

Metallurgical Assessment of Acid Etch as Anodizing Pretreatment



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Metallurgical Assessment of “Acid Etch” as an Anodizing Pretreatment

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Abstract

A number of anodizing lines in the United States and Australia have recently adopted alternate anodizing pre-treatments using fluoride-based etch solutions. The claimed benefits include shorter cycle times and freedom from streaking. The traditional caustic-based etchants are known to be sensitive to the alloy chemistry and microstructure giving rise to the well-known color or shade match problem. The current work describes a test program conducted to measure the response of the “acid etch” process to various alloy compositions. The profiles tested included some with deliberately produced extrusion streaks. The impact of “acid etch” and combined caustic etch times was assessed along with the surface topography produced by these treatments. Comparisons were also made on the same profiles when treated with conventional caustic etching. Significant differences were found between “acid etch” and caustic etching in terms of the sensitivity of the final finish to alloy composition and also the ability to hide extrusion streaks

Introduction

Anodizing is widely used as a protective decorative finish for 6XXX aluminum extrusions. The anodic film provides excellent protection against corrosion, surface damage and produces a pleasing matt finish while also providing a vehicle for coloring the surface. Normally, a sodium hydroxide-based etch is used as a pretreatment, partly as a cleaning step but also to reduce the gloss of the substrate and remove the die lines or flow lines present on all extruded profiles. The matt appearance after etching is due to light scattering at pits formed at features such as second phase particles and grain boundaries. As a result, the final appearance after caustic etching has a strong interaction with alloy composition and microstructure.^(1,2) Impurity elements such as iron, copper and zinc have a relatively strong impact⁽³⁾ on the caustic etch response and are typically controlled in 6XXX alloys for optimized anodizing response. Extrusion processing conditions that have an effect on the microstructure in terms of Mg₂Si precipitation such as quench rate and artificial ageing conditions can also influence the etched appearance. Caustic attack is also sensitive to small changes in microstructure in the original ingot and also those due to natural variations in the deformation conditions across the profile section during extrusion, which can lead to a range of streaking defects⁽⁴⁾ that are undesirable on a high quality anodized finish. For example, streaking due to the shell zone in extrusion ingots was one of the driving forces that led to the development of thin shell casting technology. Consequently today, it is found that alloy compositions, extrusion practices and billet production practices for soft alloy 6XXX extrusions are often linked to the caustic etch/anodizing process.

The adoption of “acid etch” or fluoride-based etchants by some anodizers as an alternative to caustic pretreatment in recent years appears to be based on a number of benefits^(5,6,7) including reduced metal removal and effluent generation, freedom from extrusion streaks and reduced sensitivity to billet source. However, there is little documented information on the interaction of this type of pretreatment with alloy composition and extruded microstructure. The current research was conducted to quantify the impact of metallurgical factors on the etch response of one commercially available “acid etch” system in comparison with a standard long-life caustic etch.

Experimental

A series of compositions was designed using a general purpose AA6063 as a base alloy to assess the effects of high copper, high zinc and low iron contents. AA6360 was also included as this dilute alloy developed for high press productivity⁽⁸⁾ has shown a tendency for brighter finish after anodizing than standard AA6063. The alloys were direct chill cast using air cushion technology as 4-inch diameter ingots. The compositions, as measured by OES, are given in Table 1.

Table 1. Alloy Compositions

| Alloy | AA 6063 | Hi Cu | Lo Fe | Hi Zn | AA6360 |
|-------|---------|-------|-------|-------|--------|
| Si | 0.44 | 0.44 | 0.44 | 0.45 | 0.56 |
| Fe | 0.20 | 0.20 | 0.14 | 0.19 | 0.16 |
| Cu | <.01 | 0.03 | <.01 | <.01 | 0.05 |
| Mg | 0.50 | 0.50 | 0.50 | 0.49 | 0.31 |
| Zn | <.01 | <.01 | <.01 | 0.05 | <.01 |
| Ti | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |

The billets were given a standard commercial homogenization cycle and then extruded on the RTA 780-tonne experimental extrusion press into a 50 x 3 mm profile. Press conditions were selected to ensure that a minimum exit temperature of 510°C was achieved. The profile was forced air quenched at a rate of 8°C/sec and an artificial age cycle of 5 h/185°C was applied. The extrusions were produced using a flat face die to avoid cross contamination between alloys. The standard AA6063 control was also extruded into a profile with one flat face and the reverse side featuring a series of T-slots (see Figure 1) to promote streaks on the extrusion.

