Structure and formation mechanism of rolled-in oxide areas on aluminum lithographic printing sheets

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Received 3 September 2012; revised 15 October 2012; accepted 17 October 2012
Available online 23 October 2012

Rolling is known to alter the surface properties of aluminum due to the formation of a layer below the surface. This subsurface layer, also known as “surface layer” or “Beilby layer”, is produced during rolling and is a non-uniform layer with varying thickness between 0.5 μm and 3 μm. It consists of ultrafine grains in the 40–350 nm range, cracks, a few nanometer-wide voids, aluminum oxide particles of 10–100 nm, MgO particles and finally both amorphous carbon and aluminum carbides formed from incorporated rolling lubricants [1–3].

The presence of those subsurface or rolled-in layers changes the properties of the aluminum. Many studies have revealed that regions containing rolled-in oxides are more susceptible to corrosion, giving a negative influence on the etching and electrograining of aluminum surfaces [2,4]. Few studies tried to investigate the formation mechanism of the layer during rolling. The subsurface layer is known to be produced during the first few rolling steps and remains present together with oxides during subsequent rolling steps. It has been observed that the types of oxides present differ, with MgO, Al2MgO4 and Al2O3 at the beginning of the rolling to only Al2O3 and MgO at the end of rolling [1–3]. Zhou et al. [5] recently observed the existence of small grains with grain boundaries decorated by oxide particles in the subsurface layers as well as fine grains without oxides at the grain boundaries. They assumed that high shear deformation and the presence of alloying elements are the reasons for the formation of the deformed subsurface layer.

The aim of this work is to study the microstructure and examine the presence of oxides in order to describe the formation mechanism of the subsurface layer induced by rolling. To this end, we will present orientation mapping results of the aluminum subsurface layers observed using a new technique, called automated crystallographic orientation mapping in a transmission electron microscope (ACOM-TEM) [6]. With this technique, local electron diffraction (ED) patterns are gathered by scanning the primary electron beam over the sample and acquiring a diffraction pattern in each scan point on an external charged coupled device (CCD) camera. A database of theoretical templates is then used off-line and is compared to the experimental electron diffraction pattern. The template with the best match is selected. The system also provides a correlation index and

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a value for the reliability. The correlation index is directly linked to the matching degree between the best match and the experimental pattern. The reliability is measured through the difference in the matching degree between the best match and the second best one. Besides the orientation map, it is possible to obtain maps plotting the spatial evolution of those two parameters [6–7]. Crystal orientation maps (OMs), virtual bright field maps (VBFs), correlation index maps and reliability maps can also be obtained. In the reliability map the areas that have a high reliability appear brighter. When dark or black areas are obtained the reliability is very low and the grain structure in those spots should be carefully analyzed. This means that the ED pattern comes from the overlapping of grains or the intensity from that spot is not high enough. The advantage of this technique compared with a conventional electron backscatter diffraction (EBSD) analysis is that in the latter, Kikuchi lines can become blurry when deformed layers are analyzed [7]. In addition to this, the use of electron energy loss spectroscopy (EELS) and energy-filtered TEM (EFTEM) will provide further insights into the distribution of elements and the presence of oxides on the subsurface layer.

Commercial hot rolled aluminum alloy AA 1100 sheets were provided by HYDRO R&D, Bonn. For TEM investigation, cross-sections were machined from the hot rolled aluminum specimens using a focused ion beam equipped with a liquid Ga metal primary ion source together with an Ar ion beam. A Pt layer was deposited on the sample to protect the thin foils during the Ga\(^+\) ion milling. After Ga\(^+\) milling, low energy Ar ion nanomilling was performed to remove the Ga\(^+\) implantation layers as much as possible from the internal areas of the aluminum thin foil.

A Philips CM20 TEM equipped with a LaB\(_6\) gun at 200 kV was used for the ACOM-TEM experiments. Spot sizes ranging from 6 to 35 nm and acquisition frequencies from 40 to 170 frames per second using an external CCD camera were chosen to collect orientation mappings with an acquisition time of 15 min up to 1 h according to the surface area measured.

