Mg}_2\text{Si})$ and the aluminum matrix. Considering the relatively small dimensions of $\beta'(\text{Mg}_2\text{Si})$ precipitates and their expansion ratio being similar to that of aluminum matrix after oxidation, the volume variation in the anodic film as a consequence of oxidation of $\beta'(\text{Mg}_2\text{Si})$ is negligible. Thus, a typical porous anodic film was generated (Figure 11).

Conversely, at relatively low voltages, e.g. 0–3 V (SCE), preferential oxidation of $\beta'(\text{Mg}_2\text{Si})$ phase relative to the alloy matrix occurred (Figure 2). This implies that the oxidation of the alloy matrix was restricted locally when $\beta'(\text{Mg}_2\text{Si})$ was oxidized until completion of $\beta'(\text{Mg}_2\text{Si})$ oxidation at the alloy/film interface (schematically illustrated in Figure 18 and further discussed later). The presence of voids at the location of the oxidized $\beta'(\text{Mg}_2\text{Si})$ phase and radial growth of the anodic film around the oxidized $\beta'(\text{Mg}_2\text{Si})$ at 1.5 V (Figure 16) suggest that the oxidation behavior of $\beta'(\text{Mg}_2\text{Si})$ at relatively low voltages (0–3 V) is different from that at 12 V. The mechanism for the oxidation of $\beta'(\text{Mg}_2\text{Si})$ can be explained by considering $\beta'(\text{Mg}_2\text{Si})$ as a binary magnesium-silicon alloy. Bonilla et al.$^{26}$ anodized sputtering-deposited Mg-0.4 at% W and Mg-1.0 at% W alloys in 0.3 M ammonium hydroxide/0.05M ammonium phosphate electrolyte at 293 K and found that the correlation between the anodizing behavior of alloying elements and their Gibbs free energies for the oxidation per equivalent of the elements in the binary magnesium alloy is similar to that of dilute aluminum alloys. For the magnesium-tungsten alloys, magnesium was preferentially oxidized with enrichment of tungsten immediately beneath the oxide/alloy interface. Using the previous information, for $\beta'(\text{Mg}_2\text{Si})$ phase, magnesium is expected to be oxidized while silicon is enriched. The enriched silicon would not be oxidized but incorporated into the porous anodic film in elemental form.$^{27}$ Owing to the dissolution of MgO in acidic environment, the oxidation of $\beta'(\text{Mg}_2\text{Si})$ precipitates resulted in increased porosity in the anodic film.

Preferential oxidation of $\beta'(\text{Mg}_2\text{Si})$ phase could affect not only the morphology and composition (silicon incorporation) of the anodic film, but also significantly affect subsequent film growth and the alloy/film interface profile, as revealed in Figures 13–16. Figure 18 schematically illustrates such effects. At the commencement of anodizing, the anodic film was uniformly formed on the alloy surface, with retreat of the alloy/film interface into the bulk alloy (Figure 18a). When the thickness of anodic film reached $t_1$, the alloy/film interface arrived at the top side of a $\beta'(\text{Mg}_2\text{Si})$ rod. Under the selected
anodizing condition, preferential oxidation of the β'(Mg2Si) rod occurred and the oxidation of the aluminum matrix was locally restricted (Figure 18b). During this period of time, the electric field was not uniformly distributed but concentrated at the site of β'(Mg2Si) rod with Mg being preferentially oxidized and silicon being left behind. Once the oxidation of the β'(Mg2Si) rod was completed, the electrolyte could reach the alloy matrix surrounding the β'(Mg2Si) rod through the void formed as consequence of the dissolution of MgO in the acid. Oxidation of the aluminum matrix, in both the bulk regions and the regions adjacent to the oxidized β'(Mg2Si) phase, then resumed. With progress of anodizing, anodic films with thickness $t_1$ and $t_2$ were formed in the bulk regions and the regions adjacent to the oxidized β'(Mg2Si) rods (Figure 18c).

