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REMELTING OF ALUMINIUM WITH THE ADDITION OF AlTi5B1 AND AlTi3C0,15 GRAIN REFINERS

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It was found that concentration of boron in aluminium with the addition of AlTi5B1 grain refiner is decreasing during remelting as a consequence of TiB_2 particles settling down due to gravity. TiB_2 particles remained in aluminium after four remelts shows lower effect of grain refinement compared to non-remelted samples with the same TiB_2 content. It was also found that TiC particles are still present in aluminium with the addition of AlTi3C0,15 grain refiner after four remelts and they probably participate in nucleation of α-Al grains.

Key words: aluminium, casting, solidification, grain refinement

Pretapanje aluminiuma sa dodatkom inokulanta AlTi5B1 i AlTi3C0,15. Istraživanjem je utvrđeno, da se s pretapanjem aluminiuma, kod dodavanja modifikatora AlTi5B1, koncentracija bora u leguri smanjuje, što je posljedica gravitacijske segregacije TiB_2. Kod istog sadržaja čestica TiB_2 u leguri, ima taj inokulant poslije četiri pretapanja, manji efekt na smanjenje velikosti kristalnih zrna, kao u primarno taljeni leguri. Isto tako je bilo ustanovljeno, da su u aluminiumu sa dodatkom AlTi3C0,15, i poslije četiri pretapanja još prisutne čestice TiC, koje vjerojatno sudjeluju u procesu nukleacije zrna α-Al.

Ključne riječi: aluminij, lijevanje, skrućivanje, smanjivanje zrna

INTRODUCTION

It is well known that metals and alloys usually solidify with a coarse, columnar grain structure under normal casting conditions. In industry, grain refinement is a common way of achieving a proper, uniform, fine grain structure in wrought aluminium alloys. The most widely used grain refiners are based on Al–Ti–B, notably Al-5wt.%Ti-1wt.%B (AlTi5B1). AlTi5B1 grain refiners are composed of an α_{Al} matrix, Al_3Ti and TiB_2 particles [1]. Grain refiners based on Al–Ti–B are very effective, but they suffer from poisoning in the presence of Zr, and also some other elements [2]. For this and other reasons there is increased interest in the use of alternative Al–Ti–C-based grain refiners, for example, Al-3wt.%Ti-0,15wt.%C. AlTi3C0,15 grain refiners are composed of an α_{Al} matrix, Al_3Ti and TiC particles [3]. The TiC particles, which were introduced via Al–Ti–C-based grain refiners, were found in the grain centers of the aluminium castings [4]. It has been found that TiC phase is unstable at typical conditions of grain refinement but the rate of replacement of TiC by Al_4C_3 is slow and do not significantly affect grain refinement at low temperatures and short holding times [5-7].

It is also known that effect of AlTi5B1 grain refiner is much smaller than expected if grain refined melt is held for longer time. This phenomenon is usually called fading. Consequently this means that a number of potent nucleating sites decrease with holding time [2]. This is usually attributed to either dissolution or settling/floating (or both) of nucleating particles during long holding [2]. Results of Wang et al. shows that content of Ti and B in Al-Ti-B grain refined melt is decreasing with holding time and stirring of melt can recover Ti and B content in the melt [8]. Continuous stirring can prevent the fading in Al-Ti-B grain refined aluminium melt [8,9]. Limmaneevichitr et al. have found that Ti and B contents were increased at the bottom of crucible due to settling of Al_3Ti and TiB_2 particles [10]. They also found that vigorous agitation of melt using argon purging can partly bring the particles back into the melt [10].

The objective of this work is finding out the influence of remelting on the effect grain refining of alumininum with the addition of AlTi5B1 and AlTi3C0,15 grain refiners.

EXPERIMENTAL

Commercial-purity aluminium (99,8 wt.% Al) and a commercial grain refiners in the form of 9,5 mm diameter wire AlTi5B1 (LSM – London & Scandinavian Metallurgical Co. Limited) and AlTi3C0,15 (SMC-Shiel-

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dalloy Metallugical Corporation) were used in this study. Chemical composition of aluminium is presented in Table 1 and compositions of grain refiners in Table 2.

