Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 781-786

Effect of Composition, Grain Size and Texture on the Etching Response of 6xxx Alloys

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Six different alloy compositions within the 6xxx system were extruded followed by cold rolling, solutionizing, and ageing giving a fully recrystallized structure with a random texture. Small samples from the profiles were then investigated for preferred etching of grains in the presence of different levels of Zn and Fe in the sample as well as with free Zn in the alkaline etch bath. Optical microscopy and EBSD orientation analysis of the etched surfaces have shown that not only <111> oriented grains towards the surface were preferentially etched but orientations deviating several degrees from the <111> orientation. The strength of etching appeared to be weakening from <111> oriented (strong preferential etching) to <110> (relatively less preferential etching) to100 (no preferential etching). The study has also revealed that even for an alloy with a very low content of Zn, which was not preferentially attacked in an etching bath free of zinc ions, a free-Zn content of few ppm in the etching bath is enough to initiate a preferred attack on <111> oriented grains. However the nature of the attack seems to be different from when the Zn is present in the sample. The study also showed that presence of Fe and different grain size in the same alloy had no appreciable effect on the nature of etching response in a caustic bath with free Zn. The results reported in this work are based on small scale laboratory tests in pure caustic soda solution and not in an industrial scale etching process. The study has been performed on a model material to simulate the as extruded surface.

Keywords: *Grainy appearance, Preferential etching, Aluminium, 6xxx alloys.*

1. Introduction

Etching of aluminium alloy profiles in alkaline etch solution prior to anodizing is carried out to remove natural oxide layer and scratches on the surface of profiles and to give them a uniform dull finish. However sometimes the surface of the etched profile shows a characteristic uneven etch pattern after etching with some grains on the surface etched more than the others. When examined under the scanning electron microscope a clear topography can be observed. This defect is referred to as spangling, galvanizing or grainy appearance. In the literature this effect has been attributed to free Zn in the etch bath [1, 2] but no systematic study has been reported to show the role of different factors leading to this appearance. To avoid the formation of grainy appearance, free Zn in the alkaline etch bath has to be precipitated by adding sulphides or chromates to the alkaline etch bath [1, 2].

The objective of the present study is to gain a better understanding on etching response of 6xxx alloys in caustic etch bath by isolating factors such as the effect of Zn in the profile sample or effect of free Zn accumulated in the etch bath (or the combined effect of both), the effect of Zn in presence of Fe, effect of grain size and the effect of texture.

2. Materials and Experimental Procedure

Six different alloy compositions were studied in the present work and the composition of the alloys is given in Table 1. Billets of 95mm in diameter were cast and homogenised according to industrial practice. The billet sections were extruded to profiles of 0.5 cm × 7 cm in cross section. The profiles were water cooled directly after the outlet of the die. The extrusion parameters were as follows:

temperature of container: 430^{o}C, temperature of billet: 490^{o}C, speed of profile: 30 m/min. After extrusion the profiles were stretched 0.5%.

Table 1: Alloy composition and grains size from longitudinal transversal cross-section samples after cold rolling, solution treatment and ageing

Alloy	Composition (wt %)						Grain size	
	Fe	Si	Mg	Mn	Zn	Cu	0.7 strain	1.5 strain
A1	0.15	0.42	0.46	0.02	0.01	0.01	50	41
A2	0.16	0.42	0.46	0.02	0.05	0.01	57	37
A3	0.16	0.43	0.46	0.02	0.08	0.01	53	39
A4	0.24	0.46	0.47	0.03	0.00	0.02	42	32
A5	0.25	0.46	0.47	0.03	0.04	0.02	37	27
A6	0.25	0.47	0.46	0.03	0.10	0.02	40	25

