Etching effects and the formation of Streaking Defects on Al Extrusions

Surface defects such as streaking are often present on anodized extrusions of 6xxx series alloys. The streak defect is the result of a difference in intensity and diffuse nature of the reflected light compared to the surrounding material, and is caused by an inhomogeneous distribution of surface imperfections produced during etching. Hence, the etching treatment is an important process step to influence the formation and severity of streak defects on aluminum extrusions.

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Surface appearance is an important characteristic of high quality aluminium extrusions, especially for architectural applications in the building and construction industries.

Surface defects such as streaking are often present on anodised extrusions of 6xxx series alloys, increasing the fabrication cost of these products. The origin of streak defects is a difference in intensity and diffuse reflectance of light compared to the surrounding material[1,2].

The intensity and diffuse reflectance of light is influenced by the surface roughness. Surface imperfections larger than 0.2μm on the material surface can increase the diffuse part of the reflected light and thus decrease the brightness level[3,4]. If the surface imperfections in local regions of an anodized extrusion are such that the surface is rougher than in other regions, a streak will appear in a dull colour[3,4].

During anodizing of an extrusion, an oxide layer is formed on top of the metal surface. Previous research indicates that the gloss after anodizing correlates strongly with the metal surface roughness, and to a lesser degree with the oxide surface roughness. The reason is that aluminium oxide is transparent and the metal/oxide interface, ie the extrusion surface prior to anodizing, is therefore the prevailing reflecting surface and its surface characteristics have a greater effect on the gloss of the anodized part[5]. Consequently, the intensity and diffuse reflectance of light is dependent on the micro-topography of the extrusion surface prior to anodizing[3].

Etching is an important process step to influence the topography of the extrusion surface prior to anodizing. Alkaline etching is the common pre-treatment stage for anodized aluminium sheet and extrusions, particularly for architectural applications. The aim of this process is to produce a homogeneously matt surface[6,7]. However, in the etching process, further surface imperfections can be generated due to uneven chemical attack of the microstructure.

Also, some extrusion surface defects such as pick-up and die lines may not be removed completely from the etched surface and their remains become a part of the surface imperfections on the etched surface. All these surface imperfections are barely modified by subsequent anodizing[7]. Hence, any uneven distribution of surface imperfections formed prior to anodizing can significantly influence the occurrence of streaking defects.

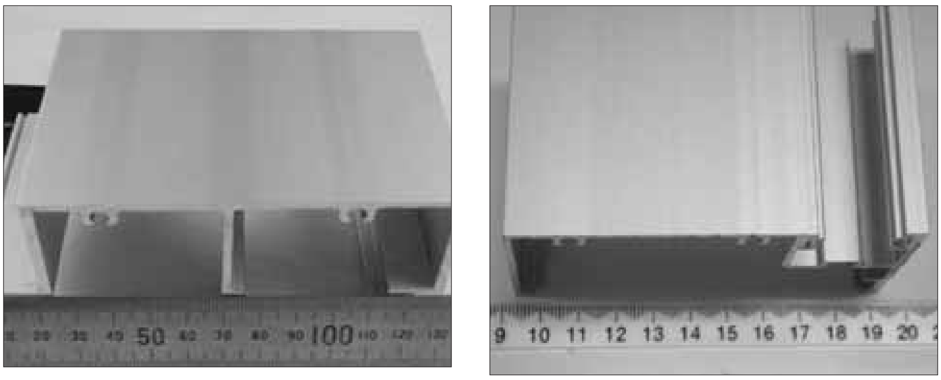

Fig.1 Streak defects on anodized aluminium extrusions of (a-l) Extrusion 1 and (b) Extrusion 2. Arrows indicate streak defects

However, so far, the effect of etching and its process parameters on the formation and severity of streak defects is less understood.

Streak Defect Formation

Streak defects on anodized aluminium extrusions are typically characterised by narrow bands with a different contrast from their surrounding materials.

The streak bands may appear darker or lighter, brighter or duller, in colour and tone compared to the surrounding material[3,4]. **Fig 1** shows examples of streaks defects on anodized aluminium extrusions. The streak bands on Extrusion 1 are located in the regions opposite the web intersections, while the streak defects on Extrusion 2 are observed between or near webs.

In this paper, the location of the surface exhibiting the streak defect is termed the streaked region and the surfaces opposite to the web and the other locations of the extrusion are referred to as web intersection region and normal region, respectively. If a streak defect is present on a web intersection, the streaked region and the web intersection region may refer to the same location as shown in **Fig 1a**.

