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AES Research Project #41: Part 4: Adhesion Failure of Electrodeposited Coatings on Anodized Aluminum Alloys

by
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Editor's Note: Originally published as D.E. Thomas, *Plating and Surface Finishing*, **69** (10), 57-62 (1982), this paper was the fourth of several reports on AES Research Project #41, a study of the technology of plating on aluminum, at the National Bureau of Standards (NBS), now the National Institute for Science and Technology. Mr. Thomas was Research Associate at NBS, working with Project Director Dr. David S. Lashmore.

ABSTRACT

Scanning electron microscopic examination of peel-test adhesion specimens from electrodeposited coatings on anodized aluminum indicates that failure can be categorized in three different modes: (1) specimens exhibiting poor adhesion strength [from 0 to 100 N/m], which fail at the anodic film/coating interface; (2) specimens with good adhesion strength [from 100 to 1,000 N/m], which fail by local fracture of the anodic film; and (3) specimens with excellent adhesion strength [greater than 1,000 N/m], which fail when the applied load is greater than the strength of the alloy substrate. The effect of anodizing parameters and alloy composition on the modes of failure are discussed.

Introduction

Porous anodizing as a pretreatment to electrodeposition was discovered more than 50 years ago,^{1,2} yet commercialization of this process has been slow. The major reason for the lack of commercial interest stems from the difficulty in developing a general process that is successful with a variety of aluminum alloys. Because of this difficulty, alternative processes using zincate or stannate electrolytes have gained much wider commercial success. However, these processes are not without problems.

First, both the zincate and stannate process require the use of cyanide solutions, which impose significant environmental and economic penalties. Second, the inner layer of zinc or tin is less than ideal from a corrosion standpoint because of potential problems with galvanic coupling. Third, the cleaning treatments required prior to the immersion treatment are critical to the success of the process. The porous anodizing process, on the other hand, poses none of these problems.

The failure of electrodeposited metal coatings on porous anodized aluminum alloys is the subject of this paper. Peel-test adhesion specimens were examined with the scanning electron microscope and energy dispersive x-ray analysis (EDAX) to determine the failure mechanism involved in the separation of an electrodeposited coating from an anodically pretreated aluminum alloy.

The anodizing process

The porous anodizing process has been investigated by many authors³⁻¹¹ with varying results. Generally, dilute phosphoric acid is the preferred anodizing electrolyte, as it provides a regular porous structure with pore diameters ranging from 15 to 45 nm. However, electrolyte concentration and temperature, anodic potential and current density, anodizing time and other conditions vary significantly from one process to the next. This is where the major problem exists: every investigator has a different method of anodizing a specific aluminum alloy.

Moreover, comparison of results is difficult because the adhesion test used to determine the effectiveness of the anodizing process is not standardized. Some authors report qualitative adhesion results from ASTM standard test method B571. Others report quantitative adhesion data using the Jacquet peel test¹² or other quantitative tests.⁹ These different data make it difficult to compare the effectiveness of anodizing processes. A review of some of the quantitative adhesion data can be found in a report by Lashmore.⁷

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Generally, phosphoric acid (1.63 sp. gr.) ranging from 3 to 30 vol% is the anodizing electrolyte. The bath is maintained near room temperature to reduce the dissolution of the anodic film, resulting in generally higher coating adhesion strength. Studies by Lashmore⁶ and Klingenmaier and Dobrash⁸ indicate that the coating adhesion strength increases with the anodizing potential. The upper limit on anodizing potential is kept at approximately 60V for repeatability.

Wittrock⁴ has shown that anodizing to a charge density of 30 Coulombs/cm² results in a good balance between anodizing time and coating adhesion. Anodizing to a higher charge density results in very little enhancement of adhesion strength and a significant cost penalty.

Experimental procedure

Specimens (6 × 50 × 100 mm) were buffed and polished to a mirror finish and chemically cleaned in a non-etching soak cleaner. Prior to anodizing, the specimens were rinsed in a mixture of nitric acid and distilled water (50:50), placed in the anodizing electrolyte and polarized to a preset anodic potential.