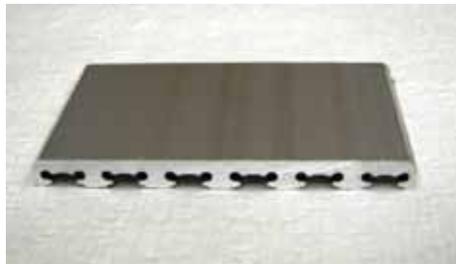


Figure 1. T-Slot Die Used to Promote Streaking

The extrusions were cut into 150-mm coupons and these were processed by the Houghton Metal Finishing Company, Alpharetta, Georgia using their 20-L pilot finishing line, as shown in Figure 2.



Figure 2. Houghton Metal Finishing, 20-L Pilot Line

The Houghton “acid etch” formulation AX-2050 (patent pending⁽⁷⁾) was used for the tests. The treatment recommended by Houghton is a 3-min acid etch followed by 40 s in a standard long-life caustic etch to remove any fluoride deposits. The acid etch time was varied from 60 to 600 s to assess the effect of this parameter on the finish and the mode of attack. Based on Houghton’s experience, the secondary caustic etch time was increased in line with the primary “acid etch” time. A parallel set of samples were processed using a standard 10-min “long-life” caustic etch. The formulation used was 7.5% NaOH, and 130 g/L aluminum at 64°C. The operating temperature for the “acid etch” bath was 46°C. The overall processing route was as follows:

- 1 Mild alkaline cleaner
- 2 Rinse
- 3 “Acid etch”
- 4 Rinse
- 5 Caustic etch
- 6 Rinse
- 7 Desmut
- 8 Rinse

Table 2 summarizes the “acid etch”/caustic etch combinations tested and the identification codes used in the subsequent analysis.

Table 2. Etch Treatments Applied in Pilot Line Trials

| acid etch time s | caustic etch time s | Identification |
|------------------|---------------------|----------------|
| 60 | 20 | 60AA + 20C |
| 180 | 0 | 180AA |
| 180 | 40 | 180AA + 40C |
| 300 | 60 | 300AA + 60C |
| 600 | 60 | 600AA + 60C |
| 0 | 600 | Caustic Only |

All samples were weighed before and after etching to determine the metal removal. Duplicate sets of samples were processed for each etch condition; one sample was retained in the as-etched condition and one was sulphuric acid anodized to give a 20- μ film. Gloss values were measured on all samples at an angle of 60°. Selected samples were examined in the SEM to reveal the surface topography produced by the different treatments.

As a reference point for the test program, a parallel set of samples was etched and anodized commercially by A&D Prevost, Richelieu, Québec using a long-life caustic etch. The etch time was 15 min and anodized film thickness was 10 μ

Results

Etched and Anodized Finish

The as-etched gloss values after the various treatments are presented in Figure 3. The data clearly separates into the caustic etch only and “acid etch plus caustic” processing routes. The 10-min pilot line caustic etching gave the highest gloss values and the 15-min commercially etched samples were typically 20-30 gloss units lower than that. All the “acid etch” treatments resulted in gloss values of <30. The 180s “Acid Etch Only” treatment gave the lowest values overall (<10) and applying the 40-s caustic treatment immediately after raised this value to ~ 20. Increasing the “acid etch” time from 60 to 600 s resulted in slightly lower gloss, and the length of the secondary caustic etch did not appear significant. For the range of “acid etch” and secondary caustic etch times used in the tests, overall the gloss varied by ~ 10 units.