Microstructural examinations of the streaked and normal regions on the anodized extrusions indicated that an inhomogeneous distribution of surface imperfections is one of the primary causes for the formation of streak defects[4,8,9].

Fig 2 shows SEM morphologies of the anodized surfaces of the streaked and normal regions of Extrusion 1. It is clear that the major difference between the streaked and normal regions is the morphology of grain boundary grooves.

Most of the grain boundary grooves in the streaked region (**Fig 2a**) are very clear though the grooves are not distributed uniformly along the grain boundaries whereas those in the normal region (**Fig**

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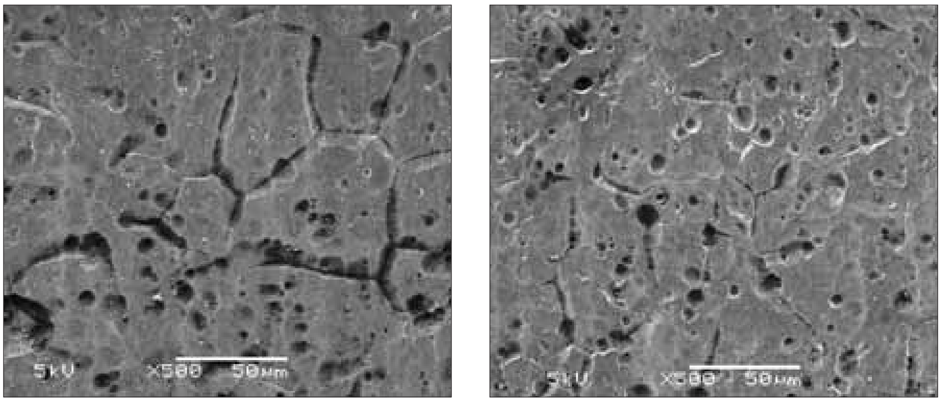


Fig.2 Surface morphology of Extrusion 1 in (l) streaked region and (r) normal region. Arrows indicate grain boundary grooves.

2b) are dim and only small segments are observed. Since the grooves cause a decrease of the diffuse part of the reflected light, the different severities of grain boundary grooves in different locations are responsible for the streak on Extrusion 1. Hence, the inhomogeneous distribution of grain boundary grooves is the primary cause for the formation of the streak defects in Extrusion 1.

Fig 3 shows OM micrographs from different locations of Extrusion 2, which has a major dull colour streak between two web intersection regions. It is evident that large amounts of die-line-remains are present in the streaked region (**Fig 3a**), the cross-section exhibits a strongly waved margin alternately concave and convex (**Fig 3b**), while almost no die line is observed in the normal region **(Fig 3c**) and the surface of the cross-section is flat (**Fig 3d**).The rough surface in the streaked region greatly increases the diffuse part of the reflected light, resulting in a dull colour streak.

Hence, the inhomogeneous distribution of die-line-remains is the primary factor for the formation of the streak in Extrusion 2. In addition, an inhomogeneous distribution of any other surface imperfections can cause streaks on the anodized extrusions. The surface imperfections are produced during etching or remains of extrusion surface defects after the etching [4].

Etching Effect

During etching, surface imperfections can be generated due to uneven chemical attack of the microstructure. Once formed, these surface imperfections are barely modified by subsequent anodizing[7]. To identify the surface imperfections on the final surface of anodized aluminium extrusions, microstructural examination was conducted on the anodized surface or polished surface for the cross-section morphology.

It was found that etching pits, grain boundary grooves and grain etching steps are the most common surface imperfections generated on the extrusion surface during the etching process. The remains of extrusion surface defects such as die lines are also observed on the etched surface under certain process and microstructure conditions[4].

Fig 4 shows the morphologies of different typical surface imperfections on anodized aluminium extrusions. As shown in **Figs 4a** and **4b**, two types of etching pits are observed on the surfaces: large etching pits with a size up to 10µm and small etching pits with a size around 0.2µm. The etching pits are produced during etching due to different reaction rates between intermetallic particles and the aluminium matrix.

Hence, the formation of etching pits is mainly related to the size and distribution of intermetallic phases on the surface. In 6xxx series alloys, the major intermetallic phases are primary Fe-rich intermetallic particles and Mg-Si particles.

