Title: ALUMINIUM ALLOY AND A PROCESS FOR PRODUCING AN ALLOY
- of inventorship (Rule 4.17(iv))

Published:
- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
ALUMINIUM ALLOY AND A PROCESS FOR PRODUCING AN ALLOY

THIS INVENTION relates to lithography. In particular, the invention relates to an aluminium alloy suitable for processing into a lithographic sheet, a lithographic sheet formed from the aluminium alloy, a cast workpiece or ingot comprising the alloy, and to a method of processing an aluminium alloy to produce a lithographic sheet.

The 1XXX alloy range, particularly AA1050A, is widely used to produce lithographic sheet. A lithographic sheet is generally required to achieve target mechanical properties and chemical or electro-graining performance to function satisfactorily. Within the AA1050 range of alloys preferred compositions usually comprise Si in the range of 0.05 - 0.1 wt.% and minimise the use of Ti based grain refiners such that free titanium in the alloy is, typically, present in concentrations of about 100ppm. Compositions having alloying additions of Mg and Mn have been generally disclosed. These alloys are said to provide adequate mechanical properties and electro graining performance and, in particular, with alloying additions of Mn are said to alleviate the adverse effects of reduced mechanical strength (known as “bake softening”) which occurs during low temperature heat treatment of the alloy to provide the finished lithographic plate.

It is an object of this invention to provide an aluminium alloy having dilute alloying additions and which has acceptable mechanical strength and electro-graining performance and which also exhibits acceptable resistance to bake softening.
It is also an object of this invention to provide an aluminium alloy having the desired properties when subjected to a low temperature interanneal stage.

In this specification the term “free titanium” means that part of the overall titanium content of an alloy not combined with boron and present as TiB₂. In order to calculate the amount of free titanium, the boron content is multiplied by a factor of 2.2 which result is subtracted from the total Ti content.

In this specification the term “rolling strain” means what is known in the art as natural strain as is explained, for example, in the Principles of Metal Working G.W. Rowe Published Arnold 1965 at page 18.

According to a first aspect of the invention, there is provided an aluminium alloy suitable for processing into a lithographic sheet, the alloy having a composition in wt.% unless otherwise stated:

\[
\begin{align*}
\text{Mg} & \quad 0.03 \quad - \quad 0.15 \\
\text{Mn} & \quad 0.03 \quad - \quad 0.07 \\
\text{Si} & \quad \text{less than or equal to 0.13} \\
\text{Fe} & \quad \text{less than or equal to 0.4} \\
\text{Ti} & \quad \text{up to 300ppm (free titanium),} \\
& \quad \text{the balance being Al and incidental impurities.}
\end{align*}
\]

The lower limit of the Mn concentration may be 0.04. The upper limit of the Mn concentration may be 0.06. Preferably, the alloy may have a Mn concentration from 0.04 to 0.06 wt% and, more preferably, from 0.04 to 0.05 wt%.
The lower limit of the Mg concentration may be 0.05. The upper limit of the Mg concentration may be 0.10. Preferably, the alloy may have a Mg concentration from 0.05 to 0.10 wt.% and, more preferably, 0.05 to 0.07 wt%.

Preferably, the alloy may have a Si concentration of from 0.06 to 0.08%. If necessary, to enhance hardening and electrograining performance the Si may be above 0.08, preferably, 0.11 – 0.12 wt%.

Preferably, the ratio of Fe to Si (Fe:Si) in the alloy exceeds 3.0. The Fe concentration may preferably be from 0.3 to 0.4 wt%.

Preferably, the Ti concentration may be up to 200ppm, more preferably, up to 150ppm, even more preferably in the range of 50 – 150 ppm.

In alloys in accordance with the invention, a Mg alloy addition, in combination with work hardening through cold reduction, is used to achieve a commercially acceptable target cold rolled yield strength of 170 – 190MPa. It has been found that low Mg additions in accordance with the invention with cold rolling strains in excess of 2.0 provide adequate strength after cold rolling. In particular, Mg additions of between 0.05 and 0.1 wt % combined with cold rolling strains of about 2.6 to 2.9 achieve a strength of 170 to 190MPa after cold rolling for an alloy containing about 0.05 wt% Mn.