Following the anodic treatment, each specimen was rinsed ultrasonically in distilled water and plated so that peel tests could be performed. In several cases, thin inner layers of copper or iron were deposited before application of the final layer of nickel. Details of the specific deposition procedure can be found in a paper by Wittrock.⁵

Results and discussion

Examination of peel-test failures in the scanning electron microscope revealed that there are three major failure modes.

When adhesion strength is low, the metal coating simply peels off the aluminum anodic film. These "Mode 1" failures are usually attributable to one or more of the following causes: (a) poor surface preparation, (b) insufficient pore diameter of the anodic film or (c) drying of the anodic film before application of the metal coating.

Poor surface preparation always results in poor adhesion, regardless of the system under study. Vigorous gas evolution during phosphoric acid anodizing does a small amount of cleaning. However, this does not imply that good surface preparation is not required. As always, organic materials such as grease or buffing compounds must be removed before anodizing.

Insufficient pore diameter of the anodic film as a result of anodizing at potentials below 25V is the major problem encountered with Mode I failures (Fig. 1). This is the case regardless of the kind of aluminum-alloy substrate being used. However, as the anodizing potential is increased above 25 V, the failure mode changes, as described below.

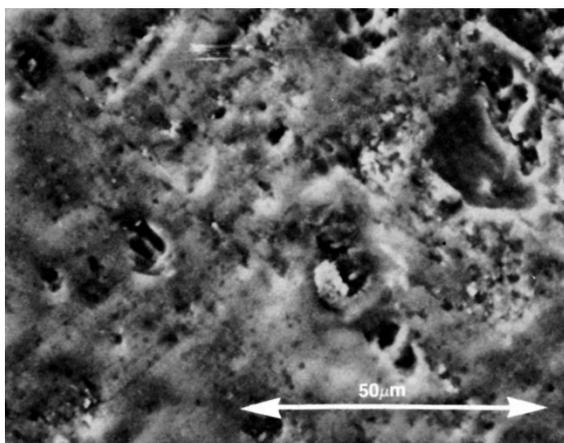


Figure 1 - SEM of substrate side of peel-tested AA 6061-T6 anodized in 10 vol% sulfuric acid at 15V and 35°C for 30 Coulombs/cm². Adhesion strength was 30 N/m.

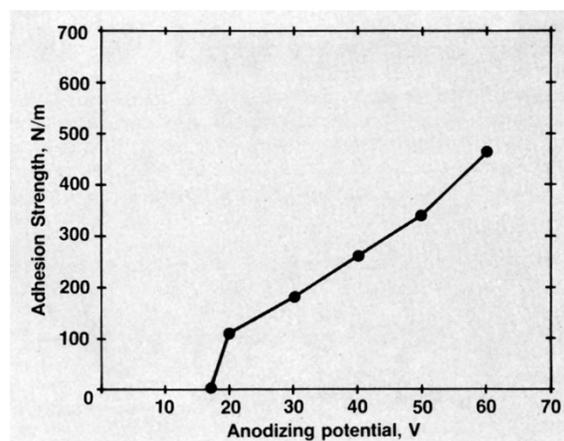


Figure 2 - Adhesion strength vs. anodizing potential using a 3 vol% phosphoric acid solution.

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O'Sullivan and Wood¹⁴ showed that the pore diameter is proportionally increased as the anodizing potential is increased. Evidently, there is a critical anodizing potential and resultant pore diameter required before a metal coating will successfully adhere to the substrate. The author has shown that anodizing below a critical potential, V_c , results in a pore diameter that is too small to provide good mechanical keying or good adhesion of the metal coating (Fig. 2).¹¹

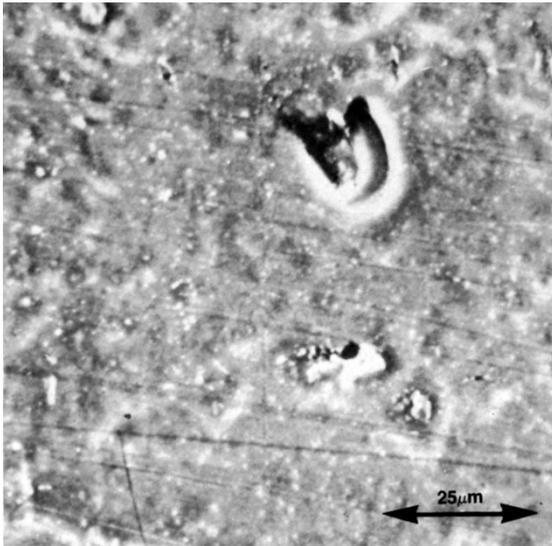


Figure 3 - SEM of substrate side of AA 6061-T6 anodized in copper sulfate solution 9 at 17V and 35°C for 30 Coulombs/cm². Adhesion strength was 80 N/m.

