DIFFERENCES IN BEHAVIOUR OF AlTiB AND AlTiC GRAIN REFINERS IN ALUMINUM

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A comparison of performance of AlTi5B1 and AlTi3C0.15 grain refiners in commercial-purity aluminum AA 1080 at contents up to 10 $\mathrm{g \cdot kg^{-1}}$ for AlTi5B1 and 16 $\mathrm{g \cdot kg^{-1}}$ for AlTi3C0.15 grain refiner is studied in this work. The results show that AlTi5B1 grain refiner is much more effective in suppressing the growth of columnar grains at the same titanium content. AlTi5B1 grain refiner in comparison to AlTi3C0.15 grain refiner also shows smaller grain size at the same titanium content except at the highest one. It was observed that the effectiveness of AlTi5B1 grain refiner decreases at the content above 4 $\mathrm{g \cdot kg^{-1}}$. Similar behaviour was not found for AlTi3C0.15 grain refiner. The differences in the behaviour of the both refiners at the high refiner content can be explained by the differences in the mechanism of the grain refinement.

Key words: casting, aluminum, grain refining

ROZDÍLY V ÚČINCÍCH PŘÍSAD AlTiB a AlTiC NA ZJEMNĚNÍ ZRNA U HLINÍKU

Příspěvek se zabývá porovnáním účinků přísad AlTi5B1 a AlTi3C0,15 na zjemnění zrna u hliníku běžné čistoty AA 1080. Účinek je sledován při dávkování do 10 $\mathrm{g \cdot kg^{-1}}$ pro AlTi5B1, resp. dávkování do 16 $\mathrm{g \cdot kg^{-1}}$ pro AlTi3C0,15. Výsledky ukázaly, že AlTi5B1 je při stejném obsahu Ti mnohem efektivnější při potlačování růstu sloupcových krystalů než AlTi3C0,15. Při stejném obsahu Ti vede AlTi5B1 i k jemnějšímu zrnu, s výjimkou nejvyššího obsahu Ti. Ukázalo se, že účinnost AlTi5B1 klesá při dávkování nad 4 $\mathrm{g \cdot kg^{-1}}$. U AlTi3C0,15 nebylo takové chování zjištěno. Rozdíly v účincích obou sledovaných přísad při vysokém dávkování lze vysvětlit rozdílným mechanizmem zjemňování zrna.

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1. Introduction

The equiaxed and fine-grained microstructure in DC-castings of aluminum and aluminum alloys can be achieved by addition of Al-Ti-B grain refiners. The advantages of the equiaxed and fine-grained microstructure include [1, 2]: improved mechanical properties, reduction of surface defects in alloys for rolling and extrusion applications, less probability of warm-cracks in shell zone of DC-cast ingots, higher casting speed without cracking, and shorter time required for homogenization treatment.

Al-Ti-B grain refiners are composed of α-aluminum matrix, Al_3Ti, and TiB_2 phases. Al_3Ti phase dissolves in the aluminum melt at typical addition content of Al-Ti-B refiners, while TiB_2 phase is stable. Al-Ti-B grain refiners are very effective but their disadvantage is the agglomeration of TiB_2 particles. Presence of Zr in aluminum alloys also reduces effectiveness of Al-Ti-B refiners. Although Al-Ti-B grain refiners are very effective, their disadvantages have led to interest in alternative Al-Ti-C grain refiners. Al-Ti-C refiners, among which the most often mentioned is AlTi3C0.15, are composed of α-aluminum matrix, Al_3Ti and TiC phases. Al-Ti-C refiners are much more resistant to poisoning in the presence of zirconium solute and more resistant to particle agglomeration [3].

Several theories for the mechanism of grain refinement have been proposed so far. The review of those theories is presented in several papers [2, 4, 5]. Mohanty et al. [6] proposed Duplex nucleation theory for the nucleation mechanism in Al-Ti-B grain refiners. They showed that the dissolved titanium is needed for the nucleation of α-aluminum on TiB_2 particles. The titanium rich layer (presumed to be Al_3Ti) was observed on TiB_2 particles at the hypoperitectic concentration of titanium. More convincing evidence for this theory was presented by Schumacher et al. [7]. They added Al-Ti-B refiner to an aluminum rich metallic glass $Al_{85}Ni_5Y_8Co_2$. They found that nucleation of α-aluminum takes place only on (0001) planes of TiB_2 particles coated with the thin layer of Al_3Ti phase.

