Precipitation and Corrosion Behaviour of Nano-Structured Near-Surface Layers on an AA6111 Aluminium Alloy

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Abstract. A nano-structured, near-surface layer has been generated by mechanically grinding an AA6111 alloy. After heat treatment at 180°C for 30 minutes, Q phase particles, ~20 nm diameter, were precipitated preferentially at grain boundaries within the nano-structured near-surface layer. No such precipitates were observed in the bulk alloy after this heat treatment. This preferential precipitation results in the near-surface layers having increased corrosion susceptibility than the bulk microstructure, due to the micro-galvanic coupling between the precipitates at grain boundary and the grain matrix. The localized attack is predominately intergranular.

1. Introduction
Recent studies have revealed that nano-structured, near-surface layers are developed during hot and cold rolling, and by mechanically grinding, or machining of the aluminium surface, due to the high levels of surface shear experienced [1-5]. Compared to the underlying bulk material, the near-surface layers are electrochemically active and susceptible to corrosion, and this promotes rapid and extensive propagation of filiform corrosion. In a most recent study [6], it was shown that the susceptibility of AA6111 automotive closure sheet alloy to filiform corrosion was significantly increased by rectification and the heat treatment to simulate the paint baking process (30 minutes at 180°C).

In order to control the corrosion properties of fabricated aluminium alloy, it is essential to understand the microstructure of the near-surface layer and its influence on the corrosion behaviour of aluminium alloys. The present study is undertaken to quantitatively characterize the near-surface deformed layer of AA6111 automotive closure sheet alloy and to determine the effect of the paint baking heat treatment on its microstructure and to advance understanding of the associated corrosion mechanism. Characterization of the mechanical grinding-induced, near-surface layer and the underlying bulk alloy was carried out using analytical transmission electron microscopy (TEM).

2. Experimental
AA6111 automotive closure sheet alloy (Mg 0.74 wt%, Fe 0.23 wt%, Si 0.63 wt%, Cu 0.74 wt%, Mn 0.20 wt%, Al rem.) was solution heat-treated (SHT) at 813 K for 30 minutes, followed by rapid quenching in ice water. In order to simulate the rectification and paint baking process, the alloy sheet was then mechanically ground with SiC paper, and heat treated at 180°C for 30 minutes. Characterization of the mechanical grinding-induced, near-surface layer and underlying bulk alloy was...
carried out using TEM of ultramicrotomed sections, generated with a diamond knife by ultramicrotomy using a Leica Ultracut ultramicrotome. The ultramicrotomed sections, of nominal thickness about 15 nm, were examined in JEOL 2000 FXII and Tecnai G2 F30 instruments.

3. Results and Discussion

Figure 1 shows transmission electron micrographs of ultramicrotomed sections of the AA6111 alloy after mechanical grinding. A near-surface layer, approximately 2 µm thick, with a relatively sharp transition to the underlying bulk alloy microstructure, is revealed (Figure 1a). The structure of the deformed layer is characterised by very fine grains, of 50-150 nm diameter, as illustrated in the increased magnification TEM dark-field (DF) image (Figure 1b). The high diffraction contrast within the near-surface layer suggests large misorientations between the nano-sized grains. This was confirmed by selected area diffraction, which revealed a ring-like pattern.

For the alloy sheet, after mechanical grinding and thermal exposure at 180°C for 30 minutes, Figure 2 shows transmission electron micrographs of an ultramicrotomed section. Two regions are shown within the section, representing the near-surface layer (upper region) and the underlying bulk alloy microstructure (lower region). Scrutiny of the DF image (Figure 2b) reveals a high population of bright spots, of approximate 20 nm diameter, distributed along preferred grain boundaries within the near-surface layer, indicating preferential precipitation of particles within the near-surface layer after 30 minutes at 180°C. Such precipitates are not seen in the underlying bulk alloy microstructure.

EDX analysis was carried out to determine the composition of the particles at the grain boundaries and of the adjacent matrix. Line profiling was performed by scanning an electron probe of nominal diameter ~2 nm, across a particle at the grain boundary and its adjacent matrix. Increased yields of copper, magnesium and silicon were detected at the grain boundary particle compared with that from the grain matrix, suggesting that the precipitates were Q phase \( \text{Cu}_2\text{Mg}_8\text{Si}_7\text{Al}_4 \) [7]. This was confirmed by HRTEM of such grain boundary precipitates. The detailed characterization of Q phase particles within the near-surface layer will be discussed in a related paper.

A transmission electron micrograph of an ultramicrotomed section through a filiform filament on the corrosion tested alloy sheet after mechanical grinding and 30 minutes at 180°C, is shown in Figure 3. The cutting direction was at 90° to the filament growth direction. It is evident that localized
corrosion is associated with the grain boundaries. Corrosion propagates along preferred grain boundaries, then, develops into the fine grains, suggesting that the localized corrosion was driven by the cathodic Q phase particles, which have relatively high electrochemical potentials due to their high copper content.

As shown in previous work [6], the corrosion behaviour of the alloy shows a great sensitivity to heat treatment. The mechanically ground surface without heat treatment, displays relatively moderate filiform corrosion susceptibility whereas the samples that were mechanically ground and heat treated at 180°C for 30 minutes show very extensive filiform corrosion. For the alloy that was mechanically ground and etched in 5 wt% NaOH at 60°C followed by desmutting in HNO₃ before heat treatment at 180°C for 30 minutes, relatively little filiform corrosion was observed, suggesting that etching and desmutting increased resistance to filiform corrosion. Thus, it is not just severe local surface shear processing to provide nano-structured, near-surface layer that promotes susceptibility to filiform corrosion. Heat treatment is required to promote preferential precipitation of Q phase particles in the deformed layers, which significantly reduces the resistance of AA6111 alloy to filiform corrosion.
This is because when copper-rich Q phase particles are formed at grain boundaries, regions adjacent to the particles are anodic with respect to copper-rich particles. The localized corrosion is galvanic corrosion in the vicinity of grain boundary driven by cathodic sites of copper-rich Q phase particles. Consequently, the near-surface deformed layer is readily corroded.

In the present study, thermal exposure at 180˚C for 30 minutes promoted the preferential precipitation of Q phase particles at grain boundaries within the nano-structured, near-surface layer in AA 6111 aluminium alloy. No in-grain precipitates were observed in the near-surface layer, indicating the precipitation behaviour is different from that in the conventional, coarse grained alloy that has composition similar to the alloy and exhibits ingrain precipitation of Q phase after similar thermal exposure [8]. Further, no β”, β’ or β phases, which coexist with the Q phase in coarse grained alloy [7, 8], was found, indicating the preferential precipitation of the more stable phase in the near-surface deformed layer, in the absence of the metastable phases.

The precipitation kinetics of Q phase particles at grain boundary within the near-surface, deformed layer is enhanced by the strain introduced by mechanical grinding and the nature of the near-surface layer, i.e. nano-sized grains. Therefore, the high population of grain boundaries as nucleation sites as well as a high-speed diffusion path. The results clearly show that the heterogeneous nucleation of precipitates at the grain boundaries, which are mostly high angle boundaries, is enhanced in the nano-structured, near-surface layer.

4. Conclusions
Thermal exposure at 180˚C for 30 minutes, promoted the preferential precipitation of Q phase particles, ~20 nm diameters, at grain boundaries within the nano-structured near-surface layer in AA 6111 aluminium alloy. No such precipitates were observed in the underlying bulk alloy microstructure after this heat treatment. Localized attack was associated with preferred grain boundary locations and was driven by the micro-galvanic coupling between the precipitates at grain boundary and the regions adjacent to the particles.

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