Performance Results for Sealed Type III Anodic Oxides

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Type III anodized aluminum is used for applications where superior hardness and wear resistance are required. In recent years there has been an expanded interest in improving the corrosion resistance and appearance of Type III anodized aluminum using sealing and dyeing processes. In this study, Type III anodized aluminum was dyed and sealed using numerous post treatment processes. The quality of the oxide was evaluated by a variety of physical tests, such as microhardness, wear resistance, corrosion resistance, and dielectric strength. The effects of the various post treatment processes on the resultant anodic oxide are discussed.

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Introduction

Hard coat (Type III) anodizing utilizes low anodizing bath temperatures (0•C) and high current densities to produce a dense anodic oxide that is used by the automotive, military, aerospace and other industries for applications where superior hardness and wear resistance are required. In recent years there has been an expanded interest in sealing and dyeing Type III anodized aluminum in order to improve the corrosion resistance and appearance of the oxide.^{1,2} However, Type III oxides are typically used without any post treatment since it is generally believed that dyeing or sealing the anodic oxide will reduce the abrasion resistance and hardness of the oxide.^{3,4} Several studies have investigated the effect of sealing and dyeing on the wear resistance of the anodic oxide.5-However, the data reported is somewhat limited and the results of different studies are contradictory.

This study was designed to investigate performance characteristics of Type III anodized 6061-T6 aluminum with eight different post treatment processes. The corrosion resistance was measured using the salt spray procedure described in ASTM B 117 in order to determine the effectiveness of each sealing method. Both wear resistance and hardness data were obtained to quantitate the adverse effect of each post treatment process. Breakdown voltages were measured to determine the effect of each seal process on the electrical properties of the sealed anodic oxide.

The post treatment processes used include a hot DI water seal where the anhydrous oxide (Al_2O_3) is hydrated to form boehmite-like $(Al_2O_3 \cdot H_2O)$ crystals.³ Boehmite has a larger volume than aluminum oxide so the pores are closed by the expansion of the cell walls. Seal times of both 30 minutes and 2 hours were examined since the time in the hot DI seal should be 1 hour per mil of oxide.³ However, spending 2 hours in a seal tank is costly, so many job shops prefer a shorter seal time. Determining the performance characteristics for both seal times will provide anodizers valuable information on whether a suitable finish can be obtained with the shorter seal time.

A mid-temperature nickel acetate seal was also used in this study. The mechanism of nickel

acetate sealing is similar to hot water sealing in that hydrated aluminum oxide is formed which closes the pores due to its increased volume. In addition, nickel hydroxide $(Ni(OH)_2)$ coprecipitates in the pores and the nickel ions play a catalytic role in hydrating aluminum oxide to the boehmite-like structure.^{9,10} Many job shops prefer to use a mid-temperature nickel acetate seal over a hot DI seal because it operates at a lower temperature and the nickel ions help to set the dye which can decrease bleed-out of the dye and improve light fastness.³

The other sealing processes used in this study include: sodium dichromate, sodium silicate, and nickel fluoride. In each of these processes, a precipitate forms to fill or plug the pores. Aluminum oxydichromate $(AlOHCrO_4)^{11}$ is formed in the case of sodium dichromate sealing. Evidence suggests that this precipitate does not completely fill the pores, but that increased corrosion resistance may be due to the corrosion inhibiting effect of Cr(VI).¹² Sodium silicate sealing involves physically plugging the pores by the formation of aluminum silicate.^{13,14} Cold nickel fluoride sealing involves the coprecipiation of aluminum fluoride (AlF₂), nickel hydroxide (Ni(OH)), and aluminum hydroxide (Al(OH₂) in hydrated forms which plug the top three to four microns of the anodic oxide.¹⁵ The initial pore plugging is followed by an aging process in which the precipitates and the water in the pores promote further hydration of the anodic film.

In addition to the sealing processes mentioned above, parts were also dyed and dyed then sealed with a mid-temperature nickel acetate solution to determine the effects of the dyeing process on corrosion resistance, wear resistance, hardness, and breakdown voltage. Unsealed parts were tested for comparative purposes.