As is set in more detail below, in accordance with another aspect of the invention, lithographic sheet material is advantageously produced from the alloy in accordance with the invention by subjecting said alloy to a low temperature interanneal. Although more cost effective, using a lower temperature interanneal impacts negatively on resistance to bake softening. The addition of Mn and Ti are known to improve a lithographic alloy’s resistance to bake softening.
Surprisingly it is found that this bake softening is alleviated by having the very low concentration levels of Mn in accordance with the invention. It has been surprisingly found Mn additions as low as the ranges suggested provide a yield strength of 100MPa after baking at 260°C for 10 minutes and above 130MPa after baking at 240°C for 10 minutes.

Additions of Mn and Ti may impair the electro-graining performance. It has also been found that by selecting the silicon content in accordance with the invention the electro-graining performance is restored to acceptable levels. In other words, the addition of Si contributes to offsetting the effects that Mn and Ti have on electrograining response.

Thus, the selected aluminium alloys with dilute additions in accordance with the invention provide lithographic sheets with acceptable mechanical properties and electro-graining characteristics and which, at the same time, may be produced by a lower temperature interanneal.

According to a second aspect of the invention, there is provided a lithographic sheet which is formed from an aluminium alloy in accordance with the first aspect of the invention.

According to a third aspect of the invention, there is provided a cast workpiece comprising an aluminium alloy in accordance with the first aspect of the invention.

Preferably, the workpiece may be a DC cast ingot.

According to a fourth aspect of the invention there is provided, broadly, a method of processing a cast aluminium alloy having a composition in
accordance with the first aspect of the invention which method includes producing a lithographic sheet material from said alloy by heat treating the alloy into an intermediate annealing stage at a temperature of between 280°C and 360°C for a period of at least 2 hours.

More particularly, according to a fourth aspect of the invention, there is provided a method of processing an aluminium alloy to produce a lithographic sheet which method includes the steps of:

casting an ingot of an aluminium alloy having a composition in accordance with the first aspect of the invention;

heating said alloy to a temperature of between 570°C and 610°C for a period of at least three hours in order substantially to homogenise said alloy;

hot rolling said substantially homogenized alloy to form a rerolled substantially un-recrystallized product;

heating said substantially un-recrystallized rerolled product to a temperature of between 280°C and 360°C for a period of at least 2 hours; and

cold rolling the rerolled product to a finished gauge.

The method may include cold rolling the un-recrystallized rerolled product prior to heating said product to a temperature of between 280°C and 360°C for a period of at least two hours.

Preferably, the method includes heating the rerolled product to a temperature of 350°C for a period of 3 hours. In a more preferred embodiment of the invention, the method includes casting an ingot of an aluminium alloy having concentrations Mg 0.05 – 0.1 : Mn 0.04 – 0.05 : Si 0.06 – 0.08 : Fe 0.3 – 0.4 in wt% and Ti : up to 300ppm and heating said rerolled product to a temperature of about 350°C for a period of about 2 hours.
Thus, according to the invention there is also provided a method of processing an aluminium alloy to produce a lithographic sheet which method includes the steps of:

1. casting an ingot of an aluminium alloy having a composition in wt% (unless otherwise stated) of Mg 0.05 - 0.1:Mn 0.04 - 0.05:Si 0.06 - 0.08:Fe 0.3 -0.4 and Ti up to 300 ppm;
2. heating said alloy to a temperature of between 570°C and 610°C for a period of at least three hours in order substantially to homogenise said alloy;
3. hot rolling said substantially homogenized alloy to form a rerolled substantially un-recrystallized product;
4. heating said substantially un-recrystallized rerolled product to a temperature of about 350°C for a period of about 2 hours; and
5. cold rolling the rerolled product to a finished gauge.

Advantageously, the method may include subjecting the rerolled product to a cold rolling strain of 2.6 to 2.9, preferably, 2.8.

The invention will now be described with reference to the following, non-limiting, examples and with reference to the accompanying diagrammatic drawings.