Results show that the nucleation of α-aluminum in Al-Ti-C refiners takes place directly on TiC particles [8, 9]. TiC particles, octahedral in shape, show cube-cube orientation relationship with the surrounding α-aluminum [8]. The grain refinement is not influenced only by the potent nucleation. The quantity of the elements dissolved in aluminum has also influence on grain refinement [10]. The growth restriction of various elements can be quantified by the growth restriction factor, GRF, which is the product of liquids slope m, concentration of element C_o, and equilibrium partition coefficient k minus one. The rate of spherical growth is inversely proportional to GRF. High GRF means that the rate of spherical growth is small as well as evolved latent heat, which limits further undercooling. Among the elements present in aluminum and aluminum alloys, titanium has the highest value of GRF/wt.%. It was experimentally demonstrated that greater growth restriction leads to finer grain size [11], and such effects were modelled quantitatively [12].

Particle size distributions of TiB_2 and TiC in AlTi5B1 and AlTi3C0.15 grain refiners show that diameters of TiC particles are approximately one third of the TiB_2 particles [8, 9, 12]. Smaller size should lead to differences in performance, particularly to greater undercooling required for the grain growth initiation [9]. Al-Ti-C grain refiners should be less effective than Al-Ti-B in suppressing columnar growth. The experiment results of Schneider [3] show that much higher additions of AlTi3C0.15 grain refiner are needed for the achievement of the completely equiaxed grain structure at the same conditions in DC casting of aluminum in comparison with AlTi5Bl.

The concentration of the dissolved titanium in the aluminum melt has an important effect on nucleation. The experimental results [7] revealed that the grain size first decreases and then increases with the increasing Ti/B ratio above stoichiometric ratio for TiB_2. Schumacher et al. [7] explained this phenomenon by the increasing thickness of Al_3Ti layer. When Al_3Ti layer is very thin, the interatomic spacing in its (112) plane is stretched by the epitaxy on TiB_2 and more closely matches the (111) α-aluminum plane. This effect disappears in thicker layer. If the additive content of AlTi5B1 refiner in aluminum is increased, the concentration of the excess titanium dissolved in the aluminum melt also increases. Higher concentration of the titanium leads to the increase in thickness of Al_3Ti layer and, consequently, to the degradation of the nucleation mechanism. The results of Greer et al. [12] show that grain sizes at the addition content of AlTi5B1 above 5 $g \cdot kg^{-1}$ are constant and do not decrease with the increasing addition content in accordance with the predictions of the free-growth model. The nucleation mechanism on TiC particles in Al-Ti-C grain refiners is probably different than in Al-Ti-B. It appears that TiC acts as a direct nucleant for α-aluminum [9]. This would mean that there is no degradation of the nucleation mechanism in the case of Al-Ti-C refiner.

The main purpose of this work is the comparison of the influence of AlTi5B1 and AlTi3C0.15 grain refiners on grain size at the addition content up to, approximately, 10 $g \cdot kg^{-1}$ for AlTi5B1 and 16 $g \cdot kg^{-1}$ for AlTi3C0.15. The differences in the behaviour of grain refiners at high addition content (> 5 $g \cdot kg^{-1}$) are expected to reveal the differences in the mechanism of grain refinement. The grain size at a high concentration of titanium ($>$ 0,02 wt.%) is expected to decrease more for AlTi3C0.15 refiner because of the absence of degradation of the nucleation mechanism in this case.

2. Experimental

Aluminum AA 1080 was grain-refined with different additions of AlTi5B1 and AlTi3C0.15 grain refiners in the form of rod. The chemical compositions of aluminum and grain refiners are illustrated in Table 1 and Table 2. Three kilograms

Table 1. Chemical composition of aluminum AA 1080 in wt.%

Alloy	Si	Fe	Ti	B	Other el.	Al
AA 1080	0.031	0.081	0.0015	< 0.0005	< 0.006	Rem.