During etching, the Fe-rich intermetallic particles have a high electrochemical potential compared to the aluminium matrix, acting as cathodic reaction sites for hydrogen evolution and stimulating anodic dissolution of the surrounding aluminium by forming aluminate[6].

The detachment of the Fe-rich intermetallic particles from the matrix results in the formation of etching pits on the etched surface[3]. The size of the etching pits is always larger than the size of the intermetallic particles and this type of pit can grow during etching to up to 10 µm in diameter[7,9].

In contrast, Mg-Si particles can act as anodes during etching, resulting in the particles dissolving in preference to the aluminium matrix. This preferential dissolution leads to the formation of smaller etching pits with size directly related to the original size of the precipitates[6].

However, not all small etching pits are produced due to the direct dissolution of Mg-Si particles. If the extrusions contain very small Fe-rich intermetallic particles or other second-phase particles, the detachment or dissolution of these very small particles may also result in the formation of small etching pits.

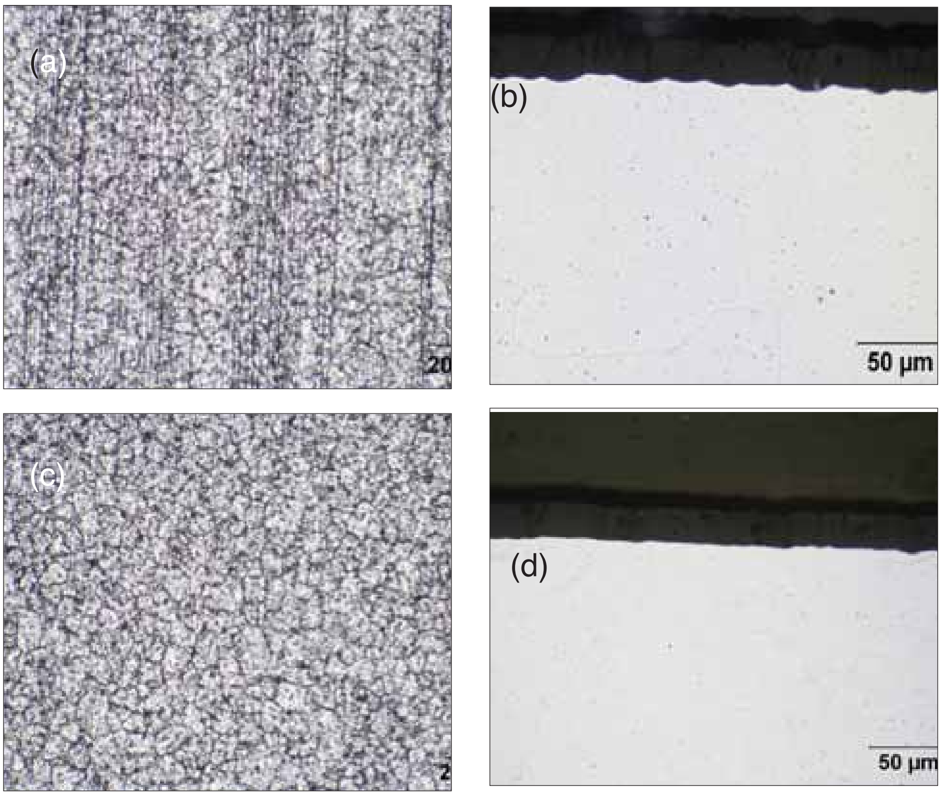
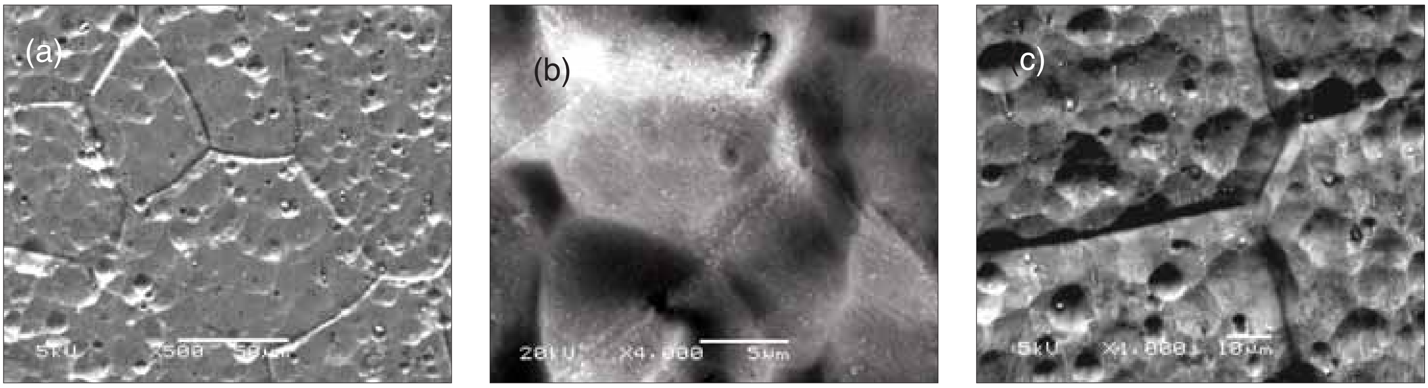