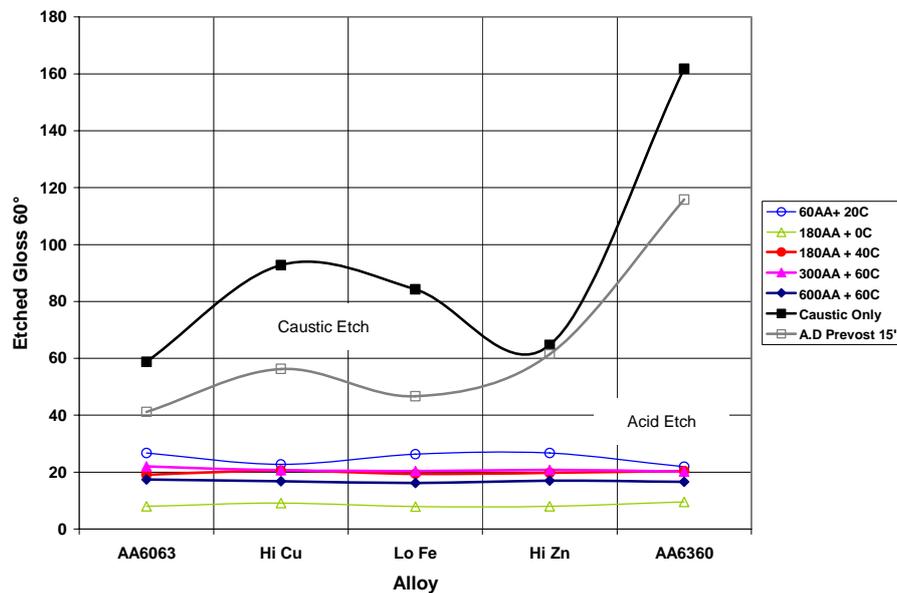


Figure 3. Etched Gloss Values

In terms of the role of alloy composition on gloss, it is clear that the “acid etch” was relatively insensitive to the changes in composition, whereas with the caustic etch treatments used, every alloy gave a significantly different value. For caustic etching, the low copper, low zinc, and standard iron AA6063 control gave the lowest values. For the

AA6063 variants, the “Hi Cu” gave the highest gloss with the “Lo Fe” and “Hi Zn” variants yielding intermediate values. The range of gloss values associated with the composition changes was ~ 20 units for the commercial, 15-min etch and 35 units, for the pilot line etch. In both cases, the AA6360 gave the highest values, some 80 – 120 units above the standard AA6063, whereas with acid etching the gloss was equivalent.

Figure 4 shows the gloss values after anodizing. As expected, the anodic film resulted in lower gloss values, but trends in terms of alloy composition and treatment were identical to those described for the as-etched condition.