In drawings:
1. Figure 1 shows the interannealing thermal history of an alloy processed in accordance with the method of the invention;
2. Figure 2 shows the thermal history of the processed alloys during bake softening;
3. Figure 3 shows a bar graph of the yield strengths for different alloys, as rolled and after bake softening treatment at 240°C and 260°C;
Figure 4 shows yield strengths after baking at 240°C and 260°C as a function of manganese content in the alloy; and

Figure 5 shows contour map of yield strength as a function of magnesium content and rolling strain, for a fixed amount of Mn at 0.05 wt%.

Figure 6 shows photographs of samples of an alloy in accordance with the invention and a standard AA1050A alloy examined in a SEM showing electrograining response.

**EXAMPLE**

10 **Alloy compositions**

A series of alloy compositions are shown in Table 1 below. Concentrations of Si, Fe, Mn, Mg, Ti and B for each alloy are shown. Alloy A is representative of a standard AA1050A alloy not in accordance with the invention. Alloys G, H and K have small alloying additions of magnesium and manganese.

Alloy G is in accordance with the invention. The electro-grainability of litho sheet is very dependent on certain trace elements. In order to minimise unwanted complications arising from variations in such elements between commercial and pilot scale production, an ingot slice of the standard commercially available AA1050 alloy was used as the base alloy for these examples. The commercial standard AA1050A reroll material, is designated HR in Table 1 with a composition as indicated. The commercial standard HR was included to provide a baseline for comparing the laboratory cold rolling behavior with known commercial performance.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ti</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.064</td>
<td>0.315</td>
<td>0.002</td>
<td>0.000</td>
<td>0.028</td>
<td>0.001</td>
</tr>
<tr>
<td>G</td>
<td>0.07</td>
<td>0.32</td>
<td>0.045</td>
<td>0.085</td>
<td>0.029</td>
<td>0.001</td>
</tr>
<tr>
<td>H</td>
<td>0.07</td>
<td>0.31</td>
<td>0.019</td>
<td>0.087</td>
<td>0.028</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Table 1: Compositions of alloy

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>0.07</th>
<th>0.31</th>
<th>0.010</th>
<th>0.085</th>
<th>0.028</th>
<th>0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR</td>
<td>0.070</td>
<td>0.330</td>
<td>0.003</td>
<td>0.000</td>
<td>0.023</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

A. Processing method

(i) Casting and scalping

Ingots of the alloy compositions described above were cast with as-cast dimensions (mm) 210x155x45, and were scalped to remove surface oxides and segregants, to provide rolling blocks of dimensions (mm) 200x150x40. Other than adjusting the major alloying elements in alloys G to K as shown, no other molten metal treatment was employed. In particular, the level of grain refiner and free titanium (since this corresponded to the target range) was not changed from the base alloy. As will be appreciated the Si and Ti level could be achieved by alloying additions if necessary.

(ii) Homogenisation

The blocks were preheated in a furnace in two stages. The first stage involved heating to a temperature of 580°C at a rate of 60°C/hour followed by a 3 hour dwell at 580°C. In the second stage the blocks were cooled at 60°C/hour to 415°C, followed by a 1 hour dwell.
(iii) **Hot Rolling**

The substantially homogenized alloy was hot rolled to a rerolled gauge of, typically, 5mm. The pass schedule was optimized to ensure the reroll material was un-recrystallized, which was confirmed metallographically.

(iv) **Heating the re-rolled product – the interanneal step**

Interanneals were employed at reroll gauge, or after further cold rolling. The interanneal practice used involved heating the sheet in a furnace at a rate of 60°C/hour in a furnace to a temperature of 350°C. The sheet was then held at that temperature for 3 hours and air cooled. Figure 1 of the drawings shows the thermal history during interannealing.

(v) **Cold Rolling**

The rerolled product was cold rolled to form lithographic sheet material having a final gauge of approximately 0.3mm. Material was retained at gauges of approximately 2, 1 and 0.5mm in order to measure the work hardening behaviour of the alloys.