Fig.3 Surface and cross-section OM micrographs of Extrusion 2. (a) Surface of the streaked region, (b) cross-section of the streaked region, (c) surface of the normal region and (d) cross-section of the normal region. Arrows indicate die-line-remains.



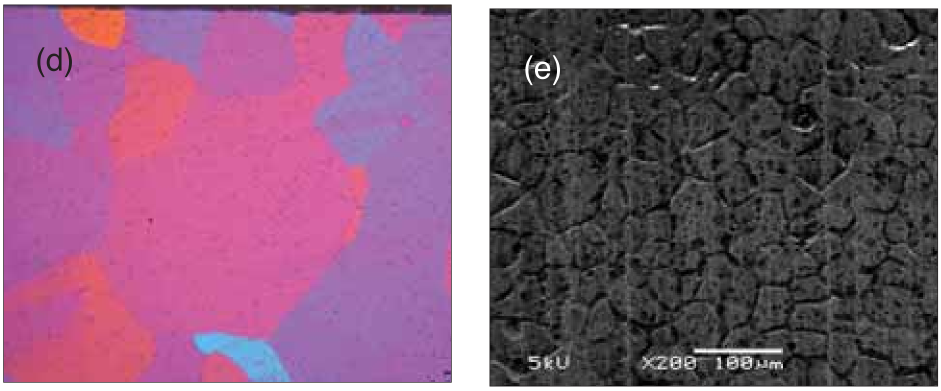


Fig 4 Morphology of various surface imperfections on anodized aluminium extrusions. (a) Large etching pits, (b) small etching pits, (c) grain boundary grooves, (d) grain etching steps and (e) die-line-remains. Arrows show various surface imperfections.

Deep and wide grooves are observed in the grain boundary regions as shown in **Fig 4c**. It appears that the grain boundary regions dissolve more quickly than the grain interiors during etching, indicating that grain boundary grooves are formed due to a preferred grain boundary attack.

The severity of grain boundary grooves depends on the kinetics of the attack. Hence, the difference in dissolution kinetics between grain boundaries and grain interiors is important for the formation and severity of grain boundary grooves. This difference is influenced by several factors such as distribution of various intermetallic particles, grain size and grain boundary characteristics etc.

For example, it was found that Mg-Si precipitates were one of the primary factors related to the formation of grain boundary grooves during etching[8,10]. In the solution-treated sample, or a location with less precipitates in the extrusion, grain boundaries are dissolved more quickly than grain interiors during alkaline etching and severe grain boundary grooves are formed.

The reason is that grain boundaries may have more segregation of solute elements than grain interiors. In contrast, in the aged samples, or a location with larger amounts of precipitates in the extrusion, Mg-Si particles can act as anodes, dissolving in preference to the aluminium matrix and resulting in the formation of small etching pits.

During further etching, a high density of small pits greatly increases the reaction area, which dramatically accelerates the dissolution of both grain interiors and grain boundary regions. Although there may be more precipitates in the grain boundary regions than in the grain interiors, the resultant difference in the dissolution rate between the two regions is not sufficiently large for the formation of serious grain boundary grooves[8].

More detailed work is required to fully understand the influence of various factors on the formation and severity of grain boundary grooves.

Grain etching steps are created at the surface of polycrystalline materials due to pronounced chemical attack of particular crystal planes during etching. As shown in **Fig 4d**, the surface of the grain between the two arrows is higher than its neighbouring grains with other orientations, indicating that this grain has dissolved more slowly than the other orientations during etching.

