Hard Anodizing Behavior of Aluminum Alloy DTD 5124 Containing Varying Amounts of Impurities Under Different Electrolytic Conditions

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The influence of various additives in hard-anodizing electrolytes to counteract the detrimental behavior of Al_{12} (FeMn)₃Si particles in aluminum alloy DTD 5124 has been investigated. Studies reveal that the addition of a small amount of hydrochloric acid, nitric acid or ammonium nitrate in sulfuric or sulfuric-oxalic acid electrolyte is capable of counteracting the inhibition of hard-anodic film growth resulting from the presence of constituent particles of impurities. The small amounts of these additives enables the electrolyte to dissolve the constituent Al_{12} (FeMn)₃Si particles during film growth. The optimum concentration of additives and other hard anodizing parameters have been evaluated.

DTD 5124 alloy is a high-strength aluminum alloy used for making a wide variety of structural components for spacecraft, rockets, aircraft and armaments. Aluminum anodization has immense technological importance. Hard anodizing is a prime requirement for improving abrasion resistance on sliding surfaces and preventing cold welding in space conditions.^{1,2} A hard anodic film provides an excellent base for dry lubricants. An anodic film is an oxide coating that imparts excellent heat resistance and electrical insulation properties.^{3,4} The infrared emissivity of a thick, hard anodic film is about 90 percent of that of a black body, providing excellent heat radiation characteristics to a surface.⁵

The quality of an anodic film depends on the chemistry and metallurgical history of the alloy treated.⁵⁻⁸ In our earlier communication,⁹ the influence of iron-rich constituent particles on the hard-anodizing behavior of aluminum alloy 7075 was investigated. It was established that both the chemistry and mode of distribution of constituent intermetallic particles are important in determining the nature and

growth of an anodic film. The iron-rich Al₁₂(FeMn)₃Si intermetallic particles survive during electrolysis in the conventional hardanodizing electrolytes. The presence of constituent intermetallics in the growth direction of an anodic film inhibits the further growth of the film. This results in a steep rise in bath voltage; consequently, the coating formed is defective, with a non-uniform, burned appearance. The degree of defects depends on the level of impurities, particle size and their orientation to the direction of film growth.

The present studies were undertaken to investigate the influence of some potential additives in hard-anodizing electrolytes to counteract the detrimental behavior of impurities. The studies were aimed at resolving an industrial problem where the specified hard anodic film thickness (80-85 μ m) could not be formed successfully on a particular supply of DTD 5124 alloy.

Experimental Procedure

Experiments were conducted on samples of DTD 5124 alloy with two different levels of impurities. Alloy 1 contained 0.12 Fe, 0.05 Si and 0.04 Mn percent by weight, and Alloy 2, 0.25 Fe, 0.27 Si and 0.25 Mn percent by weight. The specification and chemical composition of Alloys 1 and 2 are listed in Table 1.

The components of interest having a rectangular fin geometry (approx. 80 x 20 x 8 mm) were machined from a longitudinal section of round bar extrusion, where the broad surface of the fins are parallel to the extrusion direction. To examine the influence of variation in the direction of alignment of the Fe-bearing particles on the formation of a hard anodic coating, components of identical geometry were machined from the transverse section of the extrusion, where the broad surface of the fins is normal to the extrusion direction. The extrusion bar representing the sectioning pattern of the sample components is shown in Fig. 1. The longitudinal and transverse sections are labeled as LS and TS, respectively.



Fig. 1—*Extrusion bar representing sectioning pattern for fabrication of samples.*



Fig. 2—*Bath voltage-time profile for Alloys 1 and 2 samples in conventional sulfuric acid electrolyte. LS: longitudinal section. TS: transverse section.*



Fig. 3—Scanning electron micrographs: (a) cross section of Alloy 1; (b) cross section of Alloy 2.