Levinson and Mondolfo⁹ claimed that porous anodizing in a modified copper sulfate (CuSO₄) plating electrolyte and reversing the applied current after development of a porous anodic film produced a copper deposit with good adhesion. Unfortunately, the anodic film produced by this method has a small pore diameter. Typical anodizing potentials for this process range from 13 to 18 V, well below the critical anodizing potential shown previously. Not surprisingly, peel-test specimens produced using this process failed by the Mode I mechanism. Figure 3 is a photomicrograph of a typical peel-test failure using the Levinson and Mondolfo process.

Still another cause of Mode I failures is the result of allowing the anodic film to dry completely before the metal coating is applied. Most researchers concede that, on drying, the pore structure of the anodic film is closed off, thereby preventing electrodeposition of metal on the anodized aluminum surface.

The bulk of the coating adhesion failures fall into Mode II and are associated with an adhesion strength of 100 to 1000 N/m. Mode II failures are characterized by fracture of the anodic film somewhere within the porous region (Fig. 4). Thus, the strength of the anodic film is the limiting factor in the ultimate adhesion strength of the coating.

The metal coating does not separate from the anodic film in Mode II failures. Measurements obtained with energy-dispersive X-ray analysis (EDAX) showed a significant amount of coating and substrate material on both the peel tab and the bulk aluminum. EDAX results for a Mode II failure are shown in Fig. 5. This specimen was anodized in 3 vol% phosphoric acid and given a

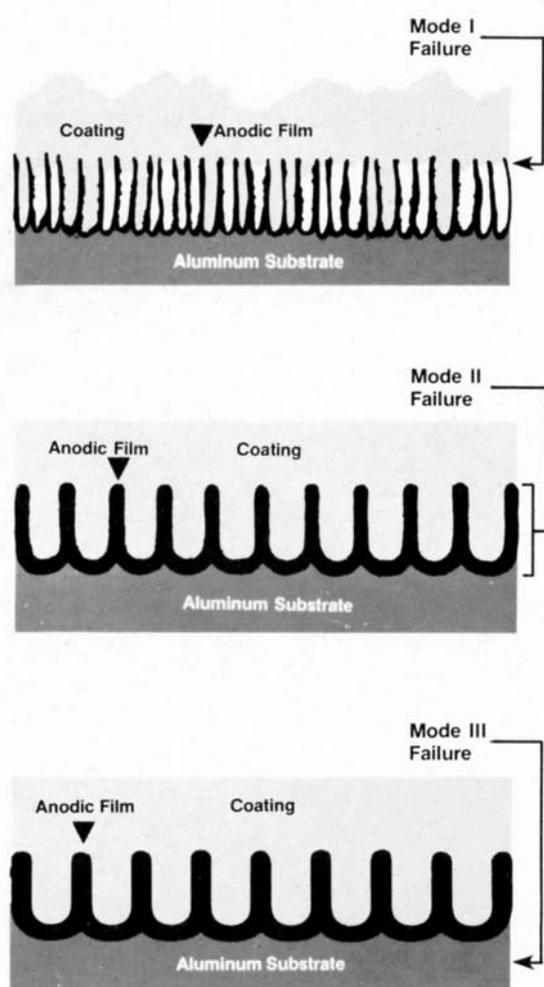


Figure 4 - Failure modes for electroplated coatings on aluminum: Mode I (upper), Mode II (center) and Mode III (bottom).