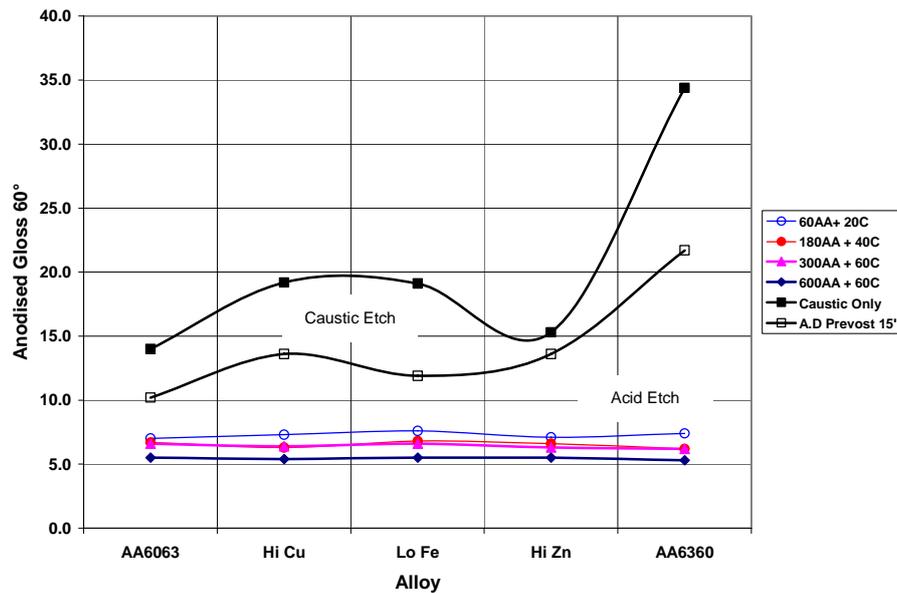


Figure 4. Anodized Gloss Values

Metal Removal Characteristics

The levels of metal removal during etching are illustrated in Figure 5. Again, the results fall into two distinct groups for the caustic and “acid etch” treatments. The pilot line 10-min caustic etch removed ~ 80 g/m² and the commercial 15-min etch removed slightly less aluminum, ~ 70 g/m². Both values are fairly typical for door and window type applications in North America. The “acid etch” processing resulted in metal removal levels from 10-30 g/m² with the aluminum dissolution increasing roughly linearly with “acid etch” time. The recommended 180-s acid etch/40-s caustic treatment gave ~ 15 g/m² metal removal.

The metal removal values varied with alloy composition for the “Caustic only” treatments as previously reported⁽³⁾. The pilot line caustic etch was the most sensitive to composition with the “Hi Cu” and AA6360 giving ~ 10% higher weight loss than the standard AA6063. The “Hi Zn” and “Lo Fe” both gave slightly lower metal removal than the control. Interestingly, the metal removal for the commercial 15-min caustic etch exhibited low sensitivity to alloy composition, with all the alloys giving similar values except for the “Lo Fe” which was ~ 5% lower.

The efficiency of gloss generation is illustrated in Figure 6, where etched gloss is plotted against metal removal. The individual points for each treatment represent the various alloy compositions. The “acid etch” treatments all generated very low gloss levels with low metal removal. There was no advantage in extending the etch time beyond 180 s as improvements in gloss were marginal for the extra metal removed. Compared to the “caustic only” treatments, the “acid etch” gave lower gloss for only 25-30% of the metal removed by caustic etching. The spread in gloss for the caustic etching represents the influence of alloy composition. It should be noted that the commercial caustic treatment resulted in lower gloss and less variation due to composition than the pilot line etch. The results suggest that with good control of the etch tank and incoming alloy composition, it is possible to achieve an etched gloss of 40 units, but the associated metal removal is still 2-3 times higher than that required to achieve an even lower gloss with acid etching.