Table 2. Titanium, boron, and carbon content (in wt.%) in AlTi5B1 and AlTi3C0.15 grain refiners

Grain refiners	Ti	B	C
AlTi5B1	5.1	1.04	
AlTi3C0.15	3.1		0.18

of aluminum were melted in medium-frequency induction furnace with a graphite crucible. The grain refiners were added at temperature of 705 ± 5 °C. The melts were stirred with a graphite stick after the addition of grain refiners for two minutes and the melt was cast into a bronze mould and rapidly ($\sim 15\,^{\circ}\mathrm{C}\cdot\mathrm{s}^{-1}$) cooled to the ambient temperature. The shape and the dimensions of the bronze mould are shown in Fig. 1. The castings were cut 13 mm above the bottom during the sample preparation for metallographic examination. The polished samples were anodized at 23 V for 2 minutes in a 2% water solution of $\mathrm{HBF_4}$ for observation in the polarized light. The samples for examination of macrostructure were ground, polished, and etched in Tucker's reagent. The widths of columnar grain regions were measured on the micrographs of the macrostructure at the magnification of 1.5×. The widths were measured at four points on the ingot circumference with millimeter scale ruler. Average value was rounded to millimeters and converted to the magnification of 1×. The average grain areas were measured on polarized light microscopy images using commercial software for image analysis. Individual grain areas were measured by automatic detection and manual corrections of detected grain boundaries. The average grain areas were converted to the mean lineal intercept lengths $\bar{l}$ according to ASTM E112-96. The term "grain size" in this paper corresponds to the mean lineal intercept length. The number of grains per mm^3,

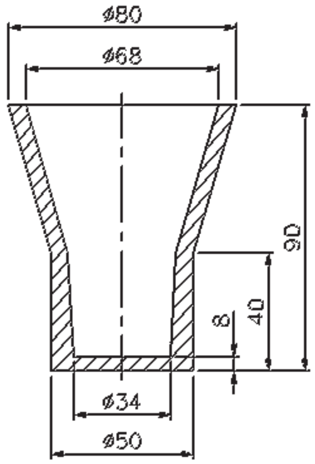

Fig. 1. The shape and dimensions of the bronze mould.

Table 3. Compositions of aluminum AA 1080 with various contents of AlTi5B1 and AlTi3C0.15 grain refiners

Samples	Additive content [g·kg^{-1}]	Ti	B	C*	Width of columnar grain region [mm]	Grain area [mm^2]	Grain area 95% CI [mm^2]**	Grain size [mm]
			[wt.%]					
0	0	0.0015			12	0.7616	0.6356	0.777
A1	0.9	0.0058	0.0008		2.7	0.0279	0.0110	0.149
A2	1.7	0.0090	0.0012		2.7	0.0222	0.0050	0.133
A3	2.6	0.0130	0.0019		2	0.0191	0.0049	0.123
A4	4.3	0.0230	0.0035		0.7	0.0121	0.0016	0.098
A5	10.1	0.0450	0.0077		0	0.0106	0.0010	0.092
B1	0.9	0.0040		0.00015	9.3	0.2518	0.1203	0.447
B2	1.7	0.0056		0.00031	8	0.1219	0.0370	0.311
B3	2.4	0.0079		0.00043	7.3	0.0733	0.0228	0.241
B4	4	0.0120		0.00072	3.3	0.0286	0.0058	0.151
B5	10	0.0300		0.00180	0	0.0144	0.0018	0.107
C1	1.4	0.0057		0.00025	8	0.1133	0.0396	0.300
C2	2.8	0.0096		0.00050	6.7	0.0685	0.0265	0.233
C3	4	0.0110		0.00073	3.3	0.0455	0.0218	0.190
C4	6.7	0.0210		0.00121	1.3	0.0269	0.0072	0.146
C5	16.7	0.0490		0.00301	0	0.0071	0.0005	0.075

* Concentration of carbon was calculated from the known addition level of grain refiner and concentration of carbon in grain refiner (Table 2)

** Values of 95% confidence intervals for the measured grain areas were determined according to ASTM E 1382-97

N_{V}, was calculated according to the equation [12]:

$$N_{\mathrm{V}} = \frac{0.5}{\bar{l}^3}.$$

The concentrations of titanium and boron in aluminum with various additions of grain refiners (Table 3) were determined by the spectrophotometric method.

3. Results

The compositions of aluminum with different additive contents of grain refiners, widths of columnar grain regions, average grain areas, 95% confidence intervals for grain areas, and grain sizes are given in Table 3. Titanium and boron concentration were determined by the chemical analysis. The carbon concentrations in Table 3 were calculated from the known addition levels and the concentration of carbon determined by the chemical analysis of the grain refiner (Table 2).