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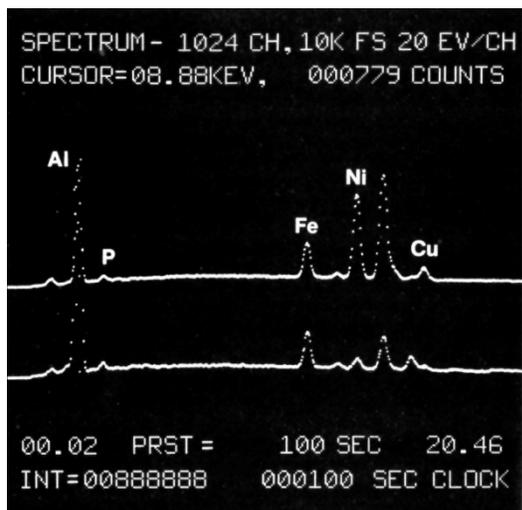


Figure 5 - EDAX of peel tab (upper line) and substrate side (lower line) of peel-tested AA 60601-T6 anodized in 3 vol% phosphoric acid at 50V and 45°C for 30 Coulombs/cm². Adhesion strength was 480 N/m.

copper strike before the final heavy deposit of nickel. Aluminum, copper, and nickel were clearly evident on both sides of the peel-test specimen.

SEM micrographs indicate there was a significant amount of aluminum anodic film adhering to the peel tab. On the other hand, the substrate had a greater amount of aluminum on its surface than the peel tab, because it was primarily composed of the aluminum alloy. Nevertheless, copper and nickel were definitely present, indicating that at least some of the metal coating remained after failure. Morphologic-ally, the surfaces appear to be composed of numerous pieces of broken anodic film adhering to both failure surfaces.

Failure surfaces are shown in Fig. 6. The peel tab and substrate surfaces are practically identical, also indicating that the failure is within the anodic film and not at one of the interfaces. Variations in peel-test adhesion strength between 100 and 1000 N/m result from a variation in the anodic film strength. For Mode II failures, the adhesion strength and microhardness of the anodic films show a strong correlation.¹¹ As the microhardness of the anodic film surface area of these regions on the peel substrate increases, adhesion strength also increases.

An SEM micrograph of the substrate of a fractured specimen with an adhesion strength of 630 N/m is shown in Fig. 7. The bulk of the anodic film adhered to the peel tab. A small amount of coating metal appeared on the mating surface near the substrate, indicating that the failure site was very near the oxide layer at the base of the pores. Typically, specimens at the low end of the adhesion-strength range (100 and 500 N/m) fail at this point.

Defects in the anodic film apparently account for the localized non-uniform fracture of the film. Study of the surface of the anodic film reveals that the grain orientation of the substrate influences the growth of the anodic film. Figure 8 is a SEM micrograph of an anodic film surface that shows such an influence. The defects for localized failure of the anodic film are formed over the grain boundaries of the substrate. Some regions of the anodic film tend to adhere to the substrate better than others. At present, the

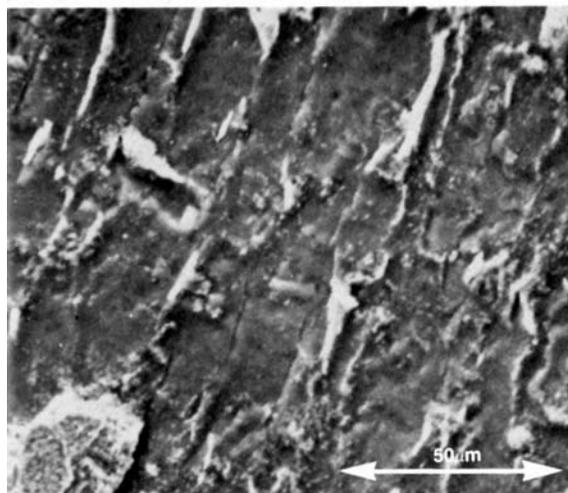
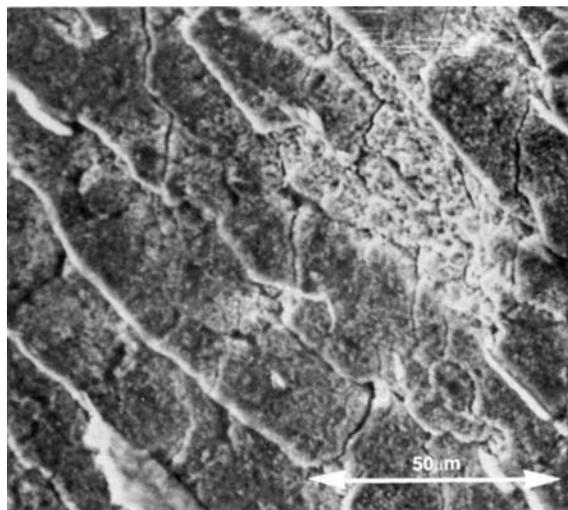


