A master alloy for grain refinement of aluminium alloys contains nucleating additives of Ti and B, in addition to unavoidable impurities. The content of Ti is 0.15 - 1.45 wt%, the content of B is 0.05 - 0.9 wt% and the Ti/B ratio is between 1.7 and 2.7.

**Fig. 1**
Description

[0001] The present invention concerns a master alloy for grain refinement of aluminium and aluminium alloys in which nucleating additives of Ti (titanium) and B (boron) are added to the master alloy as well as unavoidable impurities.

[0002] It is important to control the growth of the grain when casting aluminium in order to avoid harmful defects during casting and to increase the mechanical properties of the end product. AlTiB-based master alloys (grain refiners) with Ti/B > 2.5 and, in particular, Ti/B > 3 are usually used today for this purpose. Such an alloy primarily contains three phases, α-Al (alpha aluminium), Al₃Ti (titanium aluminide) and TiB₂ (titanium diboride). α-Al constitutes the matrix in the alloy which envelops the two other intermetallic phases. Al₃Ti is formed from the reaction 3Al + Ti → Al₃Ti and is formed only when Ti/B > 2.2. This phase exists on account of a surplus of Ti in the alloy with regard to TiB₂. There is therefore a stoichiometric ratio of Ti/B = 2.2. The titanium aluminides occur as "blocky" or plate-shaped particles with a maximum size of approximately 150 µm. The second phase, TiB₂, is the nucleating phase and is the most important for grain refinement. This phase occurs as particles in the order of < 5 µm in size and is often found together with other phases in clusters or agglomerates.

Grain refiner material is usually added as wire to liquid, flowing aluminium or aluminium alloy. Material is also added in other forms such as waffles, piglets or cut wire. When added, the alloy dissolves and the particles are distributed in the melt. Al₃Ti will dissolve immediately and the titanium level in the aluminium or its alloys will increase. The growth inhibition factor will also increase greatly with the quantity of Ti (max. 0.15 wt%). In most cases this will be positive for the control of grain growth and grain size.

Since the TiB₂ particles are very stable in the melt, they will not dissolve but be distributed in the melt. During cooling and solidification, the TiB₂ particles will attract Ti from the matrix by diffusion and a nanometer-thick layer of Al₃Ti will be formed on the TiB₂ particles' basal plane. Moreover, the rest of the melt will achieve subcooling and a motive force for nucleation will have been created. The layer of titanium aluminide formed on the titanium diboride will act as the nucleating plane and an α-Al nucleus will be formed here and grow into a crystal (grain). The level of subcooling required depends on the size of the nucleating particles. Large particles require little subcooling while the opposite is true for small particles.

[0003] Using grain refiner alloys which exist on the market today, it will be possible to control the grain size to a certain degree. However, since the alloys are made with a surplus of titanium, some of the flexibility of the alloys will be removed and it will not be possible to achieve optimal use and control of the alloys. It has also been demonstrated that only 1-3% of the particles added act as nucleants. This may be due to many factors, but the most important are size distribution, agglomeration, chemistry and morphology. Therefore, there can often be large variations in the grain refinement effect of alloys which are supplied by different producers and from batch to batch.

Attempts were previously made to make alloys which are virtually stoichiometric with regard to boron and titanium. However, only little or no grain-refining effect was achieved. The high boron content of most grain refiner alloys (~ 1 wt%) will also easily form TiB₂ agglomerates and particles > 5 µm, which can be harmful to the end product.

[0004] US patent no. 5 180 447 also describes grain refiner alloys; the titanium/boron ratio is indicated as being between 0.60 and 1.67 (substoichiometric) and each of the elements titanium and boron is indicated as being between 1.5 and 2.5 wt%. Grain refiner alloys with such a composition are not available on the market, apparently because the grain-refining effect is low and too inconsistent.

[0005] The present invention describes a grain refiner alloy containing mainly only active nucleants with a much better grain-refining effect. The size distribution of TiB₂ is much lower than for prior art alloys and the number of large TiB₂ agglomerates are much lower than for prior art alloys.

[0006] The present invention is characterised in that the alloy contains 0.15 - 1.45 wt% Ti and 0.05 - 0.9 wt% B and the Ti/B ratio is between 1.7 and 2.7.

[0007] The present invention will be described in the following in further detail using examples and with reference to the attached figures, where:

Fig. 1 shows a) phase transitions in the AlTiB system and b) the increase in the quantity of Al₃Ti on the basis of the addition of Ti,

Fig. 2 shows microstructure pictures of three different alloys a), b) and c).

[0008] Alloys in accordance with the present invention are produced by liquid aluminium reacting with KBF₄ and K₂TiF₆ salts or other sources of titanium and boron adapted to the alloy's composition and at a suitable temperature T > 670 °C and T < 750 °C in a reaction furnace. The salts KBF₄ and K₂TiF₆ are added in powder form and fed at a speed V < 30 kg/min over a time t < 15min. During this feed, the metal is kept moving by means of electromagnetic agitation. The residual salt (KAIF) or slag is removed after equilibrium has been achieved and the reactions have ceased. The alloy is then transferred to an inductive holding furnace for metal purification and maturation before it is cast as wire, bolts, piglets or waffles.