The samples were processed for hard anodizing as follows:

- 1. Ultrasonic degreasing for 3-5 min in trichloroethylene.
- Alkaline cleaning at 60 ±5 °C for 2-3 min in a solution of sodium hydroxide, 100 g/L; sodium bifluoride, 20 g/L; and trisodium orthophosphate, 2 g/L. Water rinse.
- 3. Desmutting in nitric acid (70%) solution, 350-500 mL/L for 2-3 min. Water rinse.
- 4. Hard-anodizing in the electrolytes formulated and operated as follows:

Sulfuric acid (sp. gr. 1.84)	90 mL/L
Addition agent	
Hydrochloric acid (36% V/V)	3-6 mL/L or
Nitric acid (69% V/V)	5-20 mL/L or
Ammonium nitrate	20-40 g/L
Cathode	lead or carbon
Bath temperature	-5 to +1 °C
Current density	18-36 A/ft ²
Coating thickness	80-85 µm
Post treatment	water rinse

5. Sealing of the anodic film pores in a solution containing ammonium acetate (1 g/L) operating at pH 6.5-7.0 and temperature > 98 °C for two hr. Water rinsing and drying in air.

The thickness of the anodic film was measured and microhardness was evaluated with a microhardness tester using a diamond indenter. Vickers hardness numbers were obtained by averaging five measurements on each specimen with a load of 100 g. Optical properties, namely, solar absorbance and infrared emittance of the coatings were measured using a solar reflectometer and an emissometer. Both instruments provide an average value of solar absorbance and infrared emittance digitally, over the entire solar or infrared region.

Table 1 Chemical Composition of DTD 5124 Alloy				
Element	~			
% by weight	Specification	Alloy 1	Alloy 2	
Zn	5.1-6.4	5.6	5.6	
Mg	2.1-2.5	2.5	2.5	
Cu	1.2-1.5	1.4	1.4	
Cr	0.1-0.25	0.18	0.20	
Fe	0.5 max.	0.12	0.25	
Si	0.4 max.	0.05	0.27	
Mn	0.2 max.	0.04	0.25	
Ti + Zr	0.2 max.	0.06	0.11	
Al	Balance	Balance	Balance	



Fig. 4—*Scanning electron micrographs: (a) longitudinal and (b) transverse sections of Alloy 2.*

Scanning electron micrographs were obtained on an SCM operating at 20 kv. The samples for SEM studies were prepared by conventional metallographic techniques under unetched conditions.

Results and Discussion

While hard anodizing DTD 5124 alloy components in conventional sulfuric or sulfuric-oxalic acid electrolytes within the chosen experimental operating range, it was established that the required coating thickness of 80-85 μ m can be obtained with a maximum potential of 85 V. Edge burring of fin structure components was observed when anodization continued beyond 90 V. As a result, the present studies on hard anodization were confined to a terminal bath voltage ≤ 85 .

The bath voltage-time profile of components machined from longitudinal and transverse sections of Alloys 1 and 2 are shown in Fig. 2. Alloy 1 components, irrespective of the direction of machining, show a steady increase in bath voltage. The required coating thickness ($80-85 \ \mu m$) is obtained in 120 min, within a maximum potential of 83 V, while for Alloy 2 components fabricated from a longitudinal section of the extrusion bar, a steep rise in bath voltage is observed. The cut-off potential ($85 \ V$) is attained in about 70 min, with the coating thickness in the range of $45-50 \ \mu m$. The bath voltage-time curve for transverse section components of Alloy 2, however, shows a profile more or less similar to that observed for Alloy 1. The specified film thickness is attained within the terminal potential of $85 \ V$.

Scanning electron micrographs of the cross sections of Alloys 1 and 2 are shown in Fig. 3. The photomicrograph of Alloy 1 shows continuous film growth, while the continuity of the film is greatly disturbed in the case of Alloy 2.

