Depth Profile of the Wear Resistance of Anodic Coatings Formed by Current Control Anodizing on Aluminum Alloys

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This paper reports the depth profile of the wear resistance of anodic coatings produced by the latest computerized anodizing process with current density control on three commonly used aluminum alloys, 2024-T3, 6061-T6 and 7075-T6. The results showed that the wear resistance of the anodic coating on each alloy was virtually constant in depth profile, unlike Martin Hard Coating in which the wear resistance of outer layer coating is inferior to that of inner layer. All the anodic coatings showed a depth profile of wear resistance superior to both hard chrome plating and hardened carbon steel, although the wear resistance in the depth profile of the anodic coatings on the three alloys differed from each other.

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Introduction

Hard anodic coatings on aluminum are finding increasing applications in a variety of industries, in particular, transportation industries, where aluminum materials are heavily used to save energy and reduce pollutant emission while a hard durable surface is required to extend the service lives of the aluminum parts. The hardcoatings are generally produced by anodizing aluminum in sulfuric acid electrolytes at low temperature (0 °C) and relatively high current densities (> 2 A/dm^2). It has long been recognized that the hard anodic coats on aluminum offer high abrasion resistance^[1,2]</sup>. It was reported fifty years ago^[3] that a hard anodic coating, produced by the well-known Martin Hard Coat (M.H.C.) process on aluminum75S-T6, had the abrasion resistance even better than hard chrome plating and hardened carbon steels, as shown in Figure 1. Since then, the term "file-hard" coating has been widely used to qualitatively describe the abrasion resistance of the dense anodic coatings formed on aluminum at low temperatures and high current densities.



Figure 1 Comparison of wear resistance of M.H.C. hard coating with that of other materials

Anodizing technologies have advanced substantially over the decades. Traditional constant voltage control is being replaced by current density control, incorporated with various pulsing waveforms aiming modifying coating at properties. Computerized control processes have been developed to take over manual operation in order to improve the consistency of anodizing production. Proprietary additives are commonly used in hard anodizing. It is anticipated that the coating properties will be improved by technological advances. However, there was no updated data reported for the depth profile of wear resistance in the hard anodic coatings formed on aluminum after the 1950s. Coating properties vary with aluminum alloys, as well. Figure 1 only provided the depth profile of wear resistance in the anodic coating formed on one aluminum alloy, 75S-T6. This study examined improvements in the wear resistance of the anodic coatings produced with a new commercially available anodizing process versus the well-accepted M.H.C. process. In addition, the depth profiles of the wear resistance in the anodic coatings on different alloys were determined for a comparative study. The depth profile of wear resistance on an anodic coating can provide indirect information on the uniformity of the coating composition, structure and porosity.

There are many methods available for characterizing the wear behavior of materials, yet only a few of them are used in determining the wear resistance of anodic coatings. Abrasive wheel test (ISO 8251) and abrasive jet test (ISO 8252) are specified by ISO 10074 and BS 5599 and typically used for evaluation of the wear resistance of anodic coatings in Europe. Pin-on-Disk test (ASTM G 99-95a) is sometimes used in measuring the wear resistance of anodic coatings in some special cases. Although previous studies^[4-9] were favorable to abrasive wheel test in terms of reproducibility, it is believed^[1] that the measurements of wear resistance by abrasive wheels or abrasive jets may not be an accurate guide to the behavior of hard anodized surfaces when subjected to friction or movement in contact with other materials. For this reason, the

Taber wear test (FED-STD-141) is very popular and is predominantly used for determining the wear resistance of anodic coatings in the United States. Furthermore, Taber wear tests are the only method specified for wear resistance measurement in MIL-A-8625F, ASTM D 4060, AMS 2466, and AMS 2469E specifications. Accordingly, the Taber wear test was used in this study so that the results are comparative with those reported before^[3].

Experimental Procedure

Materials

2024-T3, 6061-T6 and 7075-T6 alloys (10.2 cm x 10.2 cm x 0.1 cm coupons) were used in this work.

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 acid solution at ambient temperature for 2 minutes, and rinsed in flowing tap water for 1 minute.