Table 1. **Chemical composition of commercial-purity aluminium**

/ wt.%	Si	Fe	V	Ti	B
Al99,8	0,031	0,081	0,001	0,0015	<0,0005

Table 2. **Chemical composition of grain refiners**

	Ti / wt.%	B / wt.%	C / wt.%
AlTi5B1	5,1	1,04	–
AlTi3C0,15	3,1	–	0,18

Three kilograms of the aluminium were melted in an induction furnace with graphite crucible. Grain refiners were added at the temperature of 705°C. Melt was stirred after the addition of grain refiner and two minutes after the addition of grain refiner cast in to bronze mold presented in Figure 1. Remained melt from graphite crucible was cast in to larger gray iron mold. Casting from the larger gray iron mold was used for remelting. Casting was melted again, stirred at the temperature of 705°C and two minutes after reaching the temperature 705°C cast in to a bronze mold and the remained melt in to a gray iron mold. Remelting was repeated four times.

Casings from the bronze mold were cut 13 mm above the bottom for microstructure analysis. Samples for microstructure analysis (grain size measurement) were ground, polished and anodized for 2 minutes at 23 V in 2,5% water solution of HBF_4 for polarized light microscopy. Mean intercept grain size was calculated from the measured average grain area.

Metallographic samples for SEM were ground and polished with diamond paste. The preparation of the metallographic samples was completed with a 5-minute polish in a SiO_2 suspension after polishing with 3-μm diamond paste. The SEM examinations were preformed with a Jeol-6500F equipped with EDS at 10 kV.

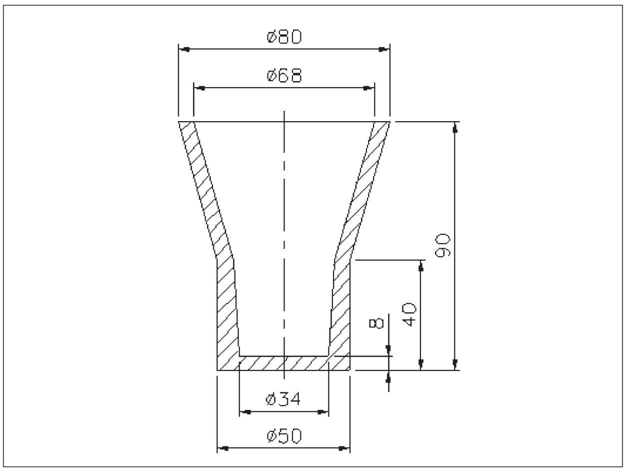

Figure 1. Shape and dimensions of the bronze mold

RESULTS AND DISCUSSION

Results of remelting of aluminium with the addition of AlTi5B1 (sample A4) and AlTi3C0,15 (sample C4) are presented in Table 3. Influence of remelting on grain size and boron concentration in aluminium with the addition of AlTi5B1 and AlTi3C0,15 grain refiners are also presented in Figure 2.

Grain size in aluminium with the addition of AlTi5B1 grain refiner increases with remelting. Grain size increase after first two remelts is larger than after third and fourth remelt.

Concentration of titanium and boron is decreasing with remelting and the Ti/B ratio is increasing (Table 3). Figure 3 shows casting from the melt remained after four remelts. On the casting are marked positions of samples taken for chemical analysis of Ti and B which are given in Table 3. Concentrations of boron and tita-

Table 3. **Grain size and composition of aluminium with the addition of AlTi5B1 and AlTi3C0,15 grain refiner after different number of remelts**

Sample	Number of remelts	Grain area / μm^2	Grain size / μm	Ti / wt.%	B / wt.%	Ti/B
A4	0	12055	98	0,023	0,0035	6,57
A4-P1	1	15577	111	–	–	–
A4-P2	2	21430	130	0,022	0,0030	7,33
A4-P3	3	24987	141	–	–	–
A4-P4	4	27048	146	0,020	0,0025	8,00
A4-P4S	4	–	–	0,020	0,0025	8,00
A4-P4Z	4	–	–	0,020	0,0024	8,33
A4-P4VRH	4	–	–	–	0,0087	–
C4	0	26898	146	0,021	–	–
C4-P1	1	25802	143	–	–	–
C4-P2	2	25768	143	0,020	–	–
C4-P3	3	30329	155	–	–	–
C4-P4	4	46801	193	0,020	–	–