(vi) **Bake softening**

Following cold rolling, lithographic sheet is generally subjected to an electro-graining process before a photoresist coating is applied. A baking step is used to harden the exposed resist coating. During baking the sheet is exposed to temperatures in excess of 200°C for several minutes. This can result in
strength loss due to recovery, or even recrystallization (the reduction in mechanical properties is known as bake softening). In order to evaluate the bake softening resistance of the alloys, the produced sheets were heated to 260°C and held at that temperature for 10 minutes. This heat treatment was applied to all alloys at the final gauges. A second set of samples of the alloys was exposed for 10 minutes at 240°C. Samples for tensile testing were cut transverse to the rolling direction, as rolled, and after bake softening at 240°C and 260°C. A preheated platen press was used to give this heat treatment. The platens were set to the desired temperature, with a sheet of thermocoupled aluminium located between the platens. Once the system had reached the stable set temperature, the thermocoupled sheet was replaced with the sample, and held for 10 minutes. This process was repeated, with the thermocoupled sheet being used between each sample anneal to confirm the system had re-equilibrated at the desired temperature. Figure 2 of the drawings shows the thermal history of the bake softening resistance testwork.

B. **Results and Analysis**

(i) **Reroll and cold rolled gauges**

Table 2 below shows actual reroll gauges and final gauges, and cold rolling strains achieved for each alloy excluding alloy A.

<table>
<thead>
<tr>
<th>Reroll (mm)</th>
<th>Gauge (mm)</th>
<th>Final Gauge (mm)</th>
<th>Cold Rolling Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>4.95</td>
<td>0.31</td>
<td>2.76</td>
</tr>
<tr>
<td>H</td>
<td>5.01</td>
<td>0.32</td>
<td>2.76</td>
</tr>
<tr>
<td>K</td>
<td>4.95</td>
<td>0.31</td>
<td>2.77</td>
</tr>
<tr>
<td>J</td>
<td>4.96</td>
<td>0.33</td>
<td>2.73</td>
</tr>
<tr>
<td>HR</td>
<td>4.91</td>
<td>0.25</td>
<td>2.98</td>
</tr>
</tbody>
</table>
Table 2: Reroll and final gauges

(ii) As Rolled Mechanical Properties

Tensile mechanical properties were determined in the as cold rolled condition at final gauge in the transverse orientation as well as after the bake softening at 240°C and 260°C. This data is illustrated for some of the alloys as a bar graph in Figure 3 of the drawings.

(iii) Bake softening resistance

As is evident from Figure 3 of the drawings, the as rolled mechanical properties (G, H and K) are relatively insensitive to the manganese content in the alloy. These values exceed the standard alloy (HR) transverse yield strength of 147 MPa. Figure 3 shows that alloys G, H and K show a transverse yield strength in the range 183-191 MPa. As is evident from the composition of alloy G in Figure 3 an alloy having a very dilute Mn composition in the preferred range of 0.04 to 0.05 wt% still exhibits favourable bake softening resistance, particularly at 240°C.

Figure 4 shows the transverse yield strength after baking at 240°C and 260°C as a function of manganese content. As is evident from Figure 4 a lower limit of about 0.03 wt% Mn still exceeds 100 MPa in the 260°C bake softening condition. Furthermore, even though low levels of Mn are used yield strengths which are comparable to alloys with higher amounts of Mn are achievable owing to the higher rolling strains used. For example, the alloy G which contains 0.085% Mg and is subjected to a yield strain of about 2.7 provides a yield strength of about 133 MPa (after baking at 240°C).
A work hardening model was developed which relates yield strength to cold rolling strain, magnesium composition and manganese composition, using the following equations: \( \sigma = K \varepsilon^\sigma \) and \( K = K_o + P_{Mg} x_{Mg}^\sigma + P_{Mn} x_{Mn}^\sigma \), where \( x_{Mg} \) and \( x_{Mn} \) are the atomic fractions of magnesium and manganese in the alloy respectively. For completeness, the key parameter values are given in Table 3 below. The parameters were derived from the alloys described in Table 1 as well as further alloys (not in accordance with the invention) which are listed in Table 4. The upper and lower bounds of the Mg and Mn concentrations may be calculated as a function of the rolling reduction based on the work hardening equation mentioned above.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA1050 hardening parameter</td>
<td>( K_o )</td>
<td>132.2MPa</td>
</tr>
<tr>
<td>Strain hardening exponent</td>
<td>( N )</td>
<td>0.18</td>
</tr>
<tr>
<td>Mg strain hardening constant</td>
<td>( P_{Mg} )</td>
<td>612.5MPa</td>
</tr>
<tr>
<td>Mn strain hardening constant</td>
<td>( P_{Mn} )</td>
<td>276.3MPa</td>
</tr>
<tr>
<td>Compositional exponent</td>
<td>( M )</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table 3: Parameters used in work hardening model for litho alloys