The scanning electron micrograph of the longitudinal section of Alloy 2 shows the presence of stringers (*i.e.*, rows of constituent intermetallics [Fig. 4a]). These stringers are formed as a result of break-up of the constituent particles during mechanical working along the extrusion direction. In transverse section, the stringers are viewed end-on and appear as non-uniformly distributed small particles across the extruded section (Fig. 4b).

Elemental X-ray mapping showed the presence of highdensity, iron-rich Al₁₂(FeMn)₃Si particles in Alloy 2.⁹ The nucleation and growth of anodic oxide films is locally inhibited when the iron-rich particles are present in the direction of film growth.⁶⁻¹² The rapid increase in bath voltage during anodization of longitudinal section components of Alloy 2 results from survival of these constituent particles. These particles become an integral part of the anodic film, adding additional resistance in the electrical path for film growth.



Fig. 5-Effect of addition of hydrochloric acid (36% V/V) on bath voltage.



Fig. 6-Effect of addition of nitric acid (69% V/V) on bath voltage.



Fig. 7-Effect of addition of ammonium nitrate on bath voltage.

The difference in the bath voltage-time profile of the alloy components machined from longitudinal and transverse sections of Alloy 2 is directly related to the difference in orientation of the Al_{12} (FeMn)₃Si stringer particles with respect to the growth direction of the anodic oxide film. In a given anodizing time, the growth front of the anodized layer encounters a much greater number of particles when the growth direction of alignment of the stringers (longitudinal section). The reverse is the case when the stringers are oriented parallel to the growth direction of film (transverse section).

Detailed characterization of the anodic film and bath voltage-time profile for Alloy 2 reveal conclusively that the steep increase in bath voltage with time, during hard anodization, is a result of the survival of Al_{12} (FeMn)₃Si particles.⁹ Attempts were made, therefore, to develop a suitable electrolyte system that can counteract the deleterious effect of these stringer particles by dissolving them during anodization. Additions of small amounts of hydrochloric acid, nitric acid or ammonium nitrate to the sulfuric acid electrolyte were made to determine their effect on the hardanodizing behavior of the alloy under investigation.

Effect of Additives

The influence of the addition of hydrochloric acid, nitric acid and ammonium nitrate on the bath voltage is shown in Figs. 5, 6 and 7, respectively. As evident from the figures, a significant drop in electrolyte voltage was achieved with the addition of these additives. The optimum concentration of different additives for obtaining the required film thickness within the terminal potential of 85 V is as follows:

Hydrochloric acid (36% V/V)	4.0 mL/L
Nitric acid (69% V/V)	7.5 mL/L
Ammonium nitrate	30.0 g/L

Although a further drop in bath voltage was achieved by increasing the amounts of these additives, a significant reduction in the rate of film growth and microhardness was observed. The latter resulted from rapid increase in the dissolution rate of the anodic film in the modified electrolytes. The coatings become rough and somewhat powdery when the concentration of additives exceeds the selected experimental ranges. In general, because of lower solvent action of the electrolyte, relatively higher coating thicknesses were obtained with the addition of ammonium nitrate; however, the microhardness of the coatings was distinctly lower than those obtained with the addition of hydrochloric or nitric acid.

Table 2 Effect of Addition Agents

Concentration of additive	Terminating voltage	Coating thickness, μm	Microhardness (VHN)	
Addition of hyd	rochloric acid (3	36% V/V)		
3 mL/L	78.4	84	380	
4 mL/L	68.0	82	378	
5 mL/L	62.7	78	364	
6 mL/L	60.0	71	358	
Addition of nitr	ic acid (69% V/	V)		
7.5 mL/L	84.2	82	374	
10 mL/L	74.6	77	370	
15 mL/L	67.2	72	364	
20 mL/L	58.5	64	348	
Addition of am	nonium nitrate			
20 g/L	84.1	86	316	
30 g/L	76.8	88	308	
40 g/L	68.0	82	300	
Current density,	18 A/Ft ² Time,	2 hr		

Effect of Applied Current Density

The higher applied current densities in hard anodization result in a higher rate of film growth and improved microhardness of the resulting coating. For difficult alloys, where the stringer intermetallic particles hinder the formation of an anodic film, it is imperative to employ lower current densities. This provides sufficient time for the electrolyte to dissolve the stringer particles at the time of film formation, leading to continuous film growth.

