RECENT DEVELOPMENTS IN GRAIN REFINING OF ALUMINIUM AND ALUMINIUM ALLOYS

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STRESZCZENIE
W pracy określono dwoma niezależnymi metodami wpływ przemysłowych i nowych podwójnych i potrójnych zapraw na rozdrobnienie ziarna w wysokowytrzymających stopach aluminium i czystym aluminium. Przecząto wpływ ilości dodatku zapraw, temperatury odlewania i czasu wytrzymania w temperaturze odlewania. Badania wykazały, znaczna efektywność przemysłowej zaprawy podwójnej Al-Ti. Następnie stwierdzono, że zaprawa potrójna Al-Ti-B jest skuteczniejsza. Bardzo dobra skuteczność stwierdzono przy zastosowaniu zaprawy Al-Ti-C opracowanej w TUB w okresie ostatnich dziesięciu lat. Porównanie pomiędzy testem w stalowej wlewnicy a Alcoa-cold-finger-test wykazały podobne tendencje do rozdrobnienia ziarna. W teście Alcoa stwierdzono tworzenie się nie tylko równoosiowych i kolumnowych ziarn ale również płatkowych. Szczególnie korzystnym przy stosowaniu zaprawy Al-Ti-C oprócz b. dobrego wpływu na rozdrobnienie ziarna jest tworzenie aglomeratów TiC o b. małych wymiarach, znacznie mniejszych niż aglomeratów TiB₂ powstających przy stosowaniu przemysłowych zapraw Al-Ti-B. Stosowanie w przyszłości zapraw Al-Ti-C dla stopów przemysłowych da w efekcie podniesienie jakości folii, płyt litograficznych i blach dla przemysłu lotniczego.

ABSTRACT
Two different grain refining test methods were used to test the effect of commercial and new binary and ternary aluminium master alloys on pure aluminium and high strength aluminium alloys. The influences of the amount of master alloy addition, pouring temperature and holding time were investigated. The grain refining tests have shown that the commercial binary Al-Ti-master alloy is very effective. Further, it was confirmed that the ternary Al-Ti-B-master alloys are more effective. A very good grain refinement effect was also prevalent in the new Al-Ti-C-master alloys, which were developed initially at the TUB during the last ten years [1]. A comparison between the two grain refining test methods, the „TUB Steel Mould Test“ and the „Alcoa Cold Finger Test“ showed similar tendencies of grain refinement. The Alcoa-Cold-Finger-Test has the advantage of exhibiting feather crystals in addition to equiaxed and columnar grains. The new Al-Ti-C-master alloys, scores over the commercial Al-Ti-B-master alloy due to the much smaller size of TiC-agglomerations in the former, than the TiB₂-agglomerations in commercial Al-Ti-B-master alloys. Thus, the Al-Ti-C-master alloys seem to have a good future for application in the industry for producing high quality products like foils, lithographic sheets and aircraft plates.
1 Introduction
In order to refine the primary $\alpha$-aluminium phase during casting of aluminium and its alloys it is the modern practice to adopt a grain refining procedure, which involves the addition small amounts of grain refiner. The nucleants of primary aluminium phase are soluble Al$_3$Ti-Phase, TiB$_2$- or TiC-particles added in the form of master alloy which contain a minimum number of these particles. The size of particles and amount of the grain refiner is to be reduced of a minimum to prevent production problems during extrusion or rolling of the alloys.

This paper presents the results of studies carried out to determine the grain refining performances of binary Al-Ti-, or ternary Al-Ti-B- and Al-Ti-C-master alloys, at varying concentrations, pouring temperatures and holding times. The master alloys AlTi6, AlTi5B0.2, AlTi6C0.1, AlTi6C0.2 and AlTi5C0.25 were tested on pure aluminium Al99.7 and AlZnMgCu1.5 (7475).

For testing the grain refining efficiency of master alloys it is helpful to use standardised test methods. These methods are quite simple in aspect of handling and preparation of the test samples. Further, it is necessary to work with test methods which can be used for all aluminium alloys. The present investigations were carried out using the TUB Steel Mould Test ("TUB Test") and the Alcoa Cold Finger Test ("ACF Test"). The TUB Test has a very easy handling, because the test mould is made of a commercial steel and a melt of only 150 g aluminium is needed to be poured into the mould with room temperature. The ACF Test mould consists of a preheated ceramic mould for 600 g aluminium. The solidification starts at a water cooled copper finger who dips on the top into the melt. This simulates the solidification at continuous casting processes.