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.114</td>
<td>0.311</td>
<td>0.002</td>
<td>0.001</td>
<td>0.029</td>
</tr>
<tr>
<td>C</td>
<td>0.072</td>
<td>0.324</td>
<td>0.003</td>
<td>0.098</td>
<td>0.027</td>
</tr>
<tr>
<td>D</td>
<td>0.063</td>
<td>0.310</td>
<td>0.104</td>
<td>0.001</td>
<td>0.028</td>
</tr>
<tr>
<td>E</td>
<td>0.115</td>
<td>0.307</td>
<td>0.002</td>
<td>0.093</td>
<td>0.028</td>
</tr>
<tr>
<td>F</td>
<td>0.119</td>
<td>0.304</td>
<td>0.107</td>
<td>0.092</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Table 4: Compositions of other alloy variants used in the mathematical model.

For a specified level of manganese, a contour map of yield strength as a function of rolling strain and magnesium content may be generated from this information: an example is shown in Figure 5 for a manganese level of 0.05wt.%.

Figure 5 indicates the acceptable combinations of strain and magnesium content, which are able to provide the required properties. Assuming a target yield strength of 175MPa the dotted line on Figure 5 shows the locus of rolling strains and magnesium additions which achieve the target properties. At one extreme, a magnesium addition of 0.09wt.% requires a rolling strain of 2 (a cold reduction of 86%), whereas a magnesium level of 0.03wt.% requires a rolling strain of about 2.7 (a cold reduction of 95%). Thus, for a selected low value of Mn concentration a combination of Mg concentration and rolling strains are disclosed which provides the target properties. Advantageously, lower levels of Mg can be used with higher rolling strains in order to achieve the desired results.
C. **Electrograining Experimental Processing**

Alloys A and G were prepared by remelting a slice of commercial AA1050 ingot, adjusting the composition, and processing to final gauge as described above. No other melt treatment was performed, and hence the trace element content was constant for all variants, reflecting the trace elements arising in the smelter. Alloy A is representative of standard AA1050 widely used in lithographic applications, whereas Alloy G is an example of the current invention. A commercial standard AA1050A litho sheet was also subjected to the electrograining laboratory treatment in order to define the laboratory electro-graining conditions.

Standard commercially rolled Hulett AA1050 litho sheet samples were used to optimise the electro-graining conditions. Eight samples were cut from the sheet. The size of the samples was 120 x 68 mm. All samples were degreased in ethanol and thoroughly rinsed in de-ionised water. Samples were then etched in 40 g/litre NaOH solution at 55°C for 15 seconds followed by thorough rinse in de-ionised water.

The voltage applied to the electrochemical cell was varied from 9.2 to 15.4 V\(_{\text{rms}}\), which resulted in a current density variation from 1420 to 3250 A/m\(^2\). In order to maintain an approximately constant total charge passed, the time of electro-graining was varied from 20 to 40 seconds. Optimal electrograining conditions were established with a current density of 3,250A/m\(^2\), and a dwell time of 20 seconds. The average charge transferred was 63,500 C/m\(^2\) (± 3,500), which compares well with the range of charge densities achieved in the commercial process.
After electro-graining, the samples were rinsed, de-smutted and thoroughly rinsed again.