In order to obtain a random crystallographic texture with different grain sizes, the extruded materials were cold rolled to strains of 0.7 and 1.5 followed by a heat treatment procedure which also was a part of the solutionising process. The samples were solutionised at 540°C and held there for 20 min followed by water quenching. Ageing treatment was done by heating the samples at a rate of 200 °C/h, holding them for 5 hours at 185 °C followed by air cooling. For each alloy a longitudinal transversal cross-section surface was studied. The etching treatment of the samples is given in Table 2. Longitudinal cross-sections (1.0 cm × 0.5 cm) of these specimens were metallographically prepared down to quarter micron diamond paste to give a plane clean surface. To study the etching response of the alloys 100 ml of etch solution was taken separately, from a 2000 ml bath, for each alloy. This was done to avoid addition of free Zn to the etching bath. The samples were desmutted after etching to remove the smut layer formed on the surface of the samples during etching (Table 1). To find out the effect of free Zn in a bath of volume 2000 ml a sample from alloy-3 was etched in the bath and the amount of Zn in ppm added to the bath was calculated from the weight loss of the dissolving sample. In this case the samples were etched one by one in the same bath and the accumulation of free Zn in the bath with time was followed carefully. The microstructure of the etched samples was studied using the Leica DMI5000 M optical microscope, Philips XL 30 S field emission gun scanning electron microscope (SEM) equipped with electron backscattered diffraction (EBSD). The EBSD data was collected and analyzed using TexSEM Laboratories (TSL) software. The EBSD orientation maps have been slightly processed to remove the unindexed or wrongly indexed pixels in the maps.

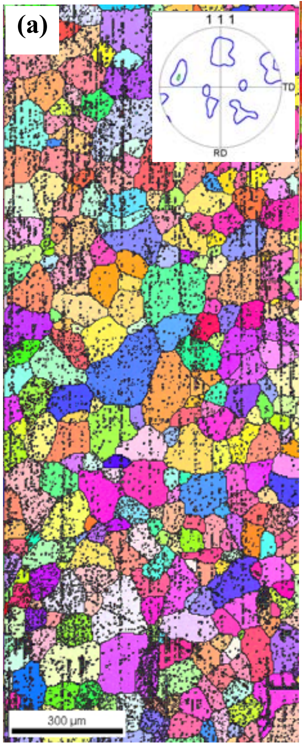
Table 2: Parameters for the etching treatment of the samples.

Step	Composition	Time	Temperature
Etching	50 g/l NaOH (2000 ml)	1min	70 °C
Rinsing	Deionised water	Dip	Room temperature
Desmutting	40 vol% HNO_3	Dip	Room temperature
Rinsing	Deionised water	Dip	Room temperature
Rinsing	Ethanol	Dip	Room temperature

3. Experimental Results

The grain structure and texture of one of the alloys (A1) in two sections (longitudinal –transverse cross section and as extruded surface) which are representative for all alloys, are shown in Fig. 1. The grain structure is seen to be fully recrystallised and uniform in both regions. There is a relatively sharp cube texture in the cross section , while it is random in the outside surface. The grain structures and crystallographic textures for the cold rolled and annealed materials are presented for one of the alloys

(A1) in Fig. 2 and show random textures for both strain variants. The grain size after cold deformation, solution treatment and ageing treatment for the six alloys obtained by EBSD orientation mapping is given in Table 1



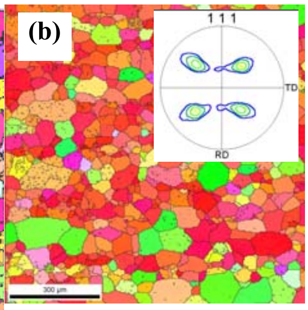


Fig. 1: Grain structure and texture in a) surface and b) longitudinal transversal cross section of variant A1 as extruded.