2 Experimental details
2.1 Description of the TUB Test and the ACF Test
A schematic diagram of the TUB Test is shown in figure 1. The TUB Test mould is made of steel, constructed for 150 g of Aluminium. The mould is used for ambient temperature and must be coated. Every commercial coating has only a negligible influence on the solidification. If only melts of 150 g, molten in electrical resistance furnaces were used this test will be called "TUB Laboratory Test" ("TUB LT"). After sample preparation the microstructure shows columnar crystals or equiaxed crystals or a mixture of both.
The ACF Test consists of a test rig for fixing a water cooled copper finger and centering the mould exactly below it [2], as shown in figure 2. A furnace for heating the mould inside of the test rig was not used. The mould was made from an insulating material and was preheated in an external furnace. Several shapes and materials of moulds can be used. The material of the mould used at TUB was calciumsilicate and contains 650 g of aluminium. The copper finger dips nearly 30 mm into the melt. In addition to the simulation of the solidification of a continuous casting process the other advantage of this test method is the appearance of columnar grains, equiaxed grains and in addition feather crystals. To avoid feather crystals at rolling bar casting is very important. The feather crystals make problems at rolling, they causes a structure of large grains in rolling sheets. This test gives the possibility to check the number and size of feather crystals.

The metallographic preparation of the samples starts with cutting of the samples. The TUB Test samples are cut horizontally, by those of ACF Test longitudinally. After surface grinding the samples are etched with a 16%-CuIICl-solution. This method of preparation produces a good quality of macro structure. The grain size measurement is done by line intercept method, see figure 1 and figure 2.

2.2 Grain refining tests

All investigated master alloys were delivered as rods. For comparison between the commercial master alloys and the new Al-Ti-C-ones, the commercial binary master alloy AlTi6 and the two commercial ternary master alloys AlTi5B1 and AlTi5B0.2 were investigated. Out of the several experimental Al-Ti-C-master alloys produced, AlTi6C0.1, AlTi6C0.2 and AlTi5C0.25 were tested. The master alloys were tested on pure aluminium (TUB Test and ACF Test) and on the high strength alloy AlZnMgCu1.5 (AA7475, ACF Test). The casting parameters were varied as follows:
- Addition amount: 0.5 / 1.0 / 2.0 / 3.0 / 4.0 and 5.0 kg/t
- Pouring temperature (T_p): 700°C and 750°C
- Holding time (t_h): 1 / 5 / 15 / 30 and 60 min

In the following figures, first results of TUB-Laboratory-Tests and later results of ACF Tests are presented. On the Y-axis of figures the diameters of equiaxed grains are called „Average Grain Size“. If columnar grains were found in the macrostructure, the average width was measured at the half of the length (TUB Test) or in the
measuring line (ACF Test). These are plotted using a second Y-axis called „Width of Columnar Grains“.  

2.2.1 TUB Test

Amounts of 150 g Al99.7 were molten in aluminium oxide crucibles using an electric resistance furnace. After adding the master alloy, the melts were poured into the TUB Test moulds, as described above.

![Figure 3 - a) and b)](image)

Grain refining tests (TUB Test) of the master alloy rods a) AlTi6, AlTi5B1 and AlTi5B0.2 in comparison with b) AlTi6, AlTi6C0.1 and AlTi6C0.2 on pure aluminium Al99.7. The pouring temperature was 700°C at a holding time of 5 min.

![Figure 4 - a) and b)](image)

Grain refining tests (TUB Test) on pure aluminium Al99.7. Comparison of the influence between pouring temperatures of 700°C and 750°C at a) the master alloys AlTi6 and AlTi5B1 and at b) AlTi6 and AlTi6C0.1. The holding time was 5 min.

At the first stage of experiments, the grain refining efficiencies of all master alloys were compared together, see figure 3. The binary master alloy AlTi6 shows a better grain refining efficiency than AlTi5B1 at a small addition amount of 1.0 kg/t. In general, the grain refining efficiencies of these two master alloys are equally good. AlTi5B0.2 shows a less good grain refining efficiency (figure 3a). The new Al-Ti-C-master alloys show grain refining efficiencies comparable to that of AlTi6. At 2.0 kg/t both are little better than AlTi6. At higher additions, AlTi6C0.1 shows a similar grain
refining efficiency to AITi6. The master alloy AITi6C0.2 has a little better grain refining efficiency than the other two master alloys (figure 3b).

At a higher pouring temperature, 750°C instead of 700°C, the master alloys AITi6, AITi5B1, AITi6C0.1 and AITi6C0.2 show a decrease of grain refining efficiencies, see figure 4a and 4b. The smallest decrease was found at AITi6C0.1 with additions of 2.0 kg/t and more.

An increase in the holding time up to 120 min results in a decrease of the grain refining efficiencies of AITi6, AITi5B1, AITi6C0.1 and AITi6C0.2, as shown in figure 5. At most interesting holding times of 1 min, 5 min and 15 min the Al-Ti-C-master alloys show better grain refining efficiencies than AITi6 and AITi5B1. At longer holding times, AITi5B1 and AITi6C0.2 show good and more stable grain refining results than the other ones.

2.2.2 ACF Test
As mentioned above, the ACF Test simulates the solidification in the continuous casting process, which is used for the production of wrought alloy products. Because of this only the results of two master alloys will be presented, which are typically used to refine wrought alloys. The first master alloy is AITi5B0.2, the second one is the experimental Al-Ti-C-master alloy AITi5C0.25. Both will be compared in their grain refining efficiencies at additions of 0.5 kg/t, 1.0 kg/t and 2.0 kg/t to melts of 15 kg Al99.7 and AlZnMgCu1.5 in an electric resistance furnace. The pouring temperature was 700°C. The holding time was varied between 1 min and 60 min.
At each holding time nearly 600 g of grain refined melt was taken from the 15 kg melt with a preheated ladle and poured into the preheated ACF Test mould in the ACF Test rig (figure 2).

