

Preferential Grain Etching of AlMgSi(Zn) Model Alloys

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Preferential grain etching is a problem occurring on aluminum products during alkaline etching prior to anodizing, especially if the etching bath contains small amounts of dissolved Zn. The visually uneven, "grainy" surface is caused by different etch rates for different grains, giving a terracelike surface topography. Polished samples of an AlMgSi alloy with different amounts of Zn were etched in NaOH solution. Grain orientations in selected areas were determined by electron backscatter diffraction. The low-Zn samples did not show preferential grain etching. On the higher-Zn alloys, grains with surface planes close to {111} were found to etch at a higher rate than those with other orientations. Secondary ion mass spectrometry depth profiling and imaging, combined with white light interferometry analysis, showed a clear correlation between the deep lying grains and a surface enriched in Zn, suggesting that Zn enrichment by alkaline etching occurred by selective dissolution of aluminum rather than a dissolution– redeposition mechanism. Zn-enriched grains become more active than the other grains as a result of a decrease in the rate of the water reduction reaction.

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Preferential grain etching, also referred to as "grainy appearance," "galvanizing," or "spangling," is caused by the presence of Zn in the alkaline etching bath. As little as only a few ppm Zn dissolved in the bath is sufficient to produce the effect.¹ The problem may occur in production lines where alkaline etching is used prior to anodizing. A common practice to avoid preferential grain etching is to precipitate zinc by adding sulfides or chromates to the etching bath.¹

Koroleva et al.² investigated preferential grain etching of high purity aluminum on neighboring grains with surface normals (334), (225), and (119). Rounding off to the nearest low-index planes, they found that the largest height difference existed between the {001} plane and the deeper {111} plane. The {112} plane was etched to about 1/3 of this distance from the higher {001} plane. They also measured the open circuit potential of the three grains and found an increasingly negative potential with grain depth after etching. The trend was linear with the grain depth, within the measurement uncertainties, and constituted a drop in the potential of about 20 mV from $\{001\}$ to the $\{111\}$ surface. Recent work by Gentile in the same group using electron backscatter diffraction (EBSD), Rutherford back scattering, and atomic force microscopy on Al alloyed with 1.1 atom % Zn showed that alkaline etching and desmutting in nitric acid gave varying degrees of Zn enrichment for grains of orientation $\{113\}, \{101\}, \text{ and } \{001\}, \text{ with the } \{001\} \text{ as the most highly enriched}$ plane.

The mechanism by which Zn promotes preferential grain etching is not well understood. It is not clear whether Zn has to be present in the etching bath or Zn alloyed with the metal is a possible cause for the preferential etching phenomenon. Furthermore, the reasons for the selectivity of grain orientation to etching and the electrochemical mechanism of selective grain etching in the presence of Zn are not clarified. The objective of this work is to provide further evidence on how the presence of Zn in the aluminum substrate affects the etch response by comparing the behavior of AlMgSi model alloys with various Zn concentrations. The interrelationship between topography, grain orientation, and Zn distribution on the etched surfaces was studied by combining white light interferometry (WLI), EBSD, and secondary ion mass spectrometry (SIMS) results acquired from the same area on the specimens.

Experimental

The specimens used in this study were model alloy extrusions containing about 0.6 wt % Mg, 0.5 wt % Si, 0.2 wt % Fe, 0.01 wt % Mn, and 0.01 wt % Cu, with various amounts of Zn added. The added Zn levels were 0.03, 0.11, 0.22, and 0.8 wt %. Direct chill cast billets of the alloys, 203 mm in diameter, were homogenized at 575°C for 2 h followed by air cooling to room temperature. The billets were then preheated to temperatures between 430 and 520°C, extruded into 75 mm \times 2 mm flat profiles in a 20 MN press, air cooled, and finally artificially aged to the peak-strength T6 temper. All alloys exhibited a fully recrystallized grain structure, with a grain size of about 100 µm.

EBSD patterns were obtained with a Hitachi S-4300SE scanning electron microscope operated at 20 kV acceleration voltage. The sample tilt was 70°, the working distance 20 mm, and the analysis grid size 5 μ m. Samples of about 1 cm² in area and 2 mm thickness were mechanically ground and polished through 1 μ m diamond paste finish. They were then electropolished to improve the quality of the EBSD images. Electropolishing was performed in a bath consisting of 1/3 volume fraction nitric acid and 2/3 volume fraction methanol at -35° C. The applied potential was 12 V, and the electropolishing time was 2 min. The deviation angles from the $\langle 111 \rangle$ direction were determined for 90 selected grains by quantitatively comparing the color codes of the EBSD image to the color values in the accompanying stereographic triangle. This method has an estimated error in the angles of about $\pm 5^{\circ}$.