All samples were examined in the SEM at magnification x330 and x2000. The electrograined litho sheets for alloys A and G are shown in Figure 6 of the drawings at a magnification of x330. Electro-graining resulted in the development of similar pit structures on the surface of both alloy A, and alloy G. The pits are of average size around 3 µm, with occasional large pits of about 20 µm. This would be an acceptable substrate for lithographic purposes. The alloy additions to alloy G have not had a discernible influence on its electro-graining performance.

The Applicant believes that it is an advantage of the invention that an alloy having very dilute and selected amounts of alloying elements is provided which lends itself to a low temperature interanneal stage while at the same time providing the requisite target properties. Magnesium addition is used in combination with cold reduction to achieve target rolled strengths. It has been surprisingly found that very low additions of magnesium are sufficient which is desirable in order to alleviate negative impact on electrograining performance.

Alloys containing magnesium are known, at elevated temperatures, to segregate to the surface where magnesium oxides are formed. This is generally undesirable and places additional requirements on the caustic cleaning process which is designed to remove surface layers. The process in accordance with the invention is carried out using a low temperature interanneal in order to limit the amount of magnesium migration. The interanneal serves to generate an equiaxed grain structure to avoid any coarse recrystallised grains from the hot mill processing which may cause streaking. A low temperature interanneal will have two other significant benefits. Firstly, it is more energy efficient than processes at elevated temperatures. Secondly, a high temperature interanneal
can create difficulties with staining on the strip surface. Rolling oil evaporates from the coil during annealing at high temperatures. Although the oil is removed, the various additives in the package remain on the surface and are cracked, forming carbon based deposits which are difficult to remove. This is especially important on mills rolling multi products where additive packages are more concentrated.

Making use of the advantages of a low temperature interanneal is usually expected to impact negatively on the bake softening response. This problem may be alleviated by making additions of Mn and Ti. The applicant has surprisingly found that the low levels of Mn and the selected Ti levels provide adequate resistance to metallurgical recovery (which is the process by which plates soften during baking). The level of Si may be selected within the range of the invention in order partly to offset the negative impact of Ti and Mn on electrograining response. Small additions of Si and Mn also make a contribution to producing a stronger litho alloy. The method in accordance with the invention surprisingly achieves good graining with cold rolling from an unrecrystallized hot rolled strip containing 0.15% or less Mg. In other words, with Mg addition recrystallization at the end of hot rolling is not required to achieve the desired results.
CLAIMS

1. An aluminium alloy suitable for processing into a lithographic sheet, the alloy having a composition in wt.% unless otherwise stated of

<table>
<thead>
<tr>
<th>Element</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.03</td>
<td>0.15</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>Si</td>
<td>less than or equal to 0.13</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>less than or equal to 0.4</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>up to 300ppm (free titanium), the balance being Al and incidental impurities.</td>
<td></td>
</tr>
</tbody>
</table>

2. An aluminium alloy as claimed in claim 1, in which the lower limit of the Mn concentration is 0.04.

3. An aluminium alloy as claimed in claim 1, in which the upper limit of the Mn concentration is 0.06.

4. An aluminium alloy as claimed in any one of claims 1 to 3 inclusive, in which the Mn concentration is from 0.04 to 0.06.

5. An aluminium alloy as claimed in claim 1 or claim 2, in which the Mn concentration is from 0.04 to 0.05.

6. An aluminium alloy as claimed in any one of claims 1 to 5 inclusive, in which the lower limit of the Mg concentration is 0.05.

7. An aluminium alloy as claimed in claim 6, in which the Mg concentration is from 0.05 to 0.07.
8. An aluminium alloy as claimed in any one of claims 1 to 6 inclusive, in which the upper limit of the Mg concentration is 0.10.

9. An aluminium alloy as claimed in any one of claims 1 to 8 inclusive, in which the Si concentration is from 0.06 to 0.08.

10. An aluminium alloy as claimed in any one of claims 1 to 8 inclusive, in which the Si concentration is above 0.08.

11. An aluminium alloy as claimed in claim 1 or claim 10, in which the Si concentration is from 0.11 to 0.12.

12. An alloy as claimed in any one of claims 1 to 11 inclusive, in which the ratio of the concentration of Fe to Si (Fe:Si) in the alloy exceeds 3.0.