At additions of 1.0 kg/t and 2.0 kg/t, the experimental master alloy rod AI\textit{T}i5C0.25 shows a better grain refining result than the commercial AI\textit{T}i5B0.2 rod. Only at longer holding times up to 60 min the boron containing master alloy has the advantage of a more stable grain refining effect.

The carbon containing master alloy shows at 60 min a considerable fading effect, as shown in figure 6. The grain refining experiments with additions from 0.5 kg/t to 2.0 kg/t AI\textit{T}i5B0.2 and AI\textit{T}i5C0.25 on the alloy AI\textit{Z}nMgCu1.5 shows similarly good grain refining results of both master alloy types at 2.0 kg/t. At small additions, the Al-Ti-C-type is a little better in grain refining than the Al-Ti-B-type, compare figure 7 and figure 8.

One of the advantages of the ACF Test is the possibility of showing feather crystals. In figure 9, macrographs of refining effect of AI\textit{T}i5B0.2 and AI\textit{T}i5C0.25 on pure aluminium and on AI\textit{Z}nMgCu1.5 are shown from ACF Tests.
### 2.3 Hard particles and agglomerations

In the production of wrought alloys only master alloys are used which have small amounts of hard particles which could form agglomerates e.g. TiB₂ or here investigated TiC. The diameters of these hard TiC-particles must be smaller than the thickness of foils, e.g. 6 μm. Their agglomerations must be very small, too. If this is not reached at the production of Al-Ti-C-master alloys (or Al-Ti-B-master alloys) there

<table>
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<tr>
<th>Macrographs of ACF Test samples showing columnar grains</th>
<th>Feather crystals</th>
<th>and equiaxed grains</th>
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<tbody>
<tr>
<td>a) 0.5 kg/t AlTi5B0.2</td>
<td>b) 1.0 kg/t AlTi5B0.2</td>
<td>c) 2.0 kg/t AlTi5B0.2</td>
</tr>
<tr>
<td>d) 0.5 kg/t AlTi5C0.25</td>
<td>e) 1.0 kg/t AlTi5C0.25</td>
<td>f) 2.0 kg/t AlTi5C0.25</td>
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Figure 9 a - f) M = 1 : 1.5; \[ = 15 \text{ mm} \]
will be problems at the later production stages i.e. at extrusion or rolling processes of grain refined alloys which can result into a very expensive scrap production.

The above mentioned aim of TiC-particle diameters below 6 μm was reached, which corresponds to below 2 μm, see Figure 10. The largest TiC-agglomerations are acceptable, because these are not compact.

3 Discussion

The new experimental Al-Ti-C-master alloys promise a successful working in foundry shops with a continuous casting production of aluminium and aluminium wrought alloys. Often the grain refining efficiency is better than the grain refining efficiency of AlTi5B0.2. Only at long holding times, Al-Ti-B-master alloys are more efficient. An unexpected result was found to be the good grain refining efficiency of AlTi6. This type of a commercial binary master alloy has been successfully developed in the last few years. It nucleates the α-aluminium only by the Al₃Ti-particles. The commercial ternary Al-Ti-B-master alloys or the newly developed Al-Ti-C-master alloys work with two nucleants Al₃Ti and TiB₂ or Al₃Ti and TiC. The combination in form of agglomerations of a stable nucleant in aluminium melts - TiB₂ or TiC - and a soluble one -Al₃Ti- increases the grain refining efficiency and decreases fading effects. The reason for this very good working together of two types of nucleants is the hindering of the solution of Al₃Ti by the other particle type in the agglomerate. Small agglomerations of TiB₂ and Al₃Ti or TiC and Al₃Ti are excellent nucleants. The new Al-Ti-C-master alloys do not make problems on the aspect of hard TiC-particles and large agglomerations of these. The diameters of the TiC-particles are dominantly very small. The sizes of agglomerations are more problematical, but on the other hand, these agglomerations are mostly not compact. For a fast testing of the grain refining efficiency a simple steel mould test, like the TUB Test, is not exact in producing of the macro structure, but good enough for investigating the grain refining efficiency. Further, it is more easy in handling than the more exact working Alcoa-Cold-Finger-Test.

4 Summary

The investigated new experimental Al-Ti-C-master alloys work often better than the commercial Al-Ti-B-master alloys on pure aluminium and on the high strength alloy AlZnMgCu1.5. There are no problems with the diameters of TiC-particles. A simple grain refining test like the TUB Test is not exact in producing of the macro structure, but good enough for investigating the grain refining efficiency. Further, it is more easy in handling than the more exact working Alcoa-Cold-Finger-Test.

5 References

1.... A. Banerji, Ph.D.-Thesis, Technical University Berlin, 1987