Anodizing

The coupons were anodized by a computerized control process to produce 2 mils of oxide coating at a current density of 3.24 A/dm² (30 A/ft²) in an electrolyte, consisting of 190 g/L H₂SO₄ + 6 g/L Al³⁺ + 9 g/L organic additives at 0 °C with air agitation. The anodized coupons were thoroughly rinsed in flowing tap water, then rinsed in deionized water for 2 minutes, and dried with oil-free pressurized air.

Taber test

Taber tests were performed on two coupons for each alloy using a Taber wear abraser in accordance with FED-STD-141, Method 6192, using CS-17 wheels, a load of 1,000 grams, and a speed of 70 rpm for 100,000 revolutions each side of every coupon. The CS-17 wheels were resurfaced after every 10,000 revolutions by running them for 50 revolutions over S-11 abrasive discs. The temperature in the testing room was 21 ± 2 °C and the relative humidity was $40 \pm 5\%$. Both weight loss and depth penetration were measured on each coupon after every 10,000 revolutions.

The depth penetration was determined by the coating thickness difference in the Taber ring area, as depicted in Figure 2, prior to and after every 10,000 revolutions. The coating thickness was measured in accordance with ASTM B 244 using a pre-calibrated eddy current instrument. To minimize systematic error and maximize reproducibility, coating thickness changes were measured by the same calibrated coating thickness gauge for each alloy.



Figure 2 A schematic diagram of a Tabered coupon

The weight loss was determined by the weight difference prior to and after Taber abrasion using an analytical balance to an accuracy of 0.1 mg. Each coupon was conditioned in a dessicator for 48 hours after anodizing, placed in the Taber room for 30 minutes prior to Taber testing, weighed with the analytical balance, abraded on the Taber abraser, placed in the room for 30 minutes, and reweighed.

Results and Discussion

The variation of the coating depth penetration with Taber abrasion revolutions is presented in Figure 3. The reported data from this work are the averages on the coating depth penetrations of both sides of two coupons. The best result reported using the M.H.C. process and the wear resistance of hard chrome plating and hardened 4130 steel are also plotted in the figure for the purpose of comparison.



Figure 3 Comparison of wear resistance of the hard anodic coatings produced by the new commercial process with that of other material and coatings



Figure 4 A schematic diagram of porous anodic coating on aluminum

It is well established that the anodic coatings formed on aluminum in sulfuric acid electrolytes are of porous structure, consisting of very large numbers of tiny hexagonal cells each with a central pore, as depicted in Figure 4. Both pore size and cell size may vary with each alloy and the anodizing parameters. Homogeneous and uniform coating structure, composition and pore size in the depth profile of an anodic coating will give rise to a constant abrasion resistance that does not change with the coating depth.

It is obvious that the depth penetrations in the anodic coatings produced on three alloys using the new commercial process increase linearly with the number of revolutions of the Taber abrader. In other words, the anodic coatings produced by the new commercial process have virtually constant wear resistance in the depth profiles. This result suggests that the resultant anodic coatings with the new commercial process are very homogeneous and uniform in structure and composition. In contrast, the wear resistance of the M.H.C. coating varied with the coating depth. Assuming that the removal of 20% of the coating thickness is regarded as a failure criterion, in accordance with the 20% allowable variation specified in MIL-A-8625F, it is then anticipated that the parts with a 50 µm coating will fail after exposure to the wear environment where the abrasion strength is equivalent to 25,000 Taber abrasion revolutions for 2024-T3, 40,000 Taber abrasion revolutions for 7075-T6, and 55, 000 Taber abrasion revolutions for 6061-T6.

It can be seen that the wear resistance of the anodic coatings produced on 2024-T3, 6061-T6 and 7075-T6 by the new commercial process is substantially better than that of hard chrome plating and hardened 4130 steel, although hard chrome plating and 4130 steel are much denser than the anodic coatings. In particular, the wear resistance of the resultant anodic coatings obtained on 6061-T6 and 7075-T6 in this study is even superior to that resulting from the M.H.C. process, as exhibited in Figure 3.

The M.H.C. $\text{process}^{[1]}$ uses a 15% v/v sulfuric acid and is operated at 2.0-2.5 A/dm² current density and 0 °C by voltage control without pulsing. To maintain the current density range specified, the initial voltage of 20-50 V is step-wisely increased to 40-60 V.