The micrograph of the cross section of a hard-anodized sample of Alloy 2 in sulfuric/hydrochloric acid electrolyte at an applied current density of 25 A/ft² showed gaps in the anodic film (Fig. 8). These gaps correspond to the size of the

 Al_{12} (FeMn)₃Si particles. The coatings obtained at a current density of 18 A/ft² have not shown such gaps. This implies that the time taken for dissolution of stringer particles is not the same as the rate of film formation; consequently, the aluminum matrix surrounding the particles is anodized faster, leaving behind the region occupied by the particles. The



Fig. 8—Scanning electron micrograph of cross section of Alloy 2 sample hard anodized in sulfuric acid. Current density, 25 A/ft².

particles eventually dissolve in the electrolyte, leaving gaps in the anodic film.

These studies suggest that the larger the size of constituent Fe-bearing particles, the lower should be the applied current density for hard anodization. It is necessary, however, to compromise between optimum applied current density to sustain continuous film growth and microhardness of the coating. This is exactly the reason why the lower current density of 18 A/ft^2 was selected.

Effect of Sealing

Sealing is done to close the pores of an anodic oxide film. Sealing produces a chemical change in the coating by converting it from simple aluminum oxide, Al_2O_3 , to stable boehmite structure, $Al_2O_3 \cdot H_2O$. In the course of this change, the coating swells and the pores are closed. The sealed anodic film provides greater corrosion resistance than an unsealed coating. For application where corrosion resistance and thermo-optical properties are of prime importance, it may be prudent to forego higher hardness.

Sealing of the hard anodic coatings was carried out in oneg/L ammonium acetate solution (pH 6.5-7.0), operating above 98 °C for one hr. Sealing results in a drop in film microhardness, the magnitude of the drop depends on the nature of the electrolyte used for hard anodization. The hard anodic films obtained in modified electrolyte systems result in comparatively higher drop in microhardness values after sealing than those obtained in sulfuric acid electrolyte. This is primarily attributed to the higher dissolution rate of the anodic film in modified electrolytes, which leads to the formation of higher porosity coatings. The drop in microhardness of hard anodic film obtained under different electrolytic formulations after sealing is in the following order: sulfuric acid < sulfuric acidammonium nitrate < sulfuric acid-nitric acid < sulfuric acidhydrochloric acid. Although insignificant, a small drop in both solar absorbance and infrared emittance values of anodic films was observed after sealing.

Table 3 Properties of Hard-anodic Oxide Coatings							
Proper cres or nard-anour oxide coactings							
	Film	Microhardness (VHN)		Solar absorbance		Infrared emittance	
Electrolyte	thickness, µm	1	2	1	2	1	2
H,SO	45-50	440	416	0.82	0.83	0.85	0.85
2 4		(425)	(385)	(0.82)	(0.83)	(0.84)	(0.83)
	80-85	430	—	0.89	—	0.88	—
		(400)	—	(0.88)	—	(0.88)	—
$^{4}\mathrm{H}_{2}\mathrm{SO}_{4}$ -(COOH) $_{2}$ ·H $_{2}\mathrm{O}$	47–52	448	419	0.83	0.84	0.86	0.86
		(428)	(386)	(0.82)	(0.82)	(0.85)	(0.84)
	80-85	438	—	0.90	—	0.88	—
		(403)	—	(0.89)	—	(0.87)	—
H ₂ SO ₄ -HCl	80-85	406	400	0.92	0.91	0.89	0.88
		(368)	(362)	(0.91)	(0.91)	(0.88)	(0.88)
H,SO ₄ -HNO ₃	80-85	410	402	0.91	0.92	0.89	0.89
2.0		(370)	(362)	(0.90)	(0.90)	(0.88)	(0.87)
H ₂ SO ₄ -(NH ₄),NO ₃	80-85	348	358	0.91	0.92	0.88	0.89
2		(310)	(308)	(0.90)	(0.90)	(0.87)	(0.88)

1: Alloy 1. 2: Alloy 2

Values in parentheses were obtained after sealing of anodic film. * Values from reference 9.