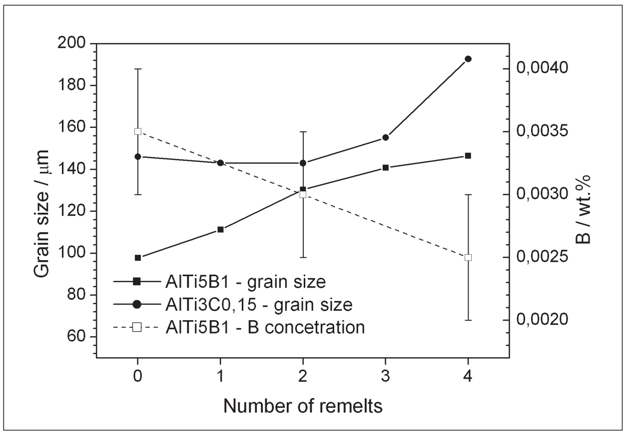

Figure 2. Grain size and boron concentration as a function of number of remelts for AlTi5B1 and grain size as a function of number of remelts for AlTi3C0,15 grain refiner in aluminium

nium in the upper part of side face A4-P4Z and bottom part of side face A4-P4S of the casting form the melt remained after four remelts are similar as in the sample A4-P4 (Table 3). Chemical analysis of the surface region at the top of the casting form the melt remained after four remelts (A4-P4VRH) presented in Figure 3 shows that concentration of boron is 3,5 times higher than in the other parts of the same casting (Table 3).

One part of titanium in melted aluminium containing AlTi5B1 grain refiner is dissolved in the melt and another part is in the form of TiB_2 particles. Decreasing concentration of titanium and boron and increasing ratio Ti/B with remelting of aluminium with addition of AlTi5B1 grain refiner indicates that quantity of TiB_2 phase is decreasing. Consequently, if we assume that TiB_2 particles are nucleants for aluminium grains then it is expected that grain size is increasing as the quantity of TiB_2 is decreasing.

Density of aluminium melt at 700°C is ~ 2,4 g/cm^3 and density of TiB_2 phase is 4,5 g/cm^3. Settling of TiB_2 is expected since there is the difference of densities between aluminium melt and TiB_2. Settling of TiB_2 particles in aluminium melt would lead to increased fraction of TiB_2 particles in aluminium melt at the bottom of crucible. Melt from the bottom of crucible is flowing out last as we pour out the melt from the crucible. All of the melt could not be flown out from the crucible because of solidification. In that way a part of aluminium melt with increased fraction of TiB_2 particles was lost. This explanation is also conformed by the fact that concentration of boron in the surface region at the top of the casting form the melt remained after four remelts (A4-P4VRH) presented in Figure 3 is much higher than in the other parts of the casting.

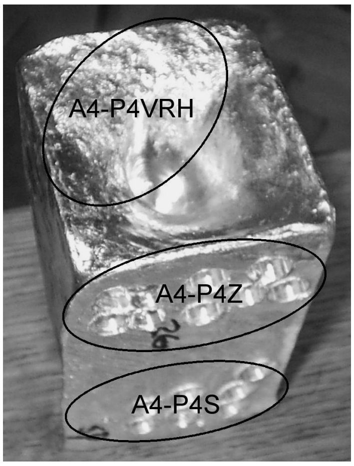

Figure 3. Casting from the melt remained after four remelts with marked positions of samples taken for chemical analysis of Ti and B given in table 3.

Table 4. **Comparison of the effect of grain refinement in sample remelted 4 times (A4-P4) and samples which were not remelted (A1, A2 and A3)**

	Ti / wt.%	B / wt.%	Grain area / μm^2	Grain size / μm
A1	0,0058	0,0008	27869	149
A2	0,0090	0,0012	22236	133
A3	0,0130	0,0019	19077	123
A4-P4	0,0200	0,0025	27048	146

It is also interesting to compare the effect of grain refinement in samples after four remelts and samples which were not remelted. This comparison is presented in Table 4. Samples A1, A2 and A3 were not remelted and present samples of aluminium with the addition of AlTi5B1 grain refiner. Samples were prepared under the same condition as the sample A4. Comparison in Table 4 shows that sample A4-P4 has similar grain size as the sample A1, which has a concentration of boron only 0,0008 wt.%. It can be concluded from this comparison that the efficiency of TiB_2 particles present in aluminium with the addition of AlTi5B1 grain refiner is decreasing with remelting. As it was proved in this work process of settling of TiB_2 particles is going on in grain refined melt. It is also likely that, since the TiB_2 particles shows a size distribution, larger TiB_2 particles would settle down faster. As it was shown by Greer at al. [11,12] larger particles needs smaller undercooling for free growth. Consequently it is completely expected that such a TiB_2 particles size distribution with smaller fraction of biggest TiB_2 particles shows lower effect of grain refinement.