Further, as revealed in Figures 13-16, a flat film/electrolyte interface and an irregularly shaped alloy/film interface are evident. It is known that anodizing can smooth a rough substrate surface through electric filed distribution that is associated with local geometry at the alloy/film interface. The preferential oxidation of the β'(Mg2Si) precipitates resulted in the roughening of the alloy/film interface. Once the oxidation of the individual β'(Mg2Si) rod was completed, through electric filed distribution, the current was concentrated on the oxidation of the aluminum matrix in the regions adjacent to the oxidized β'(Mg2Si) phase until the alloy/film interface was smoothed. The TEM images of the cross sections only reflect a time point of the roughening/smoothing cycles, therefore, revealing flat film/electrolyte interface and irregularly shaped alloy/film interface.

Discoloration of the anodic film.— It has been indicated that the discoloration of the anodized alloy is closely related to the preferential oxidation of β'(Mg2Si) phase. Plan and cross sectional examinations of the anodized alloy with different appearances suggest that one of the major consequences of preferential oxidation of β'(Mg2Si) phase is the development of the relatively rough alloy/film interface. Therefore, it is believed that the rough alloy/film interface plays an important role in the changing appearance of the anodized alloy. Considering the transparent nature of the porous anodic alumina film formed in sulfuric acid solution, most of the incident light should be reflected at the alloy/film interface. It is well known that material with smooth surfaces appear glossy, while very rough surfaces reflect little specular light and therefore appear matte. Surface roughness in the micrometer range influences the specular reflectance levels.29 Figure 19 depicts the reflection at an angle $i$ on a rough surface with a characteristic roughness height $h$. For an incident light with wavelength of $\lambda$, the path difference of the reflected light wave from the rough surface can be expressed as:

$$\Delta \phi = \frac{4\pi h \cos i}{\lambda}$$

If $\Delta \phi < \frac{\pi}{2}$, the two reflected waves are nearly in phase and therefore the specimen surface can be considered smooth. Otherwise, the surface is rough and it scatters light in different directions and the two reflected waves are not in phase, resulting in a low density of reflected light. Thus, the smooth surface condition, known as the Rayleigh criterion, is obtained as:

$$h < \frac{\lambda}{8 \cos i}$$

Taking the reflection angle as 60°, the minimum roughness height that can results in variation in reflection, which is detectable by the naked eye within the wavelength range of visible light (0.38–0.78 μm), can be calculated as:

$$h < 0.2 \mu m$$

This indicates that when the roughness height is more than 0.2 μm, the decrease of the surface gloss due to reduced specular reflection is sufficient to be detected by the naked eye.

It has been shown that β'(Mg2Si) phase are present in the AA6063-T6, 240°C-aged, and 300°C-aged alloys, with sizes in the range of 20–100 nm, 200–600 nm, and 500–800 nm, respectively (Figure 1). However, when the three alloys were anodized under the same conditions (at 1.5 V (SCE) with 1 coulomb of charge passed), only the 240°C-aged and 300°C-aged alloys displayed discolorated appearances (Figure 6). This suggests that a minimum size of β'(Mg2Si) precipitate is necessary to result in a detectable discolored appearance in addition to the required anodizing voltages for the preferential oxidation of β'(Mg2Si) phase. The smallest β'(Mg2Si) precipitate in the 240°C-aged alloy is approximately 200 nm in length, coinciding with the minimum roughness height (0.2 μm) for detectable surface gloss change, suggesting that the discolored appearance has direct correlation with the roughness of the alloy/film interface caused by the preferential oxidation of β'(Mg2Si) precipitate with minimum length of 200 nm. In fact, such correlation has been experimentally confirmed in Figure 10b, where the discolored appearance was obtained by anodizing the 240°C-aged alloy with very rough surface at 12 V (SCE) for 1 coulomb of charge passed. It is noted that anodizing the same alloy, but with a mirror finished surface, under the same conditions did not produce a discolored appearance (Figure 3d).