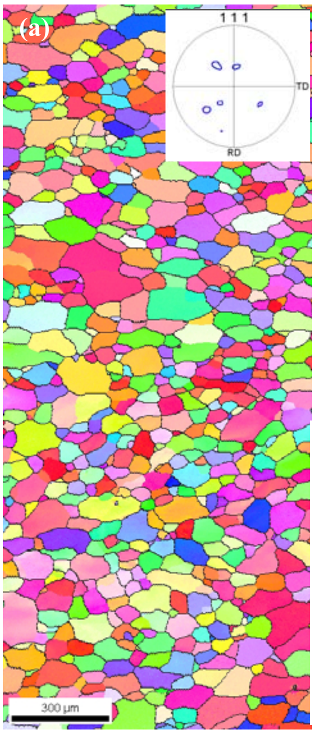


Fig. 2: Grain structure and texture after rolling and annealing the extruded profile variant A1 a) strain of 0.7 and b) strain of 1.5. The pole figure inserted in fig 2a represents the texture for Figs. 2a and 2b.

The secondary electron (SE) image and corresponding EBSD orientation maps of the same area from A1 and A3 are shown in Fig. 3. Not shown here but similar to A1 alloys A2, A4 and A5 also show only grain boundary attacks and deep pit formation. On the other hand alloys A3 and A6 show preferential etching of grains in addition to deep pit formations. As it was not possible to keep track of selected grains after etching in the alkaline etch bath, EBSD maps were obtained from the samples after etching. The orientations in the EBSD maps are according to the inverse pole figure colour key given as an insert in Fig. 3b. A comparison between Figs. 3a and 3c shows that in the same etching conditions for A1 with low amount of Fe and Zn there are nearly no preferentially attacked grains while A3 with same amount of Fe but high amount of Zn exhibits a preferential attack on <111> oriented grains. A further orientation analysis of grains in the orientation maps has shown that in the presence of high Zn in the alloy not only <111> oriented grains are preferentially etched but also grains whose <111> directions deviate up to 22° from the normal to the surface. Depth of etched grains with respect to orientation was not measured but is based on the topographic effects in a SE image. However the observations are supported by references [3, 4]. EBSD data analysis also showed that not only <111> oriented grains etch strongly but also grains with their <110> direction parallel to the surface normal. Thus it can be stated that the strength of etching appeared to be weakening from <111> oriented (strong preferential etching) to <110> (relatively less preferential etching) to <100> (no preferential etching).

The study has shown that presence of Fe in different alloys has no apparent effect on the etching response of 6xxx alloys. However it can indirectly affect the appearance of etched profiles by keeping the grain size small because the appearance of a sample etched under the same conditions but with different grain size exhibit a different surface appearance. The study has also shown that smaller grain size shows same dependence on orientation for preferential etching and also the extent of etching is the same for similar orientations given the etching conditions are the same.