Experimental Procedure

Material

6061-T6 coupons were used for all experiments with dimensions of 10.15 x 10.15 x 0.12 cm.

Post Treatment	Chemical and Concentration	pН	Temperature	Immersion		
			(•L)	time (min.)		
DI water seal	DI water 6.0		100	30		
(30 minutes)	and					
	1 g/L ammonium acetate					
DI water seal	DI water	6.0	100	120		
(120 minutes)	and					
	1 g/L ammonium acetate					
Nickel acetate seal	4% Anoseal 1000*	5.8	88	20		
Sodium	5 wt% sodium dichromate	6.0	95	15		
dichromate seal						
Sodium silicate	20% Sodium silicate solution	11.2	85	10		
seal	(41 •Bé water glass)					
Nickel fluoride	3.5% Anoseal 2020*	5.8	32	10		
seal						
Black dye	10 g/L Specialty Black BK Super**	5.0	60	20		
Black dye and	10 g/L Specialty Black BK Super**	5.0	60	20		
nickel acetate seal	and					
	4% Anoseal 1000*	5.8	88	20		

Table 1Post Treatment Processes

* Henkel Surface Technologies

** US Specialty Corporation (metal complex dyestuff)

Pretreatment

The coupons were cleaned in an inhibited alkaline solution at 62 •C for 5 minutes, rinsed in flowing tap water for 1 minute, deoxidized in a mixed acid solution at room temperature for 2 minutes, and rinsed in flowing tap water.

Anodizing

The coupons were anodized to ~50 μ m (2 mils) at a current density of 3.23 A/dm² (30 /ft²) in an electrolyte consisting of 190 g/L sulfuric acid and 6 g/L Al³⁺ ions at 0 •C.

Post treatment

The anodized coupons were rinsed in flowing tap water for 1 minute and room temperature deionized water for 1 minute. The parameters of the various post treatment processes are listed in Table 1. All dyeing and sealing solutions were prepared with deionized water. After sealing and rinsing, all the coupons were dried with oil-free pressurized air. The resultant coating thickness was measured in accordance with ASTM B 244 using a precalibrated eddy current instrument. All coupons had an oxide thickness of $50 \pm 5 \mu m$.

Corrosion resistance

Corrosion resistance testing was performed on four coupons for each post treatment process using the method described in ASTM B 117.

A failure occurred when test specimens showed more than 5 pits in a total of 387 cm^2 (30 in²) from one or more test pieces as stated in MIL-A-8625F.

Wear resistance

Wear resistance testing was performed on eight coupons for each post treatment process using a Taber abrasion instrument in accordance with FED-STD-141, Method 6192, using CS-17 wheels, a load of 1000 grams, and a speed of 70 rpm for 10,000 revolutions. The CS-17 wheels were resurfaced after every 10,000 revolutions by running them for 50 revolutions over S-11 abrasive discs. The temperature was 23 ± 2 •C and the relative humidity was $22 \pm 3\%$.

The wear resistance was measured on both sides of each coupon. Each coupon was conditioned in a dessicator for 48 hours, placed in the weighing environment for 30 minutes, weighed with an analytical balance to an accuracy of 0.1 mg, abraded, placed in the weighing environment for 30 minutes, and reweighed.

Microhardness

Vickers microhardness testing was performed on two coupons for each post treatment process in accordance with ASTM E 384. A Vickers indentor was used with a 0.050 kgf load. Three measurements were taken on a cross section of each coupon.

Dielectric strength

Voltage breakdown testing was performed on two coupons for each post treatment process using the methods described in ISO 2376 with a single ball electrode and a 500 g load. The voltage was increased 25 V/s with breakdown defined as passing 10 μ A current. The parts were cured at ambient conditions for > 48 hours prior to testing. Tests were performed at 74 •F and 24% relative humidity. Ten measurements were made per coupon.