As discussed previously, discoloration of the anodized alloy is related to preferential oxidation of β'(Mg2Si) in the alloy, which could result in void formation and silicon incorporation in the anodic film. Therefore, apart from the roughness of the alloy/film interface, the effect of structural and compositional variation in anodic film on its appearance also needs to be considered. Given the same incident light, the total amount of reflected light from an object, including specular reflectance and diffuse reflectance, is independent of the roughness of the reflecting surface. Therefore, total reflectance could be used to assess the optical nature of anodic films of different structures and compositions. Table 1 compares the integrated total reflectance and the appearance of selected specimens. The integrated total reflectance of the 240°C-aged alloy after anodizing at 12 V (SCE) for 1 coulomb of charge passed is 79%, close to that of the alloy with the mirror finished surface (83%), confirming that the typical porous anodic film is nearly transparent to the incident light and little incident light is absorbed. However, the integrated total reflectance of the 240°C-aged alloy after anodizing at 1.5 V (SCE) for 1 coulomb of charge passed is only 28%.

| Specimen | Mirror finished | 240°C/12 V anodized | 240°C/2.5 V anodized | 240°C/1.5 V anodized | 240°C/0.5 V anodized | 300°C/1.5 V anodized | T6/1.5 V anodized | 400°C/1.5 V anodized |
|----------|----------------|---------------------|---------------------|---------------------|---------------------|---------------------|-------------------|---------------------|
| Appearance | Normal | Normal | Discolored | Discolored | Discolored | Discolored | Normal | Normal |
| Integrated total reflectance (%) | 83 | 79 | 49 | 28 | 23 | 32 | 66 | 75 |
suggesting that significant amount of incident light has been absorbed by the anodic film. In fact, as shown in Table I, the integrated total reflectances of all specimens with discolored appearances are much smaller than that of the mirror finished specimen, suggesting that the discolored appearance is directly related with the total reflectance of the filmed alloy. Since the normal porous anodic alumina film is almost transparent to the incident light, the decreased total reflectance (or increased light absorption) of the anodized alloy surfaces with discolored appearances should be mainly ascribed to the structural and compositional variation in the anodic films due to the selective oxidation of $\beta'(\text{Mg}_2\text{Si})$ precipitates. Typical porous anodic alumina film can be regarded as a binary phase consisting of alumina and air. Therefore, the presence of voids in the porous anodic alumina film should not evidently change the transparent nature of the anodic film. Thus, it is believed that the incorporated silicon in the porous anodic film is largely responsible for the decreased total reflectance (or increased light absorption) of the anodized alloy surfaces with discolored appearances.

Now it is clear that the preferential oxidation of $\beta'(\text{Mg}_2\text{Si})$ could lead to two consequences that both affect the appearance of the filmed alloy: one is the roughened alloy/film interface, which reduces the surface gloss (or specular reflectance) of the filmed alloy by scattering, trapping and multiply reflecting the incident light; the other is the incorporated silicon in the porous anodic film, which increases light absorption of the anodic films. The absorption coefficient or extinction coefficient of silicon is larger than these of alumina and silicon dioxide, which are approximately zero, within the wavelength of visible light. Therefore, the discoloration of the anodized alloys is the accumulative effect of the two factors. It is difficult to quantitatively determine the contribution of each factor to the discolored appearance since these two factors either go together or interconnect with each other (e.g. trapping and multiple reflecting of incident light can lead to multiple absorptions).

Conclusions

The discoloration of anodized AA6063 aluminum alloy is related to preferential oxidation of coarsened $\beta'(\text{Mg}_2\text{Si})$ precipitates at low voltages. The minimum size of $\beta'(\text{Mg}_2\text{Si})$ precipitates that may cause discoloration of the anodized alloy is approximately 200 nm. The coarsened $\beta'(\text{Mg}_2\text{Si})$ precipitates could be preferentially oxidized in the voltage range of 0–3.0 V (SCE) during anodizing of the AA6063 aluminum alloy in 2M sulfuric acid at 20$^\circ$C. Preferential oxidation of $\beta'(\text{Mg}_2\text{Si})$ phase at low anodizing voltages proceeded through selective oxidation of magnesium, resulting in the development of a rough alloy/film interface and the incorporation of silicon in the porous anodic film. The roughened alloy/film interface decreases the surface gloss (or specular reflectance) of the anodized alloy by trapping and multiple reflecting of incident light; while the incorporated silicon in the porous anodic film led to reduced total reflectance due to the increased light absorption of the anodic film. It is believed that both the roughened alloy/film interface and incorporated silicon in the porous anodic film contributed to the discoloration of the anodized alloys. Normal appearance can be achieved when the alloys were anodized at 12 V (SCE) that would normally be employed on the production line.

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