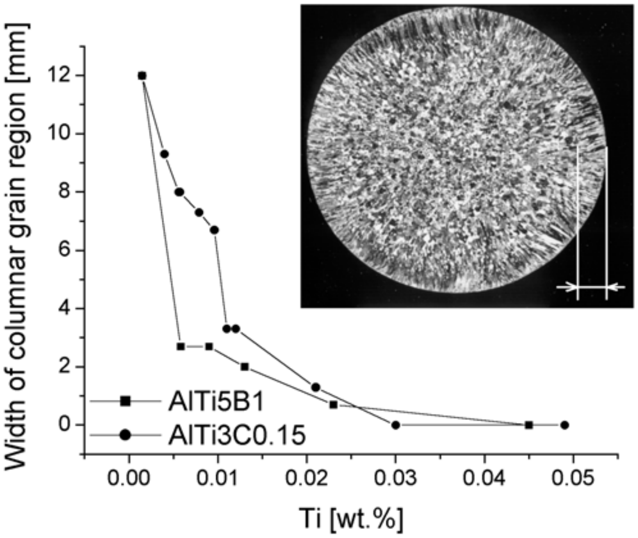

Fig. 2. The width of the columnar grain region as a function of titanium concentration in aluminum AA 1080 for AlTi5B1 and AlTi3C0.15 grain refiners. The width of the columnar grain region measurement is indicated in the micrograph.

The width of the columnar grain region as a function of titanium concentration for AlTi5B1 and AlTi3C0.15 grain refiners is shown in Fig. 2. The insert in Fig. 2 illustrates the width of the columnar grain region. The point with the smallest concentration of titanium represents aluminum without any addition of a grain refiner. The result shows that the width of the columnar grain region decreases with the increasing titanium concentration for both grain refiners. The width of the columnar grain region is smaller in aluminum with the addition of AlTi5B1 refiner at the same concentration of titanium. The columnar grain region was not observed at the concentrations of titanium higher than 0.03 wt.%.

The grain size as a function of titanium concentration for both grain refiners is shown in Fig. 3. It can be seen that the grain size decreases with the increasing concentration of titanium for both grain refiners. It decreases faster for AlTi5B1 refiner in lower concentration range of titanium (up to 0.02 wt.%). The decrease of grain size at higher titanium concentrations (> 0.02 wt.% Ti) for AlTi5B1 grain refiner is smaller in comparison to AlTi3C0.15 refiner. The grain size at the highest concentration of titanium is smaller for aluminum with the addition of AlTi3C0.15 grain refiner. Differences in grain size are illustrated in Fig. 4. Aluminum with AlTi5B1 refiner shows obviously smaller grain size at the titanium concentration of 0.023 wt.% (Fig. 4a) in comparison to aluminum with the addition of AlTi3C0.15

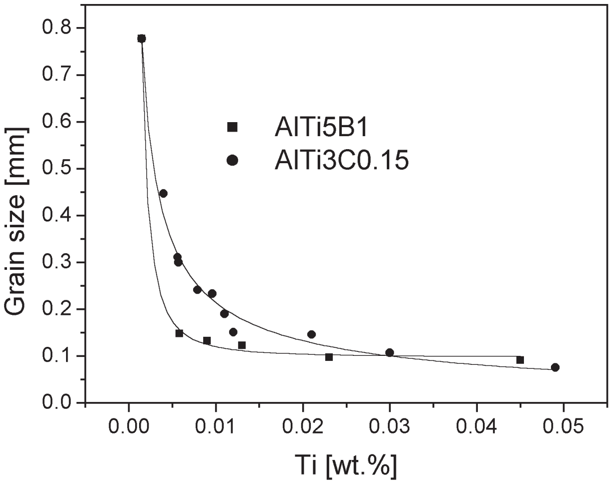

Fig. 3. The grain size as a function of titanium concentration in aluminum AA 1080 for different contents of AlTi5B1 and AlTi3C0.15 grain refiners.