The energy-filtered TEM maps in Figure 3 were acquired on a Philips CM30 FEG-TEM, operated at 300 kV using the standard three-window method on the Al–K and O–K edges. The spatially resolved EELS (STEM-EELS) maps in Figure 4 were acquired using a Titan microscope equipped with a probe corrector and a GIF QUANTUM energy filter, operated at 300 kV. The EELS data were acquired by scanning the fine electron probe over the sample in discrete steps, and acquiring an EELS spectrum containing the O–K, Cu–L, Ga–L, Al–K and Mg–K edge. To generate the elemental maps, the intensity under the background-subtracted EELS edges was plotted using an appropriate energy window. Prior to mapping, the EELS data were treated using principal component analysis (PCA) to reduce the influence of random noise.

In Figure 1a, a layer of \(\sim\)1–2 µm in thickness is observed that clearly differs from the underlying bulk aluminum, which consists of large grains. Cracks and voids are present on the subsurface region as well as small particles as seen better in Figure 1b and c, which are most likely intermetallics or small oxides [2]. The Pt deposited layer used to protect the aluminum foil against the Ga\(^+\) bombardment is present on top of the sample.

The rolling process alters the surface characteristics of the aluminum and after the first rolling introduces a subsurface layer with small aluminum grains together with oxide particles. By comparing the surface before and after rolling it was observed that just after entering the rolling mill the surface and the subsurface morphology changes. Breaking up of intermetallics and formation of holes were observed in the roll-bite. In subsequent passes, when the surface is smeared out, these holes can develop into sub-surface cracks [4]. Shingles and debris present on the surface enhance the possibility of introducing holes and cracks into the subsurface region. Small aluminum particles present on the surface can smear inside the surface and be present as small aluminum grains in the subsurface region. Surface oxides can be trapped into the subsurface area during rolling since the initial surface can be folded over, forming shingles that are incorporated into the oxide region [8].

The grain structure and the orientation are further analyzed through ACOM-TEM. As can be seen in Figure 2a, elongated grains are present on the near surface area and close to the bulk aluminum. Small, randomly orientated grains are present in the intermediate region. In order to be able to evaluate the obtained results, the reliability map is presented in Figure 2b. In regions where big elongated grains are present the reliability is high, but it is reduced in areas around the cracks where the size of the grains is very small (less than 100 nm) and possible grain overlapping occurs, which makes the indexation of the ED pattern very difficult if not impossible. Where voids or cracks are present the only signal

![Figure 1](image1)

**Figure 1.** Bright field TEM images of the subsurface layer after hot rolling of subsurface region on AA 1100 varying in thickness from 1.1 to 1.8 µm: (a) higher magnification of marked areas around the cracks (b) and (c).

![Figure 2](image2)

**Figure 2.** Orientation map (a), reliability image map of marked area with brighter grains having the highest reliability and very dark or black grains the lowest (b) and ED patterns on two different grains (c) and (d) of the subsurface region on AA 1100.
recorded is the one coming from the beam (central spot) whereas in areas with big grains a monocrystalline pattern is recorded as observed in Figure 2c. Where small grains are present a multiple crystalline pattern is recorded, due to the presence of more than one grain along the beam direction. This decreases the reliability of the measurement, as can be seen in Figure 2d. A grain gradient on the subsurface layer was observed with small, elongated grains disturbed by small aluminum grains and oxide particles.

During the rolling and within the roll gap there is a neutral plane in which the relative velocity of the sample and rolls changes direction. Therefore opposite shears are imposed on the deforming material on either side of the neutral plane, and thus material near the sample surface undergoes shearing in both directions (redundant shear), causing the elongation of the grains as observed in the subsurface layer for aluminum grains closer to the bulk and to the surface [9]. As was observed by Zhou et al. [5] the presence of three different layers in the microstructure is evident. Close to the bulk, there are large elongated grains of 100–500 nm in thickness transverse to the rolling direction. A second phase is observed with smaller grains less than 100 nm and randomly oriented. In this hot rolled sample there is only one type of near-surface deformed region, type A, as indicated by Zhou et al. That was described as layers with fine grains and grain boundaries decorated by oxide particles.