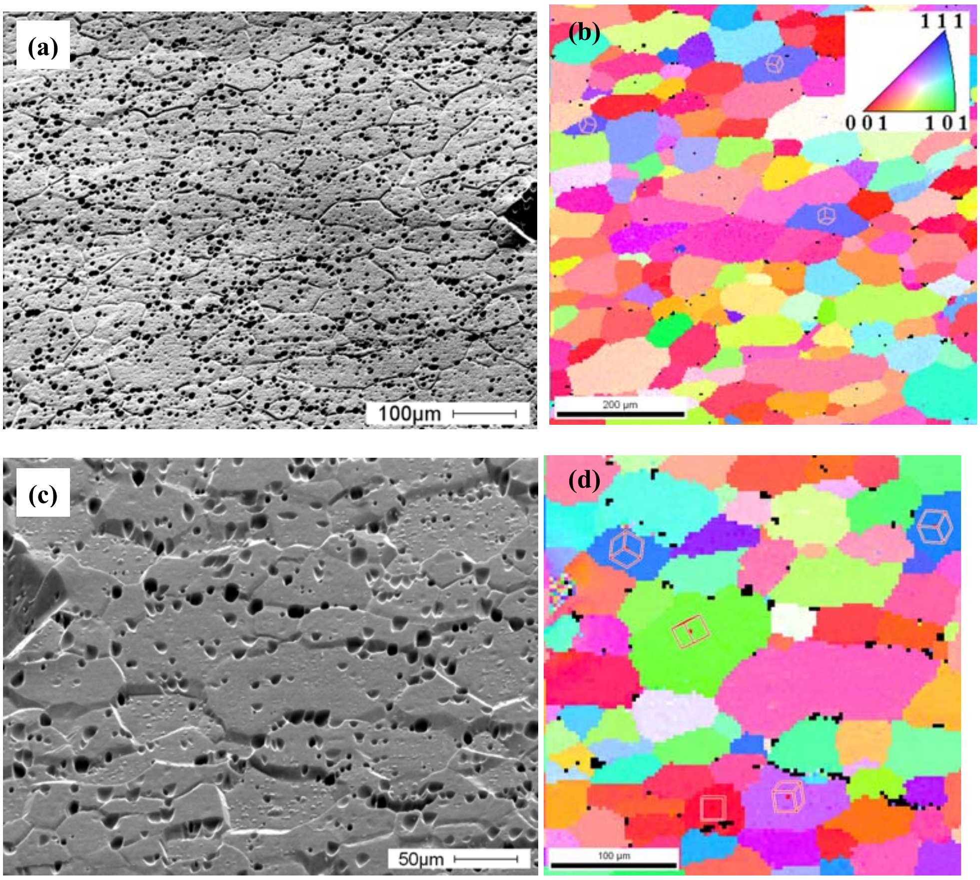


Fig. 3.
a) Secondary electron (SE) image of longitudinal transversal etched surface from alloy-1 after cold deformation and T6 treatment.
b) EBSD orientation map from the same area as in 1a.
c) SE image of longitudinal transversal from alloy-3 after cold deformation solution treatment and ageing.
d) EBSD orientation map from the same area as in 1c. Micro indents in the SE image were put to keep track of the area.

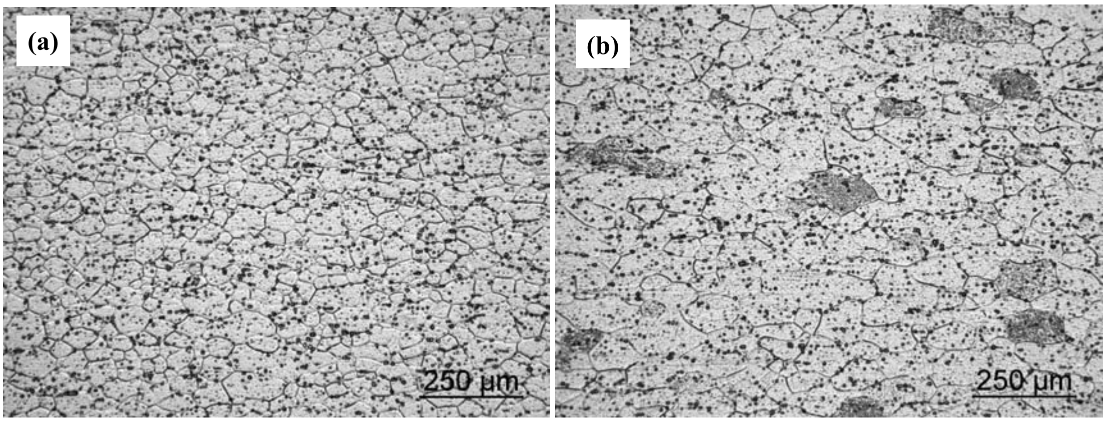


Fig. 4. Optical microscope images of A1 (0,7 strained, T6 tempered) showing etching response of samples in the presence of a) 3.7 ppm Zn, b) 5,7 ppm Zn.