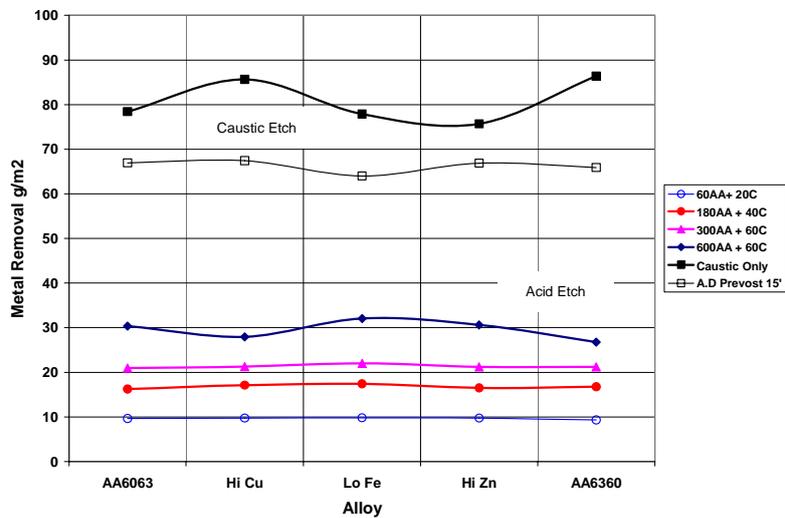


Figure 5. Metal Removal Values

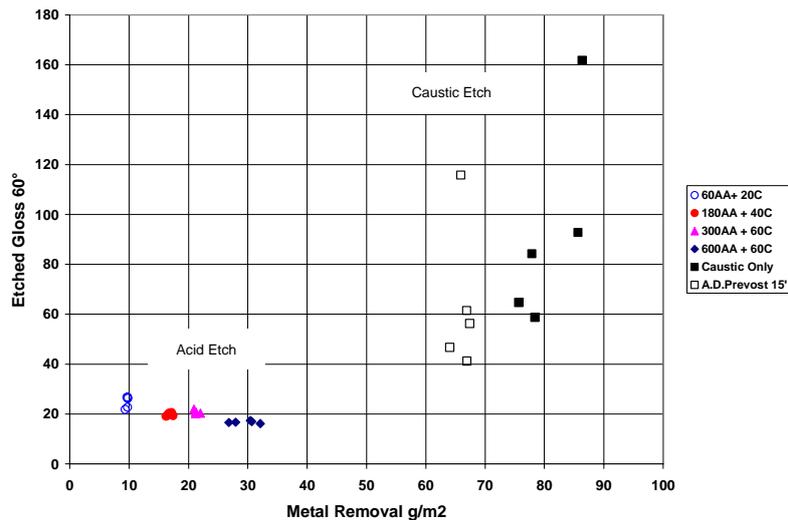


Figure 6. Etched Gloss vs. Metal Removal

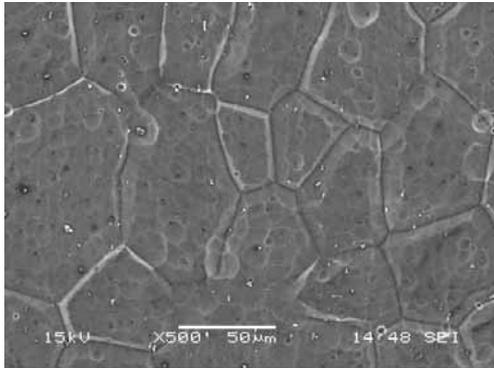
Surface Topography

Etched and de-smutted surfaces for the AA6063 control were examined in the SEM to study the mode of attack. Figure 7 shows typical images. The pilot line caustic etch (7a, 7b) had the typical features of AA6063 etched in NaOH – enhanced attack at grain boundaries combined with pitting within the matrix and on the grain boundaries at second-phase particles. The pit size was ~ 3-10 μ . In contrast, exposure to “acid etch” for 3 min (7c, 7d) gave a surface that was essentially featureless except for fine crystallographic pits of ~1-2 μ in size. There was no preferential attack at grain boundaries and in fact the grain boundaries were not visible on the surface. There was also a high density of residual iron phase particles sitting on the surface suggesting that they are not directly involved in the dissolution mechanism. The application of a 40-s NaOH treatment (7e, 7f) modified the surface in several ways. A proportion of the iron phase particles sitting on the surface was removed, the grain boundaries were lightly attacked or outlined, and the overall pit size distribution appeared to be increased to 2-5 μ . The lack of interaction between the “acid etch” and the alloy microstructure along with the fine pit size explains the insensitivity to alloy composition and the overall low gloss values produced by this process. The coarsening of the pit size, when the secondary caustic etch is applied, produces the slight increase in gloss observed.

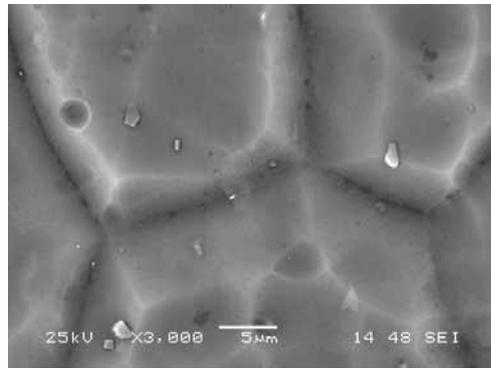
The “Hi Zn” variant of AA6063 was included in the tests as this element is known to promote the spangle defect under certain caustic etch conditions. This involves preferential attack of individual grains with preferred orientations giving a “grainy appearance” when present in concentrations of >0.03 wt%. Etched samples of this alloy were examined in the SEM where this mode of attack is easy to recognize, but no evidence of the defect was observed on any of the caustic etch or “acid etch” treated coupons.