After the EBSD analysis, the samples were again mechanically polished, but only lightly to 1 μ m finish, removing a few micrometers of material, thereby keeping the surface grain pattern essentially unchanged from the EBSD grain images. This gave a mirror finish surface with root-mean-square roughness $R_q = 18$ nm. The purpose of the mechanical polishing was to ensure that the subsequent caustic etching was not affected by the oxide film and dealloyed metal layer formed by electropolishing. The samples were etched for 30 s in 10 wt % NaOH solution at $(60 \pm 1)^{\circ}$ C, removing an average of 3–4 μ m from the polished surface. An initially smooth surface en-

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Figure 1. (Color online) Topography images of etched AlMgSi alloys with (a) 0.03 wt % Zn, b) 0.11 wt % Zn, and (c) 0.22 wt % Zn, showing increased susceptibility to preferential grain etching with Zn content in the alloy. The images have a common height scale from -400 to +400 nm relative to the average surface height.

sured that any height differences after etching were a result of different etching rates. Since previous investigations indicated that desmutting could remove elements enriched near the surface, the samples were not desmutted after etching. They were only rinsed in water and air dried.

WLI measurements were performed using a WYKO NT-2000 from Veeco Instruments. This enabled rapid and accurate determination of the etching topography. Roughness values (R_a) were obtained from the WLI images as the root-mean-square deviation from the best-fit plane to the measured surface topography. Such R_a values are generally higher than the ones obtained by a mechanical stylus since the light can penetrate deeper into crevices than a stylus with a finite radius. In this case with relatively smooth grains and a terracelike grain topography, the R_a value reflects the height deviations of the grains and not their local roughness. Since the smut layer was optically transparent, it did not affect the topography measurements. Individual grain heights were measured from threedimensional WLI images by averaging over a suitably sized rectangle within each grain, avoiding smut particles on the surface. This was done in both the x and y directions, and the average value was used as the grain height. All values were given relative to the surface mean height. The estimated uncertainty in the grain height value is 3 nm, based on the variability between the x-y pairs. WLI was also used for determining crater depths after SIMS sputtering. Here, difference images were produced by subtracting an image made before SIMS analysis from the image after SIMS depth profiling, in which craters were sputtered on selected grains. The depth of each crater could be read out directly from these difference images. The crater depths were used for calibrating the scale of the SIMS depth profiles.

SIMS measurements were performed using a CAMECA IMS 7f instrument. The primary (sputtering) ion beam consisted of 10 keV O_2^+ in order to get low detection limits for Zn and Cu. Depth profiles of selected grains were obtained from an area of 100 µm by 100 µm using a primary beam current of 100 nA. The elemental maps were recorded using a primary beam of 2 nA. The signal from the depth profiles was taken from a circular area of diameter 32 μm in the center of the crater. The sputtering time was 500 s for most craters, with an average sputtering rate of 1.2 nm/s, as found by measuring the crater depth using the white light interferometer. Profiles were made for the ionic isotopes ¹H⁺, ⁶³Cu⁺, and ⁶⁶Zn⁺. In addition, the fragment ²⁷Al₃⁺ was included to monitor the matrix signal and possible topographical effects. Before plotting the depth profiles, the intensity signals for the four species were divided by the corresponding signals from the bulk of the Al alloy to obtain normalized signals, which could be compared from grain to grain. By checking the reproducibility of the bulk signal of Zn for such profiles, the uncertainty in the SIMS quantification was estimated to be 10%

Since the samples were not desmutted, there was a composite layer of aluminum and magnesium hydroxides on the surface, which also contained individual smut particles. In order to make compositional images in the regions near the aluminum surface, the copper signal from the depth profile was used to determine the thickness of the smut layer. The 500 μ m by 500 μ m area to be imaged was sputtered rapidly (200 times faster than during the subsequent imaging) until the rising aluminum signal crossed the falling Cu signal. This typically occurred at about 75 nm depth.

Results

Alkaline etching of polished samples with 0.03, 0.11, and 0.22 wt % Zn gave increasing surface roughness (R_a) values of 0.10, 0.13, and 0.28 µm, respectively. Figure 1 shows WLI topography images of the three samples after 30 s of etching. An increasing susceptibility to preferential grain etching with Zn content is evident; i.e., the differences in the dissolution rate between individual grains increased with increasing Zn concentration in the alloy. While preferential grain etching was negligible on the 0.03 wt % Zn alloy, the deepest etched grains on the 0.22 wt % Zn alloy were about 0.8 µm deeper than the least etched ones. Weight loss measurements on a separate set of specimens showed that the overall etch rate of the alloys was between 6 and 7 μ m/min. Thus, etching under the present conditions caused the macroscopic surface of all the alloys to recede by $3-4 \mu m$. Hence, the strong effect of Zn on surface topography after etching, shown in Fig. 1, is not related to any overall differences in etch rate among the alloys.