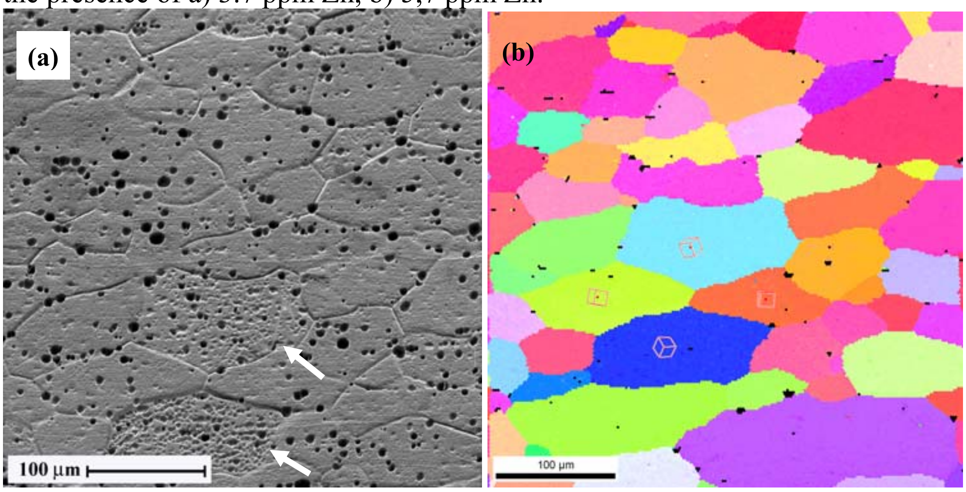


Fig. 5. SE images and EBSD orientation maps from A1 (0,7 strained, T6 tempered) showing relation between preferential etching and orientation of grains. a) SE image after etching in the bath with 5.7 ppm Zn. b) Orientation map from the same area as in (5a).

Samples from A1 and A4 each with two different grain sizes were also studied for etching response in an etch bath with free Zn. The experiment was carried out in an etch bath with larger variation, of about 2ppm, in the amount of free Zn in the bath. The test showed that at a level of about 3.7 ppm in the bath no preferential etching of grains could be seen, but for a Zn content of about 5.7 ppm in the bath preferential etching of the grains could be observed. The optical microscope images from the samples are shown in Fig.4. A comparison of images from A1 and A4, not shown here, has revealed that variation in the amount of Fe in the alloy as given in Table 1 does not affect the etching behaviour of the material.

The work reveals that as the amount of free Zn in the bath is increased the etching of certain orientation of grains also become stronger. These samples were also studied for orientation relationship with preferentially etched grains and as shown in Fig.5 the preferentially etched grains have orientations close to <111> orientation with reference to the surface. The arrows in Fig.5a highlight the grains which have relatively higher number of small pits as compared to grains whose <111> direction is not parallel to the surface normal. It can also be seen in Fig.5 that the presence of different amount of Fe in the alloys had apparently no effect on preferential etching of grains in presence of free Zn in the etch bath. Also the preferential attack of grains in the presence of free Zn in the etch bath is apparently independent of grain size. A comparison between Figs. 3c and 5a shows that the etching response of grains when Zn is present in the sample is different than when Zn is present in the etch bath. In case when Zn is present in the sample the grains etch preferentially but the surface of etched grains seem to be smooth in the present work. On the other hand when the Zn is present in the etch bath the attack on the surface of preferentially etched grains is in the form of pitting.

4. Discussion

As described above, the texture of as extruded profiles with a fully recrystallized grain structure shows a relatively strong texture gradient through thickness. The outer surface layer (approx 50 μm) has a random texture while the microstructure in the mid-thickness is strongly dominated by the cube texture. The texture just below the surface (from 50-100 μm towards the mid-thickness) is of a rotated cube type, but much less intensive as the cube texture in the centre region. The random texture in the cold deformed and solutionised profiles is most likely achieved by nucleation of recrystallisation from constituent particles (particle stimulated nucleation).