Streaking

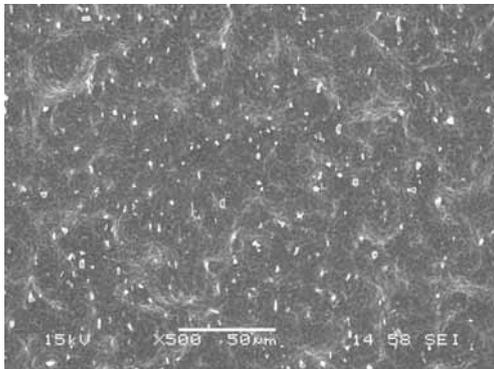
The AA6063 control alloy was utilized for this part of the study. Images of the as-etched surfaces of the T-slot profile photographed under illumination to reveal the streaking are shown in Figure 8. The treatment where the 180-s “acid etch” only was applied (8b) gave the minimum streaks on the surface although it was still not completely streak-free. Streaks and die lines were still evident after the shorter 60-s “Acid Etch”/20-s NaOH treatment (8a) probably because insufficient metal was removed. Applying the 40-s NaOH etch after the 180-s “Acid Etch” (8c) appeared to reveal some streaks, but the surface was more uniform than that produced by the standard 10-min “Caustic Only” etch (8d). The results suggest that the insensitivity of the “acid etch” to microstructure and composition results in a more streak-free surface. However, the short secondary caustic treatment appears to “bring back” some of these features.



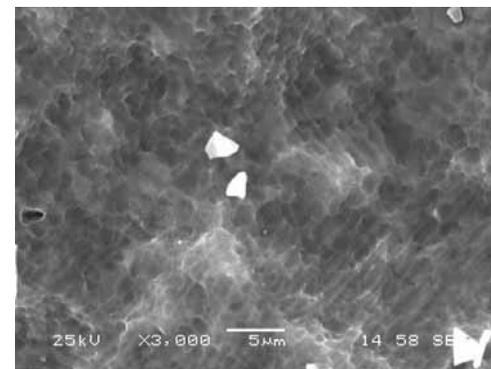
7a. 10-min NaOH



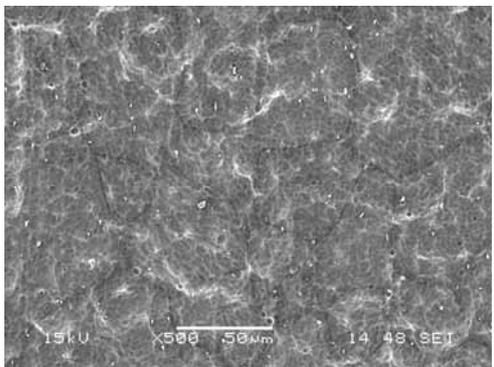
7b. 10-min NaOH



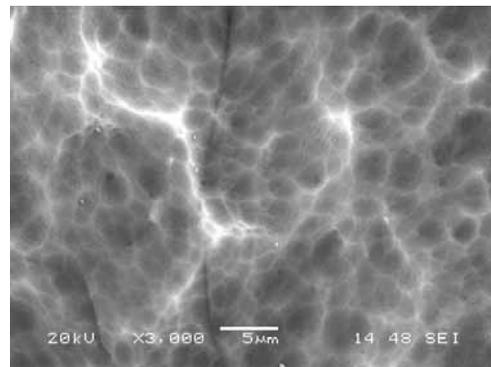
7c. 3-min "Acid Etch Only"



7d. 3-min "Acid Etch Only"



7e. 3-min "Acid Etch"/40-s NaOH



7f. 3-min "Acid Etch"/40-s NaOH

Figure 7. Secondary Electron Images of Etched and De-smutted Surfaces (AA6063 Control)