Environmental Stability

To evaluate the performance of hard anodic films during preand post-launch environments, the test coupons were subjected to humidity, thermal cycling and thermal-vacuum performance tests.

The humidity test was carried out to examine the resistance of anodic coatings to corrosive pre-launch atmospheres. The test was conducted in a thermostatically controlled humidity chamber. The relative humidity in the chamber was maintained at 95 \pm 0.5 percent at 50 °C, and the test was conducted for 96 hr.

A thermal cycling test, designed to evaluate the effect of inorbit cycling temperature likely to be encountered throughout the life span of spacecraft, was carried out in a thermostatically controlled hot and cold chamber. A total of 100 cycles was applied. A cycle consists of lowering the temperature to -100 °C for five min, then raising it to 100 °C for five min.

To examine the effect of temperature cycling on the anodic film in vacuum (space environment), a thermal-vacuum test was performed in a thermostatically controlled high-vacuum chamber. The test consisted of lowering the temperature to -100 °C for two hr and raising it to 100 °C for two hr. A total of 10 cycles of hot and cold soak was applied. A vacuum level of better than 10^{-5} torr was maintained inside the chamber throughout the test.

After humidity, thermal cycling and thermal-vacuum performance tests, the coatings were examined visually for any degradation and their optical properties were measured. The hard anodic coatings obtained with all the electrolyte compositions under investigation passed the above environmental tests without degradation in physical appearance and optical properties. These results are indicative of excellent environmental stability of the coatings for ground as well as space applications.

Measurement of Optical Properties

In the absence of an atmosphere, heat exchange in space is limited to radiation. The equilibrium temperature of any subsystem of spacecraft is controlled by the ratio of solar absorbance to infrared emittance of its surfaces. Hard anodic oxide film acts as an excellent thermal control surface. At a thickness of 80-85 μ m, hard anodic film provides high solar absorbance and thermal emittance values. This helps in improving the heat radiation characteristics of the surfaces of the components and minimizes the temperature gradient across the packages.

The physico-optical properties of hard anodic oxide film obtained in different electrolytic compositions are listed in Table 3. The optical properties of an anodic film are controlled by the coating thickness and surface characteristics. Initially, as the anodic film grows, both the solar absorbance and infrared emittance values increase sharply with the increase in film thickness. At a later stage, however, this trend slows. At about 70 μ m thickness, an anodic film attains almost constant absorbance and emittance characteristics. At the specified film thickness of 80-85 μ m, the solar absorbance and infrared emittance values of anodic coating were found to be on the order of 0.90 and 0.88, respectively, regardless of the electrolyte employed.

Conclusions

1. The presence of iron-rich constituent particles is detrimental to the growth of anodic oxide films. These particles survive during the hard-anodizing process and locally inhibit the growth of film. The added electrical resistance, because of the presence of stringer particles, results in a steep rise in bath voltage; consequently, the anodic films formed are defective.

- 2. The deleterious effect of stringer particles is influenced by their orientation, with respect to growth direction of anodic film. A much greater number of stringer particles is encountered when they are aligned normal to the growth direction of the anodic film.
- 3. The difficult alloys containing iron-rich stringer particles can be successfully hard-anodized in modified strongelectrolyte systems (*e.g.*, with small additions of hydrochloric acid, nitric acid, ammonium nitrate in sulfuric acid or sulfuric acid-oxalic acid electrolytes). The modified electrolytes dissolve the stringer particles during anodization, providing a continuous film growth. The optimum concentration of the electrolyte additives has been investigated.

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