Results and Discussion

Corrosion resistance

COLLOSION RESISTANCE RESULTS				
Post Treatment	Hours at			
	Failure*			
Black dye	21			
Black dye and	23			
Nickel acetate seal				
No dye or seal	43			
Nickel fluoride seal	70			
DI water seal (120 min.)	327			
DI water seal (30 min.)	374			
Nickel acetate seal	495			
Sodium dichromate seal	1578			
Sodium silicate seal	1578			

Table 2 Corrosion Resistance Results

*failure occurred when there was 5 pits in 387 cm^2

The corrosion resistance results are reported in Table 2 for all samples. The unsealed parts failed on the second day of testing. Both sets of parts that were dyed failed during the first day of testing, even when the parts were sealed in nickel acetate. Parts sealed with nickel fluoride failed at 70 hours. Both sets of parts sealed in hot DI water failed between 300 and 400 hours. Parts sealed in nickel acetate failed at 495 hours. The best performance was observed for parts sealed in sodium dichromate and sodium silicate. Both processes produced parts that exceeded 1500 hours.

The corrosion resistance of all these Type III parts was much lower than expected. Previous studies of Type II anodic coatings report unsealed 6061 parts to exceed 5500 hours before failure and those sealed in nickel acetate to exceed 4000 hours.¹⁶ Since the corrosion performance of all the Type III anodized parts was relatively poor, the source of corrosion may be due to crazing. Wernick, Pinner and Sheasby observed that hardcoated material is much more prone to crazing than Type II anodic oxides.³ Fissures and voids can form when the parts are transferred from the $0 \cdot C$ anodizing tank to a room temperature rinse tank. These fissures and voids may be too large to be properly sealed with the processes used in this study.

In addition, 6061-T6 alloy may be particularly susceptible to crazing since the voltage climbs dramatically, under constant current anodizing conditions, after ~38 μ m (1.5 mil) of oxide has formed. In this case, the final voltage was 75 V, the maximum rectifier voltage. A very thick barrier layer is formed at this point, since the thickness of the barrier layer is dependent on the final voltage, which may be prone to fracturing when the part is transferred from the 0 •C anodizing tank to a 25 •C rinse tank and then to an even warmer seal tank.

Further studies need to be performed to determine if the Type III anodic oxide of 6061–T6 material is indeed crazed when run under these anodizing conditions and to determine the source of the crazing.

Wear resistance

The results reported in Table 3 are an average of 16 measurements taken on both sides of 8 coupons. MIL-A-8625F states that a Type III anodic oxide have a maximum weight loss of 15 mg/10,000 revolutions. The unsealed oxide had a wear resistance of 8.4 mg/10,000 which passes the MIL-A-8625F specification.

Wear Resistance Results				
Post Treatment	Wear Resistance (mg/10,000 revolutions)*			
No dye or seal	8.4 (2.3)			
Sodium silicate seal	9.2 (2.0)			
Sodium dichromate seal	9.8 (3.7)			
Nickel fluoride seal	11.5 (2.5)			
Black dye	11.8 (3.9)			
DI water seal (30 min.)	13.9 (3.5)			
Nickel acetate seal	15.0 (4.4)			
Black dye and	17.7 (3.8)			
nickel acetate seal				
DI water seal (2 hours)	19.8 (6.5)			

Table 3Wear Resistance Results

*the numbers in parentheses are the standard deviations

The wear resistance decreased for all the post treatment process used in this study. However, those processes that sealed the pores by hydrating the aluminum oxide to the softer boehmite-like complex showed the largest weight loss. These processes include: hot DI water seal, nickel acetate seal, and black dye with nickel acetate seal. Using a hot DI seal for 2 hours instead of 30 minutes increased the weight loss by 42%.

Those processes that plug the pores with a precipitate of some form, like sodium silicate, sodium dichromate and nickel fluoride sealing, had a weight loss that still passed the MIL-A-8625F specification.

Microhardness

The Vickers microhardness results are reported in Table 4. The data range from 357 to 403 H_v for all the samples. The variation is wellwithin the repeatability of the test method. A correlation of microhardness test data between laboratories is reported as an Appendix in the ASTM E 384 specification. The results of the study state that the repeatability, differences due to test error between two test results in the same laboratory on the same material, is \pm 65 H_v for nonferrous samples with a load of 50 gf and a Vickers hardness of 375 H_v. The reproducibility, differences in test results for the same material in different laboratories, is \pm 75 H_v for nonferrous samples with a load of 50 gf and a Vickers hardness of 375 H_v.