Moreover, lower surfaces of some crystal planes than others produce asymmetric grain boundary grooves with one side in the pronouncedly etched grain lower than the other side towards the neighbouring grain. These asymmetric grain boundary grooves also influence the reflectance of the etched surface[4].

Die Lines

During etching, the extrusion surface defects such as die lines can dissolve more quickly than the other regions due to a higher surface energy in the surface defect regions. If the etching treatment is sufficient, the extrusion surface defects can be flattened.

However, if the etching time is insufficient or the temperature is low or the etching solution is not strong, the remains of extrusion surface defects can still stay on the anodized surface, resulting in surface-defect-remains[4].

Fig 4e shows die-line-remains on the anodized extrusion. Another reason for the formation of surface-defect-remains is due to intemetallic particles[4,10].

As described above, the Mg-Si or Fe-rich intermetallic particles can increase the dissolution of the extrusion surface. The dissolution of the sample containing large amounts of particles is so quick that the material on the surface of previous die lines is dissolved at the same rate as the rest of the surface. After the etching treatment, die lines cannot be removed completely and die-line-remains are present on the etched surface[4,10].

All these surface imperfections on the etched extrusion surface greatly increase the diffuse part of the reflected light and thus decrease the surface gloss. However, these surface imperfections do not always cause streaking.

Only a concentrated local distribution of these imperfections on the extrusion surface can cause an uneven reflectance of light as well as the occurrence of streak defects. As described above, most surface imperfections are generated during etching due to uneven chemical attack of the microstructure.

Hence, the uneven distribution of the microstructure in the extrusions is the major cause for the formation of the inhomogeneous distribution of surface

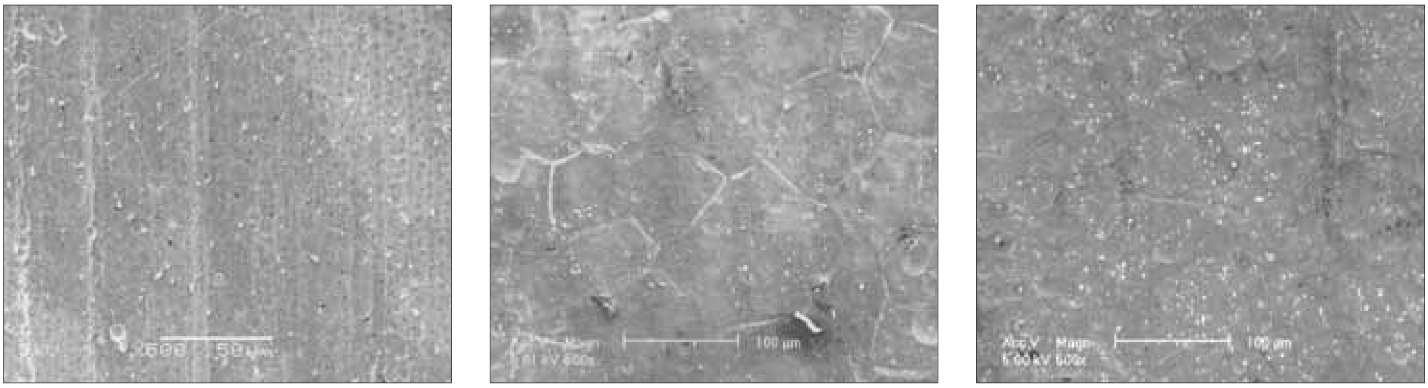


Fig 5 Surface morphology of extrusion samples etched for 5 min at (left) 40C, (middle) 70C, and (right) 90C.

imperfections. The formation of the uneven microstructure is influenced by various factors involved in the different processing steps during the fabrication of the anodized extrusions[4]. The etching treatment cannot influence the distribution of the microstructure in different locations of extrusions, but can influence the distribution of surface imperfections on the final extrusion surfaces prior to anodizing.

Surface Imperfections

To investigate the effect of etching process parameters on the severity of surface imperfections as well as streak defects, etching treatment trials were carried out at 40-90C in a solution of 10% NaOH for different time durations in the laboratory.

Fig 5 shows the surface morphologies of the normal regions in the samples after etching for 5min at different temperatures.

It is noted that the die lines are still observed on the surfaces at 40C/5min (**Fig 5a**), but completely disappeared from the etched surfaces at 70 and 90C. However, grain boundary grooves are observed on the surfaces etched at 70C/5min (**Fig 5b**).