Figure 6 - Peel tab (upper) and substrate side (lower) SEMs of AA 7146-T6 anodized in 3 vol% phosphoric acid at 60V and 30°C for 30 Coulombs/cm². Adhesion strength was 620 N/m.

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reason for the non-uniform adhesion of the anodic film is not known. However, it is known that the greater the surface area of the regions that do adhere, the greater the adhesion.

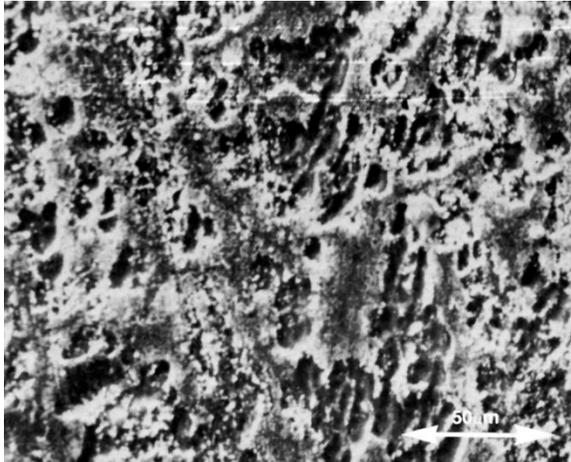


Figure 7 - SEM of substrate side of peel-tested AA 7146-T6 anodized in 3 vol% phosphoric acid at 60V and 45°C for 30 Coulombs/cm². Adhesion strength was 630 N/m.

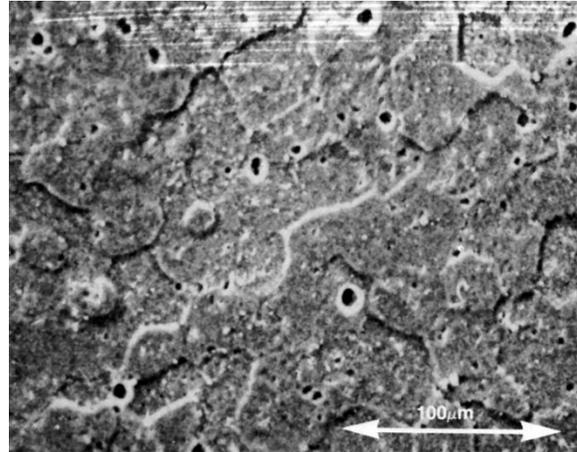


Figure 8 - SEM of anodic film on AA 6061-T6 anodized in 10 vol% phosphoric acid at 50V and 40°C for 30 Coulombs/cm².

Figure 9 is a micrograph of a mating surface adjacent to the substrate of a specimen with an adhesion strength of 675 N/m. The entire surface is covered with a thin oxide film and numerous pieces of thicker oxide film. An adhesion strength between 500 and 1000 N/m is primarily influenced by the number and size of pieces of the thicker oxide film. As the surface area of these regions on the peel substrate increases, the adhesion strength increases. Possibly, the strength of the anodic film is related to the effect of the substrate's grain orientation and structure on the growth of the anodic film.

The anodizing conditions that have the greatest effect on the adhesion strength within the Mode II failure region are anodizing potential and anolyte temperature.

The adhesion strength and the anodic film microhardness are directly proportional to the anodizing potential from 15 to 60 V.^{6,11} Beyond 60 V, rapid increases in the current density make control of the anodizing process difficult. In many cases, a high current density causes the anolyte temperature to increase rapidly, resulting in dissolution of the aluminum substrate. With a high anodizing potential, which causes the anodic film pore diameter to increase, small defects coinciding with substrate defects would have little effect on the adhesion strength. Micrographs of the anodic film surface show that the surface defects become less numerous as the anodizing potential is increased (Figs. 10-12). The higher anodizing potential decreases the ratio of the dissolving power of the electrolyte to the anodic film growth. Thus, the film has fewer defects from which the localized fracture may occur.