EBSD analyses of samples containing ≥ 0.2 wt % Zn further showed that the deepest (preferentially etched) grains had an orientation close to {111}, whereas the least etched grains had a near {001} orientation. Figure 2 summarizes WLI and EBSD data acquired from 90 individual grains on an etched specimen. It shows that there is a correlation between the depth of individual grains and their deviation from the {111} orientation: The closer the orientation of a grain is to {111}, the faster it will dissolve.

In order to investigate any correlation that may exist between topography and local variations in the Zn content on the etched surface, the surface compositions of selected grains were measured by SIMS. Depth profiles for Al, H, Zn, and Cu were acquired from grains over a range of etch depths. Since the incident beam consisted of O_2^+ ions, reliable oxygen profiles could not be obtained. Typical depth profiles for the 0.22 wt % Zn alloy are shown in Fig. 3. The Al signal in the depth profiles reached the bulk level at a local depth of about 200 nm. This corresponds to the depth where the hydrogen signal leveled off, indicating that there was no more hydroxide con-



Figure 2. Correlation between crystallographic orientation and relative etch depth of grains on AlMgSi alloy with 0.8 wt % Zn. The deepest grains had an orientation close to {111}.



Figure 3. (Color online) Normalized SIMS depth profiles obtained from within a single grain on etched AlMgSi alloy specimen with 0.22 wt % Zn.

taining smut at that depth below the original sample surface. Both Zn and Cu were significantly enriched at the surface. The Zn and Cu signals fell steadily from the surface peak at 20 nm and reached bulk levels around 300 nm or deeper.

Figure 4 shows SIMS elemental maps of Al, Zn, and Cu along with the topography image made after the SIMS analysis. The images show the correlation between the height of the etched grains ("Topo" where the deep grains are dark) and the lateral distribution of elements in the SIMS maps (Al, Zn, and Cu where brighter regions show higher concentrations of the respective elements). There was a clear correlation between the etching topography and the surface concentration of Zn. The deeper-etched grains had a higher amount of near-surface Zn and Cu than the less-etched grains. The images were obtained at a depth of 75 nm below the top of the smut layer in the transition region between smut and bulk. Thus, the images of Fig. 4 are more representative of the surface composition



Figure 4. (Color online) Topography image (Topo) of an alkaline etched sample containing 0.22 wt % Zn and corresponding SIMS elemental maps for Al, Zn, and Cu. On the topography image, the grains appear darker with increasing depression due to deep etch. On SIMS elemental maps, grains appear lighter with increasing elemental concentration. Thus, the deeper etched grains are leaner in Al and richer in Zn and Cu at their surfaces in comparison to the neighboring less deep-etched grains. Prior to imaging, 75 nm of the surface smut was removed by sputtering.



Figure 5. Zn signal from depth profiles on individual grains, integrated over the range 75–200 nm (which corresponds to the near-surface region), vs their relative etch depth.

near the aluminum metal than of the chemistry in the smut layer (0-75 nm). The elemental maps also show some smut particles with varying amounts of Al, Zn, and Cu.

An alternative way of quantifying the amount of Zn and Cu on grains of different heights is to make local SIMS depth profiles, as shown in Fig. 3, by sputtering entirely within each individual grain. In Figure 5, the near-surface Zn signal is plotted versus the height of the grain for 13 selected grains of various heights. Also here the near-surface Zn correlates with the etched grain depth, the deep grains showing more Zn on the surface. The deviations from a linear relationship are generally within the expected uncertainty of 10% in the SIMS quantification.

Comparing the 13 independent depth profile measurements of Zn that were used for obtaining Fig. 5 showed that the smut layer was not significantly thicker on the deep grains than on the shallow ones. Moreover, the largest height difference between the grains in the sample was 0.8 μ m in relation to a total etching depth of about 3.5 μ m. Assuming that the smut layer grew linearly with the etching depth, 25% thicker layers would be expected to develop on the deepest grains. Since such differences were not observed, it can be concluded that the smut layer reached a steady state thickness on all grains during etching independent of the local etching depth.