Table 4Microhardness Results

Post Treatment	Vickers	
	Microhardness	
	(H _v)*	
No dye or seal	357(7)	
No dye or seal	382(5)	
Nickel acetate seal	372(4)	
Nickel acetate seal	383(7)	
Sodium silicate seal	376(2)	
Sodium silicate seal	390(4)	
DI water seal (30 min.)	369(2)	
DI water seal (30 min.)	380(8)	
Sodium dichromate seal	358(4)	
Sodium dichromate seal	360(6)	
Black dye	360(6)	
Black dye	378(14)	
Black dye and	403(4)	
Nickel acetate seal		
Black dye and	393(6)	
Nickel acetate seal		
Nickel fluoride seal	365(4)	
Nickel fluoride seal	359(1)	

* average of three measurements; the numbers in parentheses are the standard deviations

No differences in Vickers microhardness were observed in this study between unsealed and sealed samples since the range of the data is well within the error of the test method. Data reported for 5052-H4 also showed no differences in microhardness between sealed and unsealed samples.⁶

The wear resistance data showed large differences for the various post treatment processes (see Table 3), yet the microhardness data for the various processes was all within the error of the test method. This points to a common misnomer in the anodizing industry. Wear resistance is not necessarily correlated with hardness. Wear resistance and hardness are two different physical characteristics. Wear resistance, as measured by Taber abrasion method, is the measurement of the weight loss of the surface of the oxide as an abrasive wheel is rolled over the surface. In this study, the average wear was 3 microns. It is understandable that the wear resistance of the hydrothermal post treatment processes in this study is lower than an unsealed oxide since the softer boehmite-like structure is prevalent at the surface of the anodic oxide.3

Di cunto vin Voltage Results						
Post Treatment	Oxide Thickness	Breakdown	Breakdown			
	(µm)*	voltage	voltage per			
		(kVDC)*	micron			
			(V/µm)**			
Sodium silicate seal	50.6(0.9)	0.96(0.08)	19.0(1.6)			
Sodium silicate seal	50.0(0.7)	0.94(0.06)	18.8(1.2)			
No dye or seal	50.3(1.0)	1.47(0.29)	29.2(5.8)			
No dye or seal	48.4(1.0)	1.37(0.15)	28.3(3.1)			
Nickel fluoride seal	50.3(2.0)	1.64(0.32)	32.6(6.5)			
Nickel fluoride seal	49.1(1.1)	1.44(0.14)	29.3(2.9)			
Nickel acetate seal	50.8(0.8)	1.69(0.09)	33.3(1.8)			
Nickel acetate seal	49.6(0.8)	1.57(0.15)	31.7(3.1)			
Black dye and Nickel acetate seal	49.8(0.8)	1.76(0.14)	35.3(2.9)			
Black dye and Nickel acetate seal	51.6(0.9)	1.76(0.14)	34.1(2.8)			
Sodium dichromate seal	49.5(0.9)	1.73(0.13)	34.9(2.7)			
Sodium dichromate seal	52.1(1.1)	1.88(0.10)	36.1(2.1)			
Black dye	50.0(0.9)	1.72(0.23)	34.4(4.6)			
Black dye	50.0(1.0)	1.93(0.11)	38.6(2.3)			
DI water seal (2 hours)	49.7(0.9)	1.94(0.14)	39.0(2.9)			
DI water seal (2 hours)	49.6(0.8)	1.87(0.13)	37.7(2.7)			
DI water seal (30 min.)	49.4(0.8)	1.98(0.13)	40.0(2.7)			
DI water seal (30 min.)	50.7(0.9)	1.88(0.19)	37.0(3.8)			

Table 5Breakdown Voltage Results

*numbers in parentheses are the standard deviations

** numbesr in parentheses are the absolute uncertainties

On the other hand, microhardness measurements are obtained on a cross-section of the anodized part. The diagonal of the impression made by the indentor was between 15.1 and 16.1 microns for all the samples in this study, calculated by the following equation from ASTM E 384:

 $H_v = 1854.4 \text{ x } P_1/d_1^2$

where P_1 is the load (gf) and d_1 is the length of the long diagonal (μ m).