The relationship between anolyte temperature and adhesion does not show consistent behavior when alloy, anodizing potential, anolyte concentration, and anodizing time are varied. Previous reports by Wittrock⁴ and Thomas¹¹ showed that the adhesion strength decreased as the anolyte temperature increased, but this holds true only for specific anodizing conditions. With alloys other than 6061-T6 and 7146-T6, the results have been inconclusive. In some cases, the adhesion strength increases as anolyte temperature increases. In others, the opposite relationship results, while in still other instances, there is no particular relationship. At present, there is no clear relationship between anolyte temperature and adhesion strength. Any relationship that may exist is highly dependent on the specific conditions of the anodizing system.

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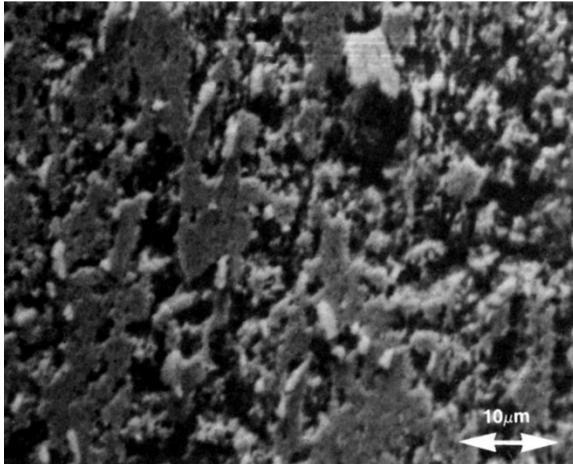


Figure 9 - SEM of substrate side of peel-tested AA 7021-T6 anodized in 3 vol% phosphoric acid at 55V and 30°C for 30Coulombs/cm². Adhesion strength was 675 N/m.

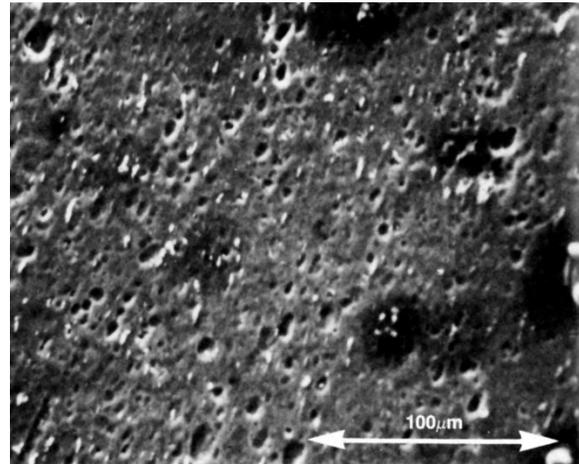


Figure 10 - SEM of an anodic film on AA 6061-T6 anodized in 3 vol% phosphoric acid at 35V and 60°C for 30 Coulombs/cm².

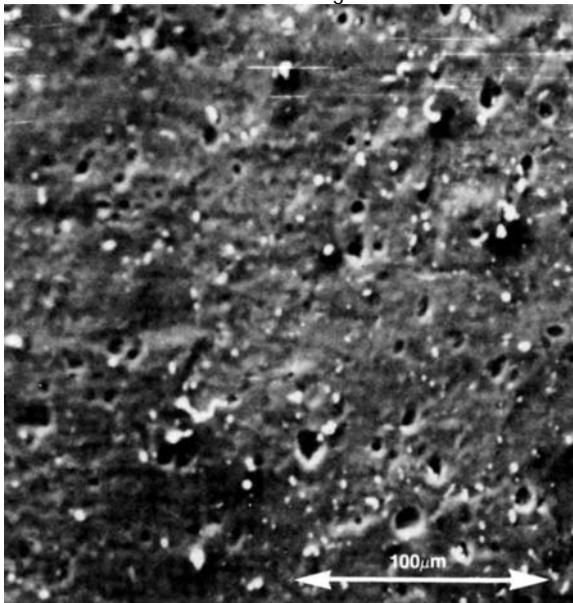


Figure 11 - SEM of an anodic film on AA 6061-T6 obtained in 3 vol% phosphoric acid at 50V and 60°C for 30 Coulombs/cm².