[0009] In accordance with the present invention,
alloys are produced with a titanium/boron ratio between 1.7 and 2.7 and with 0.15 - 1.45 wt% Ti and 0.05 - 0.9 wt% B, which only allows the formation of TiB₂ particles or (Al(x),Ti(x-1)B₂ particles, where x < 0.1, and which means that the particles cluster and form large particles to a lesser extent.

[0010] All the titanium which is added is therefore bound up in the TiB₂, which is also known as the nucleating particle. Since the grain refiner alloys do not contain a surplus of titanium, the user does not need to take this into consideration when optimising the quantity of alloys added. In other words, the user is free to optimise the free Ti level in the final cast by regulating this in the melting furnace. This can be done by using AlTi waffles, Ti tablets or other Ti sources. The fact that all the titanium in these concentrations, Ti < 0.15 wt%, dissolves is an advantage because it ensures a homogeneous mixture of Ti and the risk that Al₃Ti particles do not dissolve is eliminated.

Moreover, the speed of addition of the grain refiner alloy will regulate the number of borides added, i.e. the higher the speed, the more borides will be added. This flexibility, together with independent separate addition of titanium, will be a feature of all known grain refiner alloys as well as all other conceivable compositions with 2.2 < Ti/B < ∞. The additive can, therefore, be optimised for each individual alloy to a greater extent than was previously possible.

[0011] An important aspect of the grain refiner alloy in accordance with the present invention is that it must mainly only contain active TiB₂ nucleants (titanium diborides), see fig. 2a.

[0012] Another important feature of the present invention is that the TiB₂ particles must have identical characteristics and that the agglomeration tendency is minimised. As a result of all the TiB₂ particles having identical characteristics, the particles’ grain-refining contribution is increased. In many cases, it is doubled in relation to other known AlTiB-based alloys. An important factor for controlling this is the concentration of titanium and boron. When this increases, the difficulties in controlling particle growth and the tendency to agglomeration will increase.

Moreover, the reaction temperature and concentration of titanium and boron in the salt bath are important factors for achieving identical particle characteristics. The reaction between aluminium and the salts K₂TiF₆ and KBF₄ is very exothermic, which leads to changes in the temperature of the metal. The concentration of the salt bath will also change since the salt is added to the metal over time while the reaction is in progress. The salt is removed after the whole reaction has finished. These changes lead to changes in the preconditions when the particles are formed, which, in turn, leads to changes in the characteristics of the particles over time. This is negative. By minimising the salt additive, it is possible to achieve better control over the factors temperature, time and concentration. More identical conditions will, therefore, be achieved throughout the reaction, which will also be finished more quickly. This leads to the TiB₂ particles having an increased nucleation ability.

[0013] The new alloy can be used as a grain refiner for all types of aluminium or aluminium alloys. It is added in traditional manner in a metal channel at an expedient distance upstream of the casting equipment. Before casting, the titanium level is adjusted in accordance with the recommended or desired level and casting can begin. The temperature at which the grain refiner alloy is added is mainly in the range 690°C-730°C. For special aluminium alloys, this may be different.

Example 1. Grain refining of 6063 Ø 203 mm billets.

[0014] The previous practice is as follows.

[0015] The titanium level in the base metal is approximately 40 ppm. Grain refiner is added as AlTi5B1 wire in a quantity of approximately 40 ppm Ti and 8 ppm B, i.e. approximately 0.8 kg per tonne. The grain size achieved is approximately 100 µm.

The new practice can be:

The titanium level in the base metal is approximately 40 ppm. The titanium level is adjusted to 100 ppm using Ti tablets (mm. 75 wt% Ti). Grain refiner is added as Hydloy in a quantity of approximately 7.2 ppm Ti and 3 ppm B, i.e. approximately 0.6 kg per tonne. The grain size achieved is approximately 100 µm.

Example 2. Grain refining of 6060 Ø 178 mm billets.

[0016] The previous practice is as follows.

The titanium level in the base metal is approximately 20 ppm. The Ti level is increased by 50 ppm in the form of AlTi5B1 waffles added to the furnace. Moreover, grain refiner is added as AlTi5B1 wire in a quantity of approximately 50 ppm Ti and 10 ppm B, i.e. approximately 1.0 kg per tonne. The grain size achieved is approximately 110 µm.

[0017] The titanium level in the base metal is approximately 20 ppm. The titanium level is adjusted to 100 ppm using AlTi10 waffles. Grain refiner is added as Hydloy in a quantity of approximately 7.2 ppm Ti and 3 ppm B, i.e. approximately 0.6 kg per tonne. The grain size achieved is approximately 100 µm.