Discussion

The present work verified the information in the literature that grains which have near {111} orientation on aluminum alloys are more susceptible to alkaline etching than grains with other orientations.^{2,4,5} It was further verified that the presence of Zn in the alloy increases the degree of preferential etching. A concentration of 0.2 wt % Zn created height differences large enough that the individual grains could be distinguished by the naked eye. Grains with surface planes near {111} were always the deepest. In addition, the surface of the grains with this orientation should exhibit a more active potential than that of the grains with the other orientations. This potential difference is necessary as the driving force for the expected microgalvanic coupling between the more active and nobler grains, which gives the difference in the observed etching rates. Activation of Zn-enriched {111} grains is likely caused by a decrease in the rate of the water reduction reaction in relation to the Zn-lean grains, assuming that the enriched surface Zn is metallic. The water reduction reaction is known to occur at a much lower rate on Zn than on Al in alkaline solutions.⁶

A new result of the present work was the enrichment of the {111} planes by Zn in the alloy rather than by Zn already present in the etching bath. This result was based on SIMS characterization of surfaces which were not desmutted after etching. Preliminary work

on desmutted samples did not show Zn enrichment on deep grains. After attempting to desmut by use of a hot chromic-phosphoric acid stripping bath (ASTM G1-72), the sample studied in Fig. 4 showed, after new SIMS analysis of the same region, that Zn was redistributed on the surface into a nearly homogeneous layer. Desmutting after etching may thus radically change the distribution of Zn caused by alkaline etching. This observation complicates the analysis of the true near-surface Zn after etching. Moreover, enrichment of Zn on the more active grains by dealloying is an expected result,⁷ assuming that the aluminum matrix is more active in alkaline solution than the Zn component of the alloy. If Zn enrichment were a result of a dissolution-redeposition mechanism, then Zn enrichment of the surface of the more noble grains would be expected. This would result from the galvanic coupling of the active and noble grains, causing selective oxidation of Zn from the active grains to form zincate ions and reduction of these as metallic Zn on the noble grains. There was no indication of such enrichment from our SIMS data. On the contrary, both the SIMS images and the depth profiles showed enrichment of Zn and Cu on the deepest grains having near $\{111\}$ orientation. Recent results by Gentile et al.^{3,4} for a solid solution AlZn alloy indicated that a {100} grain had a higher Zn enrichment than three grains with orientations {225}, {314}, and {113}. However, those results cannot be compared with the present results because grains close to the {111} orientation were not investigated by Gentile et al.

Several studies have shown that $\{111\}$ grains etch faster even in very pure Al, ^{2,5,8-10} in agreement with the present results. This indicates that Zn simply promotes an effect already present: that the $\{111\}$ surfaces are electrochemically more active than the other grain orientations.

Conclusions

Using WLI, EBSD, and SIMS to study the topography, grain orientation, and local chemical composition of alkaline etched surfaces of AlMgSi alloys with varying amounts of Zn, we find the following: • The deepest grains have crystallographic orientations close to {111}.

• The deepest grains also have more near-surface Zn than the other grains, with a linear trend toward less Zn for the higher grains.

• Zn enrichment occurs by selective dissolution of the active aluminum component (dealloying) rather than dissolution and redeposition of Zn.

• Zn-rich grain surfaces oxidize at a higher rate than the neighboring Zn-lean grains because Zn reduces the rate of the water reduction reaction, creating galvanic driving force between the two types of grains.

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References

- S. Wernick, R. Pinner, and P. G. Sheasby, in *The Surface Treatment and Finishing of Aluminium and its Alloys*, 6th ed., Vol. 1, p. 203, Finishing Publications Ltd., Stevenage, UK (2001).
- E. V. Koroleva, G. E. Thompson, P. Skeldon, and B. Noble, Proc. R. Soc. London, Ser. A, 463, 1729 (2007).
- M. Gentile, P. Skeldon, and G. E. Thompson, Abstract 644, The Electrochemical Society Meeting Abstracts, Vol. 901, San Francisco, CA, May 24–29, 2009.
- M. Gentile, E. V. Koroleva, P. Skeldon, G. E. Thompson, P. Bailey, and T. C. Q. Noakes, *Surf. Interface Anal.*, 42, 287 (2010).
 M. Gentile, E. V. Koroleva, P. Skeldon, and G. E. Thompson, Abstract 1710, The
- M. Gentile, E. V. Koroleva, P. Skeldon, and G. E. Thompson, Abstract 1710, The Electrochemical Society Meeting Abstracts, Vol. 902, Vienna, Austria, Oct 4–9 2009.
- M. D. Zholudev and V. V. Stender, J. Appl. Chem. USSR, 31, 711 (1958).
 M. Gentile, E. V. Koroleva, P. Skeldon, G. E. Thompson, P. Bailey, and T. C. Q. Nacker, Grange Grange Grange (2010).
- Noakes, Corros. Sci., **52**, 688 (2010). 8. G. M. Treacy and C. B. Breslin, *Electrochim. Acta*, **43**, 1715 (1998).
- 9. S. Lee and H. S. White, J. Electrochem. Soc., **151**, B479 (2004).
- M. Miakova, M. Plchova, and H. Halasa, Collect. Czech. Chem. Commun., 52, 88 (1987).