Increasing the etching temperature to 90C, the grain boundary grooves are completely absent from the etched surface (**Fig 5c**). These results demonstrate that increasing the etching temperature from 40C to 70C, the die lines can be flattened due to a quicker dissolution in the die line region than in the surrounding surface of the extrusion.

However, the difference in the amount of material loss between the grain boundaries and grain interiors due to different dissolution kinetics become so large during etching at 70C that serious grain boundary grooves are formed. Further increasing the etching temperature to 90C, the dissolution of both grain interiors and grain boundary regions are accelerated so much that the difference in dissolution rates between the two regions is greatly decreased, preventing the formation of grain boundary grooves.

In addition, the distribution of the major die lines is very different between the web intersection and normal regions after etching at 40C. This difference can cause a different reflectance of light between these two regions.

However, there is no significant difference in the morphology of grain boundary grooves between the web intersection and normal regions after etching for 5min at 70C and 90C.

This would prevent the formation of streaking defects. Also, the etching time has a similar effect on extrusion surface defects as the etching temperature. Increasing the etching time at 40C, the severity of extrusion surface defects such as die lines decrease whereas grain boundary grooves increase, and the difference in the morphology and distribution of surface imperfections between different locations on the extrusions decreases.

Fig 6 shows photos of etched samples for different etching temperatures for 5min. A streak defect is observed in the 40C/5min etched sample (left sample) due to larger difference in severity of die line remains between the web intersection and normal regions, while there is no evident streak defect on the 70C/5 min and 90C/5min etched samples.

Moreover, the 40C/5 min etched sample exhibits a dull appearance compared to the other two samples due to a rougher surface. These results confirm that increasing etching temperature can decrease the intensity or prevent the formation of some streak defects formed due to extrusion surface defects.

Therefore, it is important to control the etching process to prevent the formation of streaking defects in aluminium extrusions.

Fig 6 Etched extrusion samples. Left: 40C/5 min; middle: 70C/5 min; right: 90C/5 min. The arrow indicates a streaking defect.

Summary

Streak defects on anodized aluminium extrusions are formed due to an inhomogeneous distribution of surface imperfections.

The etching treatment produces surface imperfections including etching pits, grain boundary grooves and/or grain etching steps due to uneven chemical attack of the microstructure. Insufficient etching can also result in the remains of extrusion surface defects such as die lines.

The etching temperature and time are the most important etching process parameters to influence the severity and inhomogeneous distribution of the surface imperfections.

With increasing etching temperature and time, the severity of the surface defects and the difference in the morphology and distribution of the surface imperfections among different locations decreases, and thus the streaking defect may disappear.

Therefore, it is important to control the etching process to decrease the intensity or even prevent the occurrence of the streak defects.

References

[1] K.Karhausen, A.L.Dons and T.Aukrust: Mater. Sci. Forum Vol. 217-222 (1996),

pp.403-408.
[2] P.Ratchev, R.Labie, B.Verlinden and R.V.D.Broeck: Z.Metallkd. Vol. 91(2000), pp.510-515.
[3] X. Zhang, H. Zhu, M.J. Couper, A.K. Dahle, Proceedings of the 9th International Aluminum Extrusion Technology Seminar & Exposition, May 13-16 2008, Orlando, Florida, Vol. 2, pp.455-464.
[4] H.Zhu, X.Zhang, M.J.Couper, A.K.Dahle, JOM 62 (2010): 46-51.
[5] Y Wang, H. Kuo and S.Kia: Proceedings of AESF SUR/FIN 2003, pp.150-166.
[6] R.Akeret, H.Bichsel, E.Schwall, E.Simon and M.Textor, Trans. Inst. Metal. Finishing 67 (1989) 20.
[7] T.Hauge and K.F.Karhausen: Aluminum extrusion, 1998, V3(1), pp.32-37.
[8] H.Zhu, X.Zhang, M.J.Couper, A.K.Dahle, Metall. Mater. Trans. A 40(2009): 3264 - 3275.
[9] H.Zhu, X.Zhang, M.J.Couper, A.K.Dahle, Mater. Chem. Phys. 113 (2009) 401-406.
[10] H.Zhu, X.Zhang, M.J.Couper, A.K.Dahle, Proceedings of the Seventeenth Annual International Anodizing Seminar & Exposition, Oct. 28-30 2008, San Francisco, California.

This is an extended version of an article which appeared in the May/June 2011 edition of Aluminium International Today.

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