Example 3. Grain refining of 6082 Ø 203 mm billets.

[0018] The previous practice is as follows.

The titanium level in the base metal is approximately 40 ppm. Grain refiner is added as AlTi5B1 wire in a quantity of approximately 50 ppm Ti and 10 ppm B, i.e. approximately 1.0 kg per tonne. The grain size achieved is 100 µm.

[0019] The new practice can be:

The titanium level in the base metal is approximately 40 ppm. The titanium level is adjusted to 100 ppm using Ti
tablets (mm. 75 wt% Ti). Grain refiner is added as Hyd-
loy in a quantity of approximately 9.6 ppm Ti and 4 ppm
B, i.e. approximately 0.8 kg per tonne. The grain size
achieved is approximately 100 µm.

Claims

1. A master alloy for grain refinement of aluminium
   alloys containing nucleating additives of Ti and B, in
   addition to unavoidable impurities.
   characterised in that the content of Ti is 0.15 - 1.45
   wt%, the content of B is 0.05 - 0.9 wt% and the Ti/B
   ratio is between 1.7 and 2.7.

2. A master alloy in accordance with claim 1,
   characterised in that the content of Al₃Ti is maxi-
   mum 0.5 wt%.

3. A procedure for grain refinement of an aluminium
   alloy by adding a master alloy of aluminium which
   contains nucleating additives of Ti and B,
   characterised in that a master alloy of aluminium is
   first added to the alloy and contains, apart from
   unavoidable impurities, 0.15 - 1.45 wt% Ti and 0.05
   - 0.9 wt% B. The Ti/B ratio is between 1.7 and 2.7
   and Ti is subsequently added to the alloy in the
   form of AlTi plates, Ti piglets or other Ti sources.
**Fig. 1**

![Diagram showing the relationship between Ti/B, AlB₂, and TiB₂](image)

- **Ti/B** axis:
  - Y-axis: 0, 2.2, 2.4
  - X-axis: AlB₂ → TiB₂

- **wt%Ti** axis:
  - Y-axis: 2.0, 2.2, 3.0
  - X-axis: Al₃Ti → X

- **Note**: Al₃Ti is formed at a certain point on the Ti/B axis.
Fig. no. 2  a. Hydloy, b. AlTi3B1, c. AlTi5B1, all at 75X
### Documents Considered to Be Relevant

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<th>Category</th>
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<th>Relevant to claim</th>
<th>Classification of the Application (Int.Cl./7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>DATABASE WPI&lt;br&gt; Section Ch, Week 1992/48&lt;br&gt; Derwent Publications Ltd., London, GB; Class M26, AN 1992-396403&lt;br&gt; XP002139115&lt;br&gt; &amp; SU 1 700 078 A (BRATSK ALUMINIUM WKS), 23 December 1991 (1991-12-23)&lt;br&gt; * abstract *</td>
<td>1-3</td>
<td>C22C1/03</td>
</tr>
<tr>
<td>X</td>
<td>L. ARNBERG ET AL: &quot;Grain Refinement of Aluminium Part 1&quot;&lt;br&gt; METALS TECHNOLOGY, vol. 9, no. 1, 1982, pages 1-6, XP000910316&lt;br&gt; London&lt;br&gt; * page 3, column 1, line 2 - line 5; table 1 *</td>
<td>1,2</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>EP 0 601 972 A (RHEINFELDEN ALUMINIUM GBH) 15 June 1994 (1994-06-15)&lt;br&gt; * claims 1,4 *</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>GB 1 333 957 A (GRAENGES ALUMINIUM AB)&lt;br&gt; 17 October 1973 (1973-10-17)</td>
<td></td>
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</tr>
</tbody>
</table>

The present search report has been drawn up for all claims

Place of search: THE HAGUE<br> Date of completion of the search: 30 May 2000<br> Examiner: Gregg, N

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<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int.Cl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P,X</td>
<td>CHEMICAL ABSTRACTS, vol. 131, no. 10, 6 September 1999 (1999-09-06) Columbus, Ohio, US; abstract no. 133024</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SPITTLE, J. A. ET AL: &quot;The grain refinement of Al7Si alloys with boron containing refiners&quot; XP002139114</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims

Place of search | Date of completion of the search | Examiner |
<table>
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<tr>
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<tr>
<td>THE HAGUE</td>
<td>30 May 2000</td>
<td>Gregg, N</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU 1700078 A</td>
<td>23-12-1991</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA</td>
<td>30-06-1994</td>
</tr>
<tr>
<td>GB 1333957 A</td>
<td>17-10-1973</td>
<td>SE</td>
<td>25-09-1972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE</td>
<td>16-09-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA</td>
<td>05-02-1974</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE</td>
<td>11-11-1971</td>
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<tr>
<td></td>
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<td>FR</td>
<td>14-01-1972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL</td>
<td>01-11-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO</td>
<td>24-06-1974</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US</td>
<td>15-01-1974</td>
</tr>
</tbody>
</table>

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