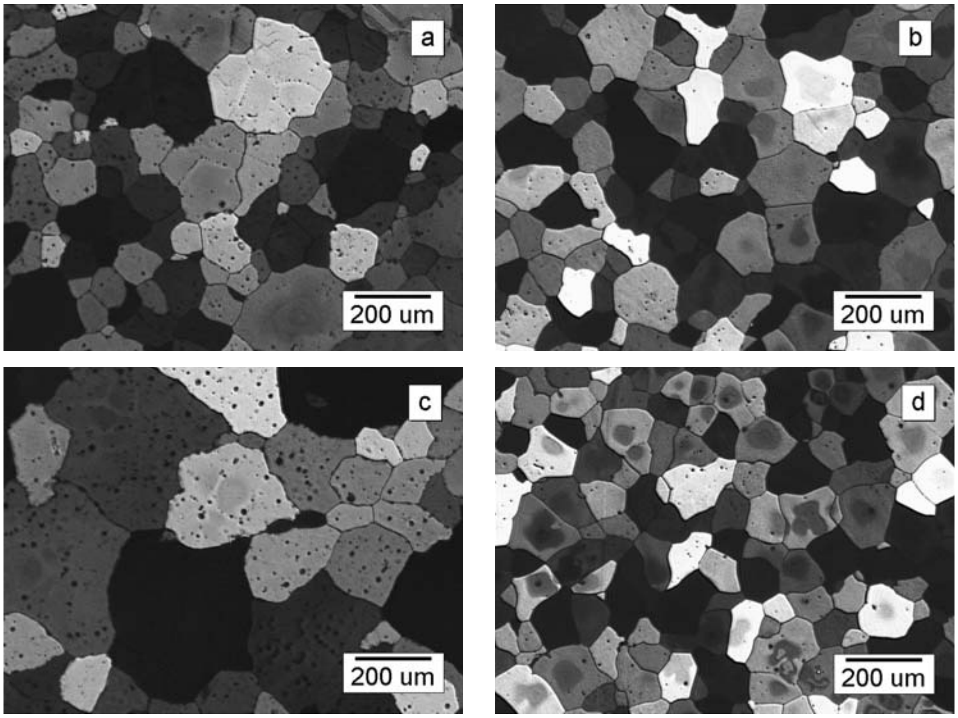

Fig. 4. Microstructures of samples A4 (a) and A5 (b) with the addition of AlTi5B1 grain refiner and C4 (c) and C5 (d) with the addition of AlTi3C0.15 grain refiner. Titanium concentrations are: 0.023 wt.% in A4, 0.045 wt.% in A5, 0.021 wt.% in C4, and 0.049 wt.% in C5.

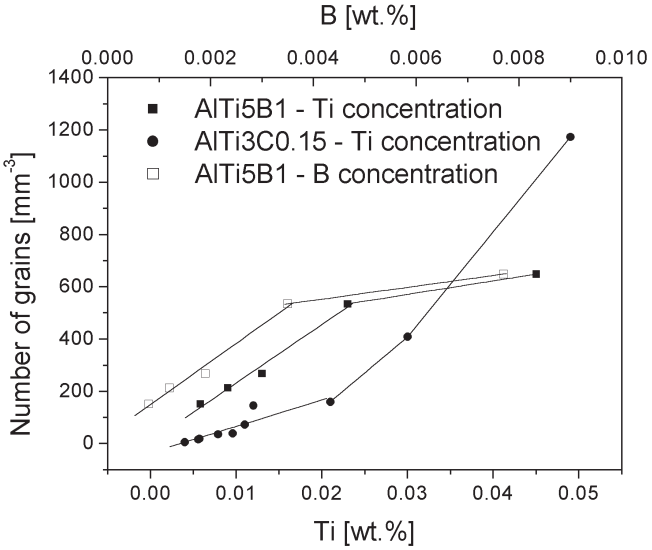

Fig. 5. Number of grains per mm^3, N_V, as a function of titanium and boron concentration in aluminum AA 1080 for different contents of AlTi5B1 and AlTi3C0.15 grain refiners.

refiner at the titanium concentration of 0.021 wt.% (Fig. 4c). The smaller grain size at the highest grain refiner additions shows aluminum with the addition of AlTi3C0.15 grain refiner (Figs. 4b,d).

The differences between grain refiners are more clearly seen in Fig. 5 which shows the diagram of the number of grains per mm^3 N_V as a function of the titanium concentration for both grain refiners and as a function of the boron concentration for AlTi5B1 refiner. N_V increases linearly with the increasing titanium concentration up to 0.02 wt.% of titanium for both grain refiners. The slope is greater for AlTi5B1 refiner in this range of titanium concentrations. At the concentrations of titanium above 0.02 wt.%, the slope decreases for AlTi5B1 grain refiner and increases for AlTiC0.15 compared to the slope in the low concentration range of titanium (< 0.02 wt.%). The number of grains per mm^3, N_V, as a function of boron concentration for AlTi5B1 refiner is identical to N_V as a function of the titanium concentration. N_V as a function of the titanium concentration calculated from the known grain refiner content shows similar behaviour.