The etching experiments show that when Zn is below 0.05 wt% in the alloy (as in alloys A1, A2, A4 and A5) the grains do not etch preferentially in the alkaline etch bath. The attack is on the grain boundaries. Only in the case of relatively high amount of Zn (0.1 wt%) the grains are etched preferentially. However, when alloys A1 and A4 with amount of Zn $\leq$ 0.01 wt% are etched in an alkaline bath with free-Zn, {111} oriented grains etch preferentially. The preferential attack of grains in an alkaline bath with and without Zn can be explained as follows. Gentile et al. [5] has shown that in an alkaline etch bath there is a varying degree of Zn enrichment in an Al 1.1 at% Zn alloy on different crystallographic planes with {100} plane as the most highly Zn enriched plane. A maximum number of Zn atoms will make {100} planes more cathodic as compared to {110} and {111} planes with less number of Zn atoms. Thus in an alkaline bath without free Zn a {100} plane will be most resistant to chemical attack, {111} plane will be attacked most while {110} plane will be attacked to a degree in between the {111} and {110} planes. Work by Koroleva et al. [6] has shown that even in super purity aluminium the anodic potential decreases in the order of {334} most anodic, {225} and {119} least anodic and preferential etching of {334} oriented grains took place even on high purity aluminium in an alkaline bath. The question then rises; why do the alloys A1 (Fig. 3a),A2, A4 and A5 not show preferential etching in the etch bath without free-Zn but the same alloys show preferential attack in the presence of free-Zn in the etch bath (Figs. 4 and 5). One explanation could be the strength of the etchant. The solution used by Koroleva et al. [6] was 1.5M while the solution used in present work is 1.25M. Preferential attack on near {111} grains in stronger alkaline etch bath could be due to galvanic action between intimately coupled grains. The second explanation of this observation could be: as the attack when Zn is present in the sample is very uniform on the whole surface of a grain (Fig. 3c) and the Zn content is low in case of alloys A1, A2, A4 and A5 the difference of attack on differently oriented grains will not be high enough to see with ordinary SE imaging. The reason why A1 and A4 show preferential attack (Figs. 4 and 5) in presence of free-Zn in the bath could be attributed to collection of Zn in the smut layer causing galvanic action between Zn in the smut and aluminium surface as shown by Holme, et al. [3] that there is a high content of Zn in the smut layer on top of deeply etched grains. Hence it can be deduced that free Zn entrapped in the smut layer give rise to microgalvanic action causing the preferential attack in the form of pitting on {111} plane surface. The deep pits seen in the SE images of all the alloys might be due to α-Al (Fe, Mn)Si particles. These particles in an alkaline solution serve as cathodic as compared to the matrix leading to dissolution of matrix [7].

5. Summary

The OM and SE imaging and the EBSD orientation mapping have shown that in the high Zn alloys the grains having <111> direction parallel to the normal to the etched surface etch strongly. Pole figure analysis further showed that the grains still etch preferentially even their <111> plane normal have a deviation of up to 22° from the surface normal. The strength of etching appeared to be weakening from <111> oriented (strong preferential etching) to <110> (relatively less preferential etching) to <100> (no preferential etching). Under the given experimental conditions the alloys with Zn content ≥ 0.1 wt% show strong preferential attack of grains due to Zn enrichment of {100} grains more than other grains. However this effect is very weak in case of low Zn alloys. A higher content of Fe does not show appreciable effect on the preferred etching response of 6xxx alloys in an alkaline bath with or without free-Zn. However the deep pits in the alloy A6 profile sample appears to be higher as compared to alloy A3. The experiments have shown that even an alloy with low content of Zn ≤ 0.01 wt % exhibits a preferential etching of grains when Zn content in the bath crosses the level of few ppm. The work has also shown that in case of an alkaline bath containing free-Zn the preferential attack is in the form of pitting and not a uniform attack. This could be due to Zn in the smut layer causing microgalvanic action. The pitting attack becomes stronger as the amount of free-Zn in the etchant increases few ppm. The grain size seems to have no effect on the etching response of the grains. The results reported in this work are based on small scale laboratory tests in pure caustic soda solution and not in an industrial scale etching process.

6. References

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