The shear strain produced during rolling is higher at the surface [1,10]. The subsurface region consists mainly of high angle grain boundaries as can be seen in Figure 2. The small aluminum particles present in the subsurface region introduce high strains which enforce the existence of smaller grains. Zhou et al. [5] observed that the strain and the temperature of the subsurface region are sufficient enough to cause dynamic recrystallization. In addition, Zenner pinning of the grain boundaries caused by oxides or other precipitates suppress or prevent the grain growth and therefore stabilizes the structure [11]. Those two phenomena can clearly explain the three types of grain structures appearing on the subsurface layer reported in this study.

In Figure 3a, EFTEM results are displayed. The Al and O maps in Figure 3b clearly show the distribution of oxygen around the cracks and in between the grain boundaries in the subsurface layer. Further evidence for elemental segregation in the sample is given by the spatially resolved electron energy-loss spectroscopy results presented in Figure 4. Elemental maps for Al, O, Mg, Cu and Ga are displayed. The magnesium can be seen to be segregated towards the crack surface, promoting the possible development of MgO or spinel oxide. The latter has been reported to be created only at the first rolling passes and only MgO is seen at the end of the hot rolling step. EELS maps were acquired from the marked area in Figure 4 (left). In Figure 4 (right) the presence of Mg close to the crack together with aluminum is illustrated. In the same area a higher concentration of oxygen is recorded in the oxygen map, pointing towards the presence of MgO on the subsurface region. Ga and Cu are present on the subsurface region around the cracks. They are deposited on the aluminum cracks during the sample preparation and as small particles of a few nanometers in the main matrix of the layer. The distribution of the oxides around the grain boundaries seen with EFTEM confirms the existence of Zenner pinning of the grain boundaries in the subsurface region.

The oxides present in the subsurface region are known to be amorphous but some crystalline structures are possibly present on the subsurface layer. The presence of γ-Al2O3 and spinel MgAl2O4 was reported mainly during the first rolling passes and the particle size of those oxides was 28 to 300 Å [1]. In the present study, the ACOM-TEM technique could not evaluate such small crystalline structures. Therefore the presence and the crystalline structure of oxides were not mapped due to their small size.

As a conclusion, automated crystallographic orientation mapping in a transmission electron microscope has been used for the observation and characterization of thin AA 1100 samples. After the rolling procedure a specific area of interest was prepared by focused ion beam. The grain orientation and structure in highly deformed layers can be clearly seen. Using this technique we were able to observe the texture of subsurface layers on commercial AA 1100. Specifically, a grain gradient is observed on the subsurface layer. Elongated grains appear closer to the bulk and to the upper surface layer whereas small grains of random orientation are present in the intermediate area of the layer. Small aluminum grains are present on the subsurface layer with oxides around the grain boundaries and the voids. Al2O3 is present in the subsurface layer of the hot rolled AA 1100.

Figure 3. (a) Bright field TEM image of a subsurface region of AA 1100. (b) Color overlay of Al (in red) and O (in green) EFTEM maps of the same region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Figure 4. Left: HAADF-STEM overview image of a crack region, with the spectrum image region indicated by Si. Right: STEM-EELS elemental maps for Al, O, Mg, Ga and Cu. The color map is an overlay of the Al (in green) and Mg (in blue) signals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Around the cracks and in between the grain boundaries, oxides are present, which leads to Zenner pinning. The latter, together with the high strains introduced around small hard particles, enhances the presence of small aluminum grains in the subsurface region. These effects together provide an explanation for the observed three gradient layer.

The authors would like to thank OCAS NV for the preparation of the thin aluminum cross-section with FIB. S.T. gratefully acknowledges financial support from the Fund for Scientific Research Flanders (FWO). The Titan microscope used in this study was partially financed by the Hercules Foundation of the Flemish Government. S.G. acknowledges the FNRS and the MG the financial support of the Walloon Region.