13. An alloy as claimed in any one of claims 1 to 12 inclusive, in which the Fe concentration is from 0.3 to 0.4.

14. An aluminium alloy as claimed in any one of claims 1 to 13 inclusive, in which the Ti concentration is up to 200 ppm.

15. An aluminium alloy as claimed in any one of claims 1 to 13 inclusive, in which the Ti concentration is up to 150 ppm.

16. An aluminium alloy as claimed in claim 1 or claim 15 in which the Ti concentration is from 50 to 150 ppm.

17. An aluminium alloy as claimed in claim 1 having a composition Mg 0.05 - 0.1: Mn 0.04 - 0.05 “ Si 0.06 - 0.08 : Fe 0.03 - 0.04 and Ti up to 300 ppm.

18. An aluminium alloy as claimed in claim 1 having a Mg concentration of 0.05 to 0.1 and a Mn concentration of about 0.5 which has been subjected to a
cold rolling strain of between 2.6 and 2.9 and which has a yield strength of between 170 and 190 MPa.

19. A lithographic sheet which is formed from an aluminium alloy having an alloy composition in accordance with any one of claims 1 to 18 inclusive.

5 20. A cast workpiece comprising an aluminium alloy having an alloy composition in accordance with any one of claims 1 to 17 inclusive.

21. A method of processing a cast aluminium alloy having a composition in accordance with any one of claims 1 to 17 inclusive which method includes producing a lithographic sheet material from said alloy by heat treating the alloy in an intermediate annealing stage at a temperature of between 280°C and 360°C for a period of at least 2 hours.

22. A method of processing an aluminium alloy to produce a lithographic sheet which method includes the steps of:

15 casting an ingot of an aluminium alloy having a composition as claimed in any one of claims 1 to 147 inclusive;

heating said alloy to a temperature of between 570°C and 610°C for a period of at least three hours in order substantially to homogenise said alloy;

hot rolling said substantially homogenized alloy to form a rerolled substantially un-recrystallized product;

heating said substantially un-recrystallized rerolled product to a temperature of between 280°C and 360°C for a period of at least 2 hours; and

cold rolling the rerolled product to a finished gauge.

23. A method as claimed in claim 22 which includes the step of cold rolling the un-recrystallized rerolled product prior to heating said product to a temperature of between 280°C and 360°C for a period of at least two hours.
24. A method as claimed in claim 22 or claim 23 which includes the step of heating the rerolled product to a temperature of about 350°C for a period of 3 hours.

25. A method as claimed in any one of claims 22 to 24 inclusive which includes subjecting the rerolled product to a cold rolling strain of 2.6 to 2.9.

26. A method as claimed in claim 25, which includes subjecting the rerolled product to a cold rolling strain of 2.8.

27. A method of processing an aluminium alloy to produce a lithographic sheet which method includes the steps of:
   - casting an ingot of an aluminium alloy having a composition in wt% (unless otherwise stated) of Mg 0.05 - 0.1:Mn 0.04 - 0.05:Si 0.06 - 0.08:Fe 0.3 -0.4 and Ti up to 300 ppm;
   - heating said alloy to a temperature of between 570°C and 610°C for a period of at least three hours in order substantially to homogenise said alloy;
   - hot rolling said substantially homogenized alloy to form a rerolled substantially un-recrystallized product;
   - heating said substantially un-recrystallized rerolled product to a temperature of about 350°C for a period of about 2 hours; and
   - cold rolling the rerolled product to a finished gauge.

28. An aluminium alloy as claimed in claim 1, substantially as herein described with reference to any one of the examples.

29. A method as claimed in claim 21, 22 or 27, substantially as herein described with reference to any one of the examples.
30. A lithographic sheet as claimed in claim 19, substantially as herein described.

31. A cast workpiece as claimed in claim 20, substantially as herein described.
FIG. 2
FIG 3
Commercial standard AA1050, electro-grained in the laboratory

Alloy G: lab processed and lab electro-grained

FIG 6