Since the current density used in the M.H.C. process is lower than that in the new commercial process, it takes about 15 minutes longer for the former process to produce 50 µm coating. The dissolution rates of the anodic coatings were obtained by immersing anodized coupons in the anodizing electrolyte without current passing through. After 1.5 hour immersion, the coupons were taken out of the electrolyte to measure the coating thickness reduction resulting from the acid attack. The results are shown in Table 1. It appears that anodic coatings dissolve very slowly, relative to the coating thickness (~ 50 μ m) and coating formation rate (~1.2 μ m/min at 3.25 A/dm²), according to the data in Table 1. However, such dissolution rates are large enough to substantially enlarge the pore size of the outer layer in the anodic coatings in 15 minutes of dissolution, considering that the typical pore size of the anodic coatings produced in sulfuric acid electrolytes is only in the order of 100 Å and the cell wall thickness in the order of 1,000 Å^[1], respectively. It is understandable that the wear resistance of an anodic coating decreases as the cell wall thickness is reduced. This principle may be used to explain why the wear resistance of the anodic coatings produced by the new commercial process is better than that resulting from the M.H.C. process.

 Table 1

 The dissolution rate of anodic coating in the anodizing electrolyte

| Substrate material | 2024-T3 | 6061-T6 | 7075-T6 |
|---------------------------|---------|---------|---------|
| Dissolution rate Å/min | ~85 | ~40 | ~55 |

The wear resistance of the anodic coatings formed on 6061-T6 and 7075-T6 is better than that on 2024-T3, as expected, since the coatings on 6061-

T6 and 7075-T6 are denser than that on 2024-T3. The content of soft aluminum sulfate in 2024 is close to or higher than that in 6061 and 7075, as presented in Table $2^{[10]}$.

Table 2 The coating density and aluminum sulfate content of hard anodic coating

| Substrate | 2024-T3 | 6061-T6 | 7075-T6 |
|-------------------|---------|---------|---------|
| material | | | |
| Coating density | 2.29 | 2.45 | 2.39 |
| g/cm ³ | | | |
| $Al_2(SO_4)_3$ | 41 | 35 | 42 |
| content % | | | |



Figure 5 Depth profile of wear resistance in anodic coatings by weight loss

The weight loss of the anodic coatings was also measured after every 10,000 Taber wear revolutions in this study. The average results from both sides of two coupons are presented in Figure 5. Like the trend in depth penetration, the weight loss of the abraded anodic coatings demonstrate a linear increase with the Taber wear revolution. The reasonably consistent weight loss for each 10,000 abrasion revolutions indicates the uniformity of the coating composition and structure in the depth profile. The average wear indices of the anodic coatings produced on the three alloys with the new commercial process are listed in Table 3. The abrasion resistance specified by MIL-A-8625F for these three alloys are also included in the table for a comparative purpose. It is clear that the new commercial anodizing process produces hard anodic coatings on aluminum alloys with an excellent wear resistance that far exceeds the requirements specified in MIL-A-8625F. In particular, the wear index for alloy 2024 is three times lower than the allowable wear index for 2XXX series alloys in MIL-A-8625F.

Table 3 Wear resistance of the resultant anodic coatings on three alloys (mg/1,000 revolutions)

| | Measured wear index (average)* | Maximum allowable wear |
|---------|-----------------------------------|---------------------------|
| Alloy | | index |
| 2024-T3 | 1.18 (0.10) | 3.50 |
| 6061-T6 | 0.80 (0.06) | 1.50 |
| 7075-T6 | 0.94 (0.14) | 1.50 |

^{*}The numbers in parentheses are the standard deviations.

For comparison, the coating depth penetrations were also calculated from the coating weight loss caused by Taber abrasion, in terms of the coating density for each alloy given in Table 2 and the wear ring area (2.18 cm^2) , respectively, using the following equation:

$$\delta = \frac{w}{Ad}$$

 δ and w represent the coating depth penetration and the coating weight loss resulting from Taber abrasion, respectively, A stands for the surface area of a Taber abrasion ring left on the coating surface, and d is the coating density.