The indentation site for the microhardness measurements are typically chosen to be as close to the aluminum substrate as possible in order to test the most recently formed harder oxide. Yet, care must be taken not to indent the softer aluminum substrate. In this study, the anodic oxides produced were ~50 µm and the diagonal of the impression was ~16 µm. The indentations were made in the 25 microns (1 mil) of anodic oxide closest to the aluminum substrate. No differences were observed in microhardness between the various post treatment processes, indicating that the affects of the sealing processes may not progress to the oxide formed closest to the aluminum substrate. This hypothesis should be further tested with methods that can examine the chemical nature of the anodic oxide.

Breakdown Voltage

Breakdown voltage data are reported in Table 5. The breakdown voltage was measured in ten locations and the data averaged. Unsealed parts had a breakdown voltage of 29 V/ μ m. Sodium silicate sealing drastically reduced the breakdown voltage to 19 V/ μ m. All the other post treatment processes used in this study increased the observed breakdown voltage. Parts sealed in hot DI water had breakdown voltages close to 40 V/ μ m.

Conclusions

Type III 6061 parts exhibit poorer corrosion resistance than Type II 6061 parts.

Sodium dichromate and sodium silicate seals provide the best corrosion resistance for Type III anodized 6061 aluminum.

All post treatment processes used in this study decrease the wear resistance. However, the hydrothermal sealing processes showed the most degradation of the wear resistance. The best wear performance was observed for parts sealed with sodium silicate.

There were no variations observed in the Vickers microhardness data between sealed and unsealed samples.

Sodium silicate sealing drastically decreases the breakdown voltage of the anodic oxide.

Hot DI sealing significantly increases the breakdown voltage of the anodic oxide.

Corrosion resistance, breakdown voltage and microhardness data for parts sealed in Hot DI for 30 minutes versus 2 hours are similar. However, increasing the sealing time from 30 minutes to 2 hours decreased the wear resistance by 42%.

References

- 1. Mark Jozefowicz, Proc. IHAA 7th Annual Hard Anodizing Technical Symposium, (1998).
- Tina Gaddy, Proc. AESF, SUR/FIN '99, p. 209 (1999).
- S. Wernick, R. Pinner and P.G. Sheasby, *The Surface Treatment and Finishing of Aluminum and Its Alloys*, 5th ed., Vol. 2, Finishing Publications Ltd., Teddinton, England, 1996; p. 662-856.
- 4. A.W. Brace and P.G. Sheasby, *The Technology of Anodizing Aluminum*, 2nd ed., Technicopy Ltd., England, 1968; p. 217-238.
- 5. H.J. Gohausen, *Aluminum* **55**(8), 515 (1979).
- 6. Jean Rasmussen, Proc. IHAA 7th Annual Hard Anodizing Technical Symposium, (1998).
- Scott Olbrantz and Jean Rasmussen, Proc. AESF SUR/FIN '98, (1998).
- 8. B. Rachel Cheng and L. Hao, *Metal Finishing*, manuscript accepted for publication (2000).
- R. C. Spooner and W.J. Forsyth, *Plating*, 55(4), 336 (1968).

- 10. G.C. Wood and V.J. Marron, *Trans. Inst. Met. Finish.* **45**, 107 (1967).
- 11. N.D. Tomashov and A. Tyukina, *Light Metals*, **9**, 22 (1946).
- F. Mansfeld, C. Chen, C.B. Breslin, and D. Dull, J. Electrochem. Soc., 145(8), 2792 (1998).
- 13. L. Whitby, Metal Industry, 72, 400 (1948).
- 14. G.C. Wood, Trans. Inst. Met. Finish, 36, 220 (1959).
- 15. B. Yaffe, Met. Finish., 88(5), 41 (1990).
- T. Westre Corrosion Testing Results of MLT-II Anodized Aluminum METALAST Internal Report, METALAST International, Inc., Minden, NV 89423 (1999).

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