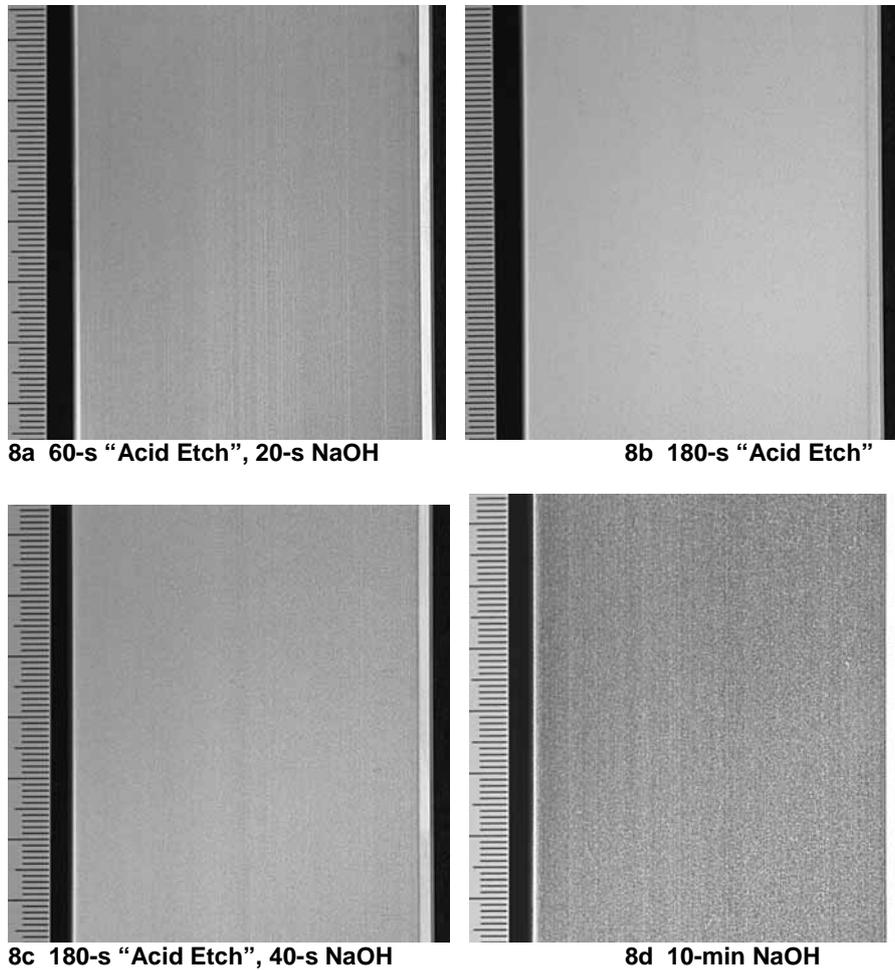


Figure 8. Optical Images Showing Extent of Streaking after Etching

Discussion

The relative performance of an "acid etch" as compared to caustic etching can be explained by differences in the underlying mechanism of aluminum dissolution at the surface. In caustic etching, smooth bottomed pits up to 10 μ in size are formed at microstructural features, in particular the Al-(Fe,Mn)-Si intermetallics and grain boundaries and, as a result, the final finish is highly sensitive to small changes in the original extruded microstructure. In the case of acid etching, the attack appears to take place in the form of crystallographic pitting, resulting in a finer more uniform pit distribution that is independent of the microstructure. The application of a secondary caustic treatment does modify the acid etched surface, but the underlying features are retained such that the recommended processing conditions of 3-min "acid etch"/40-s NaOH gave significantly lower gloss than typical 10-15-min caustic etching with 1/3 of the metal removal.

Today, streaking is a major quality issue for anodized extrusions. There are a variety of causes of streaks, but the most common and difficult to avoid are those simply due to variations in flow due to inevitable features of the die design required to produce the required profile. In these simple tests, the “acid etch” clearly showed a reduced level of streaking compared to 10-15-min long-life caustic etching.

Acid etching also appears insensitive to alloy composition both in terms of impurities and the principal alloy elements, magnesium and silicon. This has some implications for alloy selection and design. For example, the iron additions typically made to AA6063, to promote a matt finish, are not required with acid etching. The use of lower levels of this element would improve the extrudability and mill finish of this alloy for non-anodized applications. Currently, many extruders using AA6360 restrict it to non-anodized applications because of the increased brightness after caustic etching and resulting matching problems. With acid etching, this restriction is no longer required and the increase in press productivity associated with AA6360 can be obtained.

Conclusions

Acid etching appears to offer the following advantages over conventional caustic etching:

1. The etched surface topography has a finer more uniform pit distribution with very low sensitivity to microstructural features.
2. A lower gloss surface can be produced with ~ 1/3 of the metal removal.
3. The etched and anodized surface has low sensitivity to alloy composition.
4. The appearance of extrusion streaks is reduced.

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