4. Discussion

AlTi5B1 refiner is much more effective in suppressing the columnar growth of grains than AlTi3C0.15 refiner at the same concentration of titanium (Fig. 2). It is known that the increase of the alloy content and nucleating particles with smaller undercooling for nucleation promote transition from the columnar to the equiaxed grain growth. The undercooling needed for the nucleation on the nucleant particle is the function of their diameter [12]. TiC particles represent one third of the diameter of TiB_2 particles [8, 9, 12]. The undercooling needed for the nucleation on TiC is higher compared to TiB_2. Despite higher concentration of solute titanium in aluminum with AlTi3C0.15 grain refiner, AlTi5B1 refiner is more effective in suppressing the columnar grain growth. Schneider [3] also showed that AlTi5B1 refiners are more effective in suppressing the columnar grain growth compared to AlTi3C0.15.

The influence of the content of grain refiners on grain size (Fig. 3) and the number of grains per mm^3, N_V, (Fig. 5) show the substantial differences between the both grain refiners. AlTi5B1 refiner is more effective in comparison to AlTi3C0.15 in the concentration range of titanium up to 0.02 wt.%. Grain size does not decrease much with the increasing concentration of titanium for AlTi5B1 grain refiner in higher concentration range of titanium (> 0.02 wt.%). AlTi3C0.15 grain refiner is more effective in comparison to AlTi5B1 at the highest concentration of titanium. The experiment results of Greer et al. [12] also show that the grain size does not change with the addition of AlTi5B1 grain refiner above 5 $g \cdot kg^{-1}$ in TP-1 test. The addition level of 5 $g \cdot kg^{-1}$ for AlTi5B1 refiner corresponds to 0.025 wt.% of titanium. Figure 3 shows the same behaviour of AlTi5B1 refiner compared to the experiment results of Greer et al. [12] at almost the same concentration of titanium. This behavior is more obvious in Fig. 5. N_V as the function of boron concentration for AlTi5B1 grain refiner, which is also presented in Fig. 5, agrees with the observed behaviour and suggests that it is not a consequence of changes in the chemical composition. The behaviour of AlTi5B1 grain refiner at higher concentrations of titanium can be explained by the Duplex nucleation theory [7]. If the addition content of the grain refiner in aluminum increases, then the concentration of excess titanium dissolved in aluminum also increases. It leads to a thicker Al_3Ti layer on TiB_2 particle. Schumacher et al. [7] suggested that the nucleation is most effective when Al_3Ti layer on TiB_2 particle is very thin. For a thin layer, interatomic spacing in Al_3Ti layer is stretched by its epitaxy on TiB_2 and more closely matches α-aluminum. In a thicker layer this effect disappears. Higher content of the grain refiner lead to higher excess of titanium and consequently increased growth restriction factor, GRF. The increased content also increases the concentration of TiB_2 particles. The increased GRF and the concentration of TiB_2 particles would lead either to the decrease of grain size or to the increase of N_V. As the results, Figs. 3 and 5 show that grain size decrease or N_V increase are very small as a consequence of the degradation of the nucleation mechanism.

AlTi3C0.15 grain refiner does not show the behavior observed for AlTi5B1 refiner in Figs. 3 and 5. The results in Fig. 5 indicate that the slope of the increasing

N_V with the concentration of titanium in higher concentration range of titanium (higher than 0.02 wt.%) increases. On the assumption that the mechanism for AlTi3C0.15 refiner in comparison to AlTi5B1 refiner is different, this result which does not indicate any degradation of nucleation mechanism is expected. There is no evidence for a layer similar to that in the case of TiB_2 particles in AlTi5B1 grain refiner. This is possibly because the nucleation of α-aluminum occurs directly on TiC particle [8, 9].

5. Conclusions

The performance of AlTi5B1 and AlTi3C0.15 grain refiners has been tested in aluminum AA 1080. The comparison of the widths of the columnar grain region showed that AlTi5B1 refiner is much more effective in the suppressing growth of the columnar grains than AlTi3C0.15 at the same additive content of titanium. AlTi5B1 grain refiner shows smaller grain size compared to AlTi3C0.15 at the same titanium content except at the highest content of titanium. The effectiveness of AlTi5B1 grain refiner decreases at high additive content. Similar behaviour was not observed for AlTi3C0.15 refiner. That is the reason for smaller grain size achieved with AlTi3C0.15 grain refiner compared to AlTi5B1 at the highest content of titanium. The difference in behaviour of both grain refiners can be explained by the differences in the nucleation mechanisms. The Duplex nucleation theory explains the decrease in the effectiveness at high content of AlTi5B1 grain refiner.

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Received: 18.12.2003
Revised: 18.3.2004