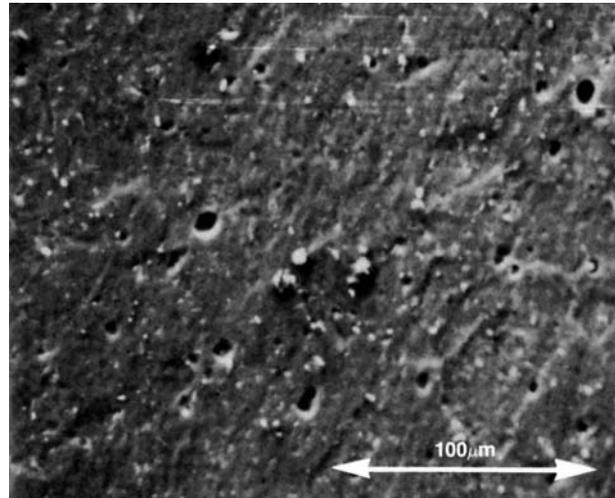


Figure 12 - SEM of an anodic film on AA 6061-T6 obtained in 3 vol% phosphoric acid at 60V and 60°C for Coulombs/cm².

Conditions for maximum adhesion

Mode III failures are characterized by fractures completely within the aluminum substrate. Adhesion strength is so high that the coating cannot be stripped from the substrate until the load is sufficient to rupture the substrate. This type of failure represents the maximum adhesion because failure is wholly within the substrate alloy. Typically, the peel strength exceeds 1000 N/m.

There is no general set of anodizing conditions that will guarantee this type of failure mode. Mode III failures can be achieved only by optimizing the anodizing process to the specific alloy being coated. However, it is possible to give a general range of anodizing conditions that can serve as a starting point for the optimizing process.

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Generally, the anodizing potential should be maintained at 50 to 60V for the entire anodizing period. Evidence indicates that removal of the specimen from the anodizing electrolyte with the current flowing may be beneficial.¹¹ The only anolyte that consistently produces good results is phosphoric acid in concentrations of 3 to 30 vol%. Usually, the higher-concentration anolytes work on less heavily alloyed aluminum. The simplest method of controlling the anodizing time is to anodize to a specific charge density. Charge densities of 25 to 35 Coulombs/cm² give the best compromise between adhesion, strength and required power output. Charge densities of this magnitude require anodizing for 10 to 30 min, depending on the other conditions.

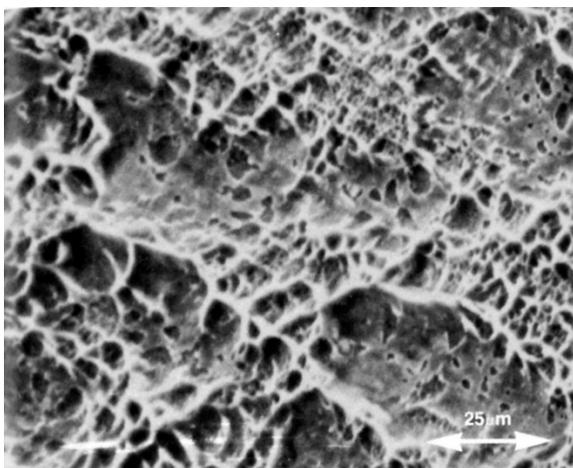


Figure 13 - SEM of substrate side of peel-tested 99.9 percent aluminum anodized in 10 vol% phosphoric acid at 60V and 30°C for 30 Coulombs/cm². Adhesion strength was 1350 N/m.