The calculated results are provided in Table 4. It can be seen that the calculated depth penetrations are reasonably consistent with the measured ones. It is also noticed that the calculated depth penetrations are slightly lower than the measured ones. This discrepancy may be attributed to the facts that the calculated depth penetration is equivalent to the average coating thickness reduction over the entire wear ring area, and the measured depth penetration tends to represent the coating thickness reduction in the center of wear ring. However, the thickness reduction at the edges of the wear ring is slightly less than that in the center of the wear ring in a Taber abrasion test. The results in Table 4 indicate that the weight loss and depth penetration due to Taber abrasion can be converted to each other within an acceptable experimental error, providing the coating density is predetermined properly.

Conclusions

The wear resistance of the anodic coatings on 6061-T6 and 7075-T6, produced by the new commercially available process, is superior to the best results obtained from the M.H.C. process.

The anti-wearing performance of the anodic coatings on 2024-T3, 6061-T6 and 7075-T6 is substantially better than that of both hard chrome plating and hardened 4130 steel.

All the anodic coatings produced on the three alloys using the new commercial process showed virtually constant wear resistance in the depth profiles, indicating that the anodic coatings are very homogeneous and uniform in structure and composition.

The depth profile of wear resistance in an anodic coating is alloy-dependent.

The new commercial anodizing process produces hard anodic coatings on aluminum alloys with excellent wear resistance that far exceeds the requirements specified in the MIL-A-8625F specification. In particular, the wear index for alloy 2024 is three times lower than the allowable wear index for 2XXX series alloys in the MIL-A-8625F specification.

Table 4 Comparison of calculated and measured coating depth penetrations on three typical alloys from Taber abrasion

| Taber wear | 2024-T3 | | 6061-T6 | | 7075-Тб | |
|------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| cycles | $\delta_{cal}/\mu m$ | $\delta_{mea}/\mu m$ | δ _{cal} /μm | $\delta_{mea}/\mu m$ | δ _{cal} /μm | $\delta_{mea}/\mu m$ |
| 10,000 | 3.5 (0.6) | 5.8 (0.7) | 1.8 (0.5) | 2.7 (1.1) | 2.3 (0.9) | 4.5 (2.1) |
| 20,000 | 5.7 (1.3) | 8.5(0.9) | 3.4 (0.7) | 4.6 (0.5) | 3.8 (0.7) | 6.3 (1.7) |
| 30,000 | 8.2 (1.8) | 11.0 (1.9) | 4.8 (0.8) | 6.8 (1.2) | 5.7 (1.2) | 8.5 (1.0) |
| 40,000 | 11.1 (0.9) | 13.8 (0.9) | 6.3 (1.0) | 8.1 (1.3) | 7.4 (0.7) | 10.2 (1.8) |
| 50,000 | 13.2 (1.80 | 16.1 (1.6) | 7.7 (0.9) | 9.4 (1.3) | 9.0 (0.8) | 11.5 (1.5) |
| 60,000 | 15.7 (1.9) | 18.3 (1.8) | 9.3 (0.8) | 10.7 (1.6) | 10.9 (1.2) | 13.3 (1.2) |
| 70,000 | 17.6 (1.5) | 19.9 (1.4) | 10.8 (1.0) | 12.1 (1.6) | 12.4 (1.6) | 14. 8(1.6) |
| 80,000 | 19.8 (1.5) | 22.3 (1.5) | 12.3 (1.3) | 13.8 (1.7) | 14.0 (1.9) | 16.2 (1.7) |
| 90,000 | 21.8 (1.3) | 24.2 (1.1) | 13.6 (1.2) | 15.0 (1.7) | 15.8 (2.8) | 17.9 (2.0) |
| 100,000 | 23.6 (1.9) | 25.8 (1.8) | 14.9 (1.1) | 16.1 (1.1) | 18.1 (2.6) | 20.4 (1.8) |

^{*}The numbers in parentheses are the standard deviations.

 δ_{cal} : the coating depth penetration calculated from the weight; δ_{mea} : the coating depth penetration measured in terms of an eddy current instrument.

Acknowledgment

This study was supported by METALAST International, Inc.

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