Grain size in aluminium with the addition of AlTi3C0,15 remained unchanged after first two remelts and increases after third and fourth remelt. Increase in grain size after forth remelt is larger than increase in grain size after third remelt. Although decrease in concentration of titanium in Table 3 is found the difference is much smaller than accuracy of titanium concentration measurement.

Titanium carbide is thermodynamically unstable and decompose [5-7,13]. According to aluminium corner of equilibrium phase diagram Al-Ti-C at 700°C proposed by Vandyoussefi et al. [6] all compositions important for

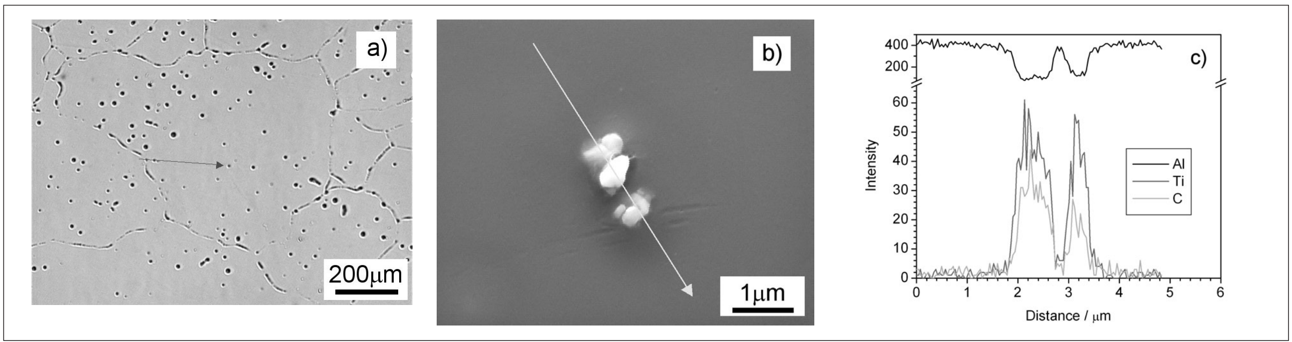

Figure 4. SEM-EDS analysis of sample C4-P4 a) Optical micrograph b) Secondary electron image of region marked with arrow on optical micrograph and c) distribution of Al, Ti and C along the arrow in secondary electron image

industrial use are in region L+Al_4C_3. Sample C4 with composition of 0,0021 wt.% of titanium and 0,0012 wt.% of carbon also lie in L+Al_4C_3 region. Carbon content in sample C4 was calculated from the chemical composition and addition of grain refiner. According to proposed phase diagram [6] TiC particles present in melt as a consequence of AlTi3C0,15 grain refiner addition are thermodynamically unstable and decompose.

Results in Table 3 and Figure 2 shows that grain size starts to increase after third remelt. This means that based on the TiC thermodynamic instability in aluminum melt decomposition of TiC is not instant, what was also found by other authors [7]. SEM analysis of aluminum with the addition of AlTi3C0,15 grain refiner after fourth remelt (sample C4-P4) is shown in Figure 4. SEM analysis conforms that TiC particles are still present in the aluminum melt after four remelts and can possibly participate in nucleation of α-aluminium grains.

It is also interesting to compare the effect of both grain refiners (AlTi5B1 and AlTi3C0,15) with remelting. In the case of AlTi5B1 grain refiner the effect of grain refinement is decreasing immediately after first remelt as shown in Figure 2 and that the increase in grain size is lower with every remelt. On the other hand the effect of grain refinement remained unchanged after first two remelts in the case of AlTi3C0,15 grain refiner. The effect of grain refinement decreases after third and fourth remelts and grain size increase is larger with every remelt. This difference between grain refiners indicate that the reasons for decreasing effectiveness with remelting are probably not the same in the case of AlTi5B1 and AlTi3C0,15 grain refiners. Similar grain size increase acceleration with holding time by modeling has been also found by Tronche et al.[7].

CONCLUSIONS

Grain size is increasing and boron content is decreasing with remelting of aluminium with addition of AlTi5B1 grain refiner. Decreasing boron content with remelting is a consequence of TiB_2 particles settling down due to gravity. It was also found that TiB_2 particles remained in aluminium with the addition of AlTi5B1 grain refiner after four remelts shows lower effect of grain refinement compared to non-remelted samples with the same TiB_2 content. This could be explained by the difference in TiB_2 particle size distribution, formed during settling.

TiC particles are still present in aluminium after four remelts and they probably participate in nucleation of α-Al grains.

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Note: Linguistic Adviser / English language Paul Mc Guiness, Ljubljana, Slovenia