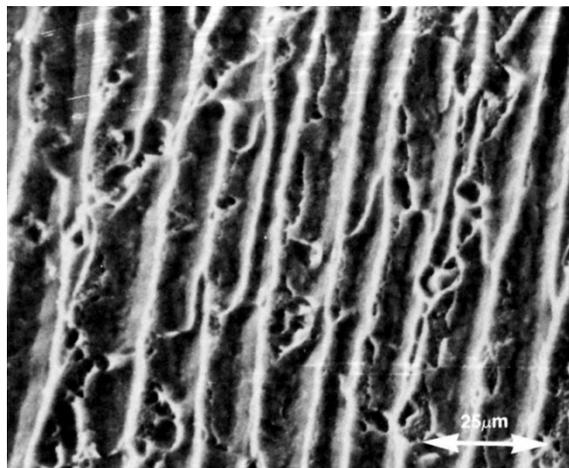


Figure 14 - SEM of substrate side of peel-tested AA 7129-T6 anodized in 3 vol% phosphoric acid at 60V and 60°C for 30 Coulombs/cm². Adhesion strength was 1680 N/m.

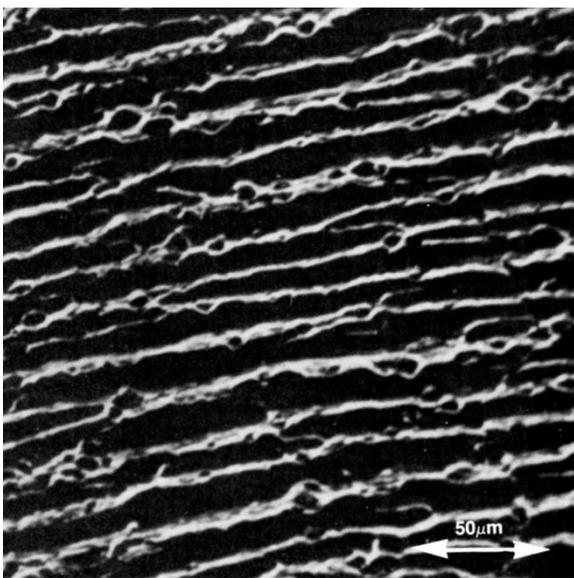


Figure 15 - SEM from peel tab of AA 7129-T6 anodized in 3 vol% phosphoric acid at 60V and 45°C for 20 Coulombs/cm². Adhesion strength was 1860 N/m.

Anolyte temperature is the most difficult parameter to generalize. The relationship between adhesion strength and anolyte temperature is dependent on both the aluminum alloy being coated and the other anodizing conditions. Temperatures should be kept above room temperature to prevent possible cracking of the anodic film, but below approximately 60°C to prevent excessive dissolution of the substrate. The best temperature will depend on the alloy being anodized. Microhardness measurement of the anodic film may prove useful in optimizing some of these anodizing parameters.

Rinsing after anodizing to remove all of the anolyte is very important to the success of the process. Any phosphoric acid remaining in the pores of the anodic film will severely reduce the adhesion strength of the final electrodeposited specimen. In some cases, ultrasonic rinsing in distilled water or dilute sulfamic acid will increase the adhesion substantially.

why Mode III failure specimens exhibit such outstanding adhesion strength. Since the failure is not interfacial in nature, but a bulk failure of the substrate, the bonding interface between the metal coating and the anodic film cannot be examined.

An examination of micrographs showing peel failure surfaces (Figs. 13-15) does not reveal any information as to

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Consequently, examination of Mode III failure surfaces provides little information as to the reason for the excellent adhesion strength.

Conclusions

Three distinct modes of failure occur in the peel testing of electrodeposited coatings on anodized aluminum.

Mode I failures, on specimens with adhesion strengths between 0 and 100 N/m, are characterized by complete separation of the deposited coating from the porous anodic film. The primary causes for this mode of failure are (1) poor surface preparation, (2) low anodizing potential [or insufficient pore diameter], and (3) drying of the anodic film prior to electrodeposition.

Mode II failures, on specimens with adhesion strengths between 100 and 1000 N/m, are characterized by failure of the porous anodic film, which appears to fracture locally near the base of the pores at defects caused by the substrate structure. The more defects present in the anodic film, the lower the adhesion strength. Variations in adhesion strength between 100 and 1000 N/m are primarily caused by these defects, their size and number.

Mode III failures, generally on specimens having adhesion strengths greater than 1000 N/m, are the result of optimum adjustment of anodizing parameters. This type of failure is characterized by fracture completely within the aluminum-alloy substrate and is achieved only through careful optimization of the anodizing process for the specific alloy employed.

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