

MICROSTRUCTURE AND GRAIN REFINING EFFICIENCY OF TiC PARTICLES IN Al-Ti-C GRAIN REFINING MASTER ALLOYS

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ABSTRACT Master alloys from the Al-Ti-B ternary system are commonly used as grain refiners for cast aluminium and its alloys. However, the desire to reduce particulates in the finished product has led to the investigation of alternative master alloys based on the Al-Ti-C system. Currently little is known about the structure of the TiC particles that form in this system, or their grain refining mechanism. In the work reported, it has been found that an Al-3wt%Ti-0.15wt%C master alloy has a grain refining efficiency comparable to that of a conventional Al-5wt%Ti-1wt%B master alloy, when used at the same Ti concentration. The individual TiC particles formed during the reaction process were observed to be strongly faceted and smaller than the TiB₂ particles, typically seen in Al-Ti-B grain refiners. The TiC particles were found to grow as polycrystalline chains comprised of several particles, which are broken up on processing to rod. TEM studies of the TiC particles showed the presence of stacking faults and voids within the individual particles. In a model, metal-matrix-composite, sample α -Al grains were found to nucleate epitaxially on large artificially added TiC particles.

Keywords: Al-Ti-C, grain refiners, microstructure, TEM.

1. INTRODUCTION

The most common method of controlling the grain structure of cast Al-alloys is by the deliberate addition of heterogeneous nucleation sites into the melt [1] through the use of a grain refining master alloy. The fine, uniform, equiaxed grain structure, promoted by effective grain refinement, allows higher casting speeds in the DC cast house and reduces losses through ingot cracking [2]. Traditionally, master alloys based on the Al-Ti-B system have been used to fill this role. Although the grain refinement mechanism in these alloys is still controversial, it is thought that they refine by introducing TiB₂ particles into the melt and that a Ti/TiAl₃ layer forms on the TiB₂ particles during cooling, which nucleates the α -Al grains [3]. Grain refiners, based on the Al-Ti-C system, are currently being investigated as an alternative to Al-Ti-B master alloys. This recent interest in Al-Ti-C grain refiners stems from the potential benefits of this system over that of Al-Ti-B. It is thought that the TiC particles formed in Al-Ti-C refiners may be smaller than the TiB₂ particles in Al-Ti-B alloys and could be less prone to clustering [4]. In one of very few studies Mayes *et al* [5] has shown that in the particular Al-Ti-C grain refiner investigated the TiC particles were submicron and faceted and with an octahedral morphology. Moreover, it has been reported that grain refining results similar to those obtained by Al-Ti-B alloys can be achieved with lower volume fractions of inoculant particles in Al-Ti-C based refiners [5]. If these claims are realised Al-Ti-C grain refiners could lead to important improvements, such as a better surface finish for wrought products, a reduced incidence of tearing of thin sheets during drawing, and a reduction in the need for melt filtration.

In Al-Ti-C grain refiners both TiAl₃ and TiC particles are introduced into the melt [6]. However, in contrast to Al-Ti-B refiners it is thought that the TiC can act as a direct nucleant for the Al grains, without the need for an excess Ti concentration [7]. This may be because TiC has a cubic NaCl crystal structure that is more similar to the FCC structure of α -Al [8] than that of the tetragonal TiB₂ phase. However, TiC and Al have lattice parameters of 0.433 and 0.405 nm respectively [9], which represents a substantial lattice mismatch of ~7% and it has not been confirmed how α -Al nucleates on the surface of TiC particles. Furthermore, it is well established that "TiC" is a non-stoichiometric phase whose more accurate notation is Ti_(1+x)C_(1-x), 0 ≤ x ≤ 0.36 [10], leading to a variation in lattice parameter, with composition.

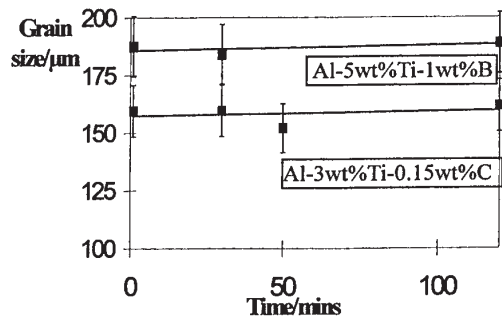
Despite their potential technological importance, there have been few studies of Al-Ti-C grain refiners at sufficient resolutions to reveal the detailed structure of the TiC particles. In this present work, the grain refining efficiency of a developmental Al-Ti-C grain refiner has been investigated and compared to that of a commercial Al-Ti-B master alloy. The microstructure of the TiC particles has been studied in detail using HRSEM and TEM techniques and related to their grain refining performance.

2. EXPERIMENTAL

The experimental Al-3wt%Ti-0.15wt%C and commercial Al-5wt%Ti-1wt%B master alloys investigated were supplied by Anglo Blackwells, Widnes, Cheshire. The Al-3wt%Ti-0.15wt%C alloy was produced by reacting graphite powder with an Al-Ti alloy. The grain refining efficiency of the two extruded master alloys was compared by making additions to commercial purity aluminium (99.7% Al) and using a modified Aluminium Association TP-1 grain refining test [11]. As the two master alloys had different concentrations, additions were made such that the total Ti concentration was diluted to the same level of 0.005wt% Ti in the casting for both master alloys. The first addition method is more representative of the grain refining performance of the two different systems, than comparing the effect of equal masses of master alloy rod, as it measures the relative grain refining effect for equal concentrations of addition. The relative grain sizes were measured using the linear intercept method on the standard section through the cone. For the analysis of the size and morphology of the TiC and $TiAl_3$ particles, extractions were carried out from samples of the Al-3wt%Ti-0.15wt%C master alloy in the cast condition directly after the reaction process, using a technique involving the dissolution of aluminium in anhydrous butanol originally developed by Siemens [12]. The extracted particles were subsequently characterised by examination in a Philips XL30 FEG high resolution SEM. To study the internal structure of the TiC particles in more depth, TEM foils were prepared by mechanically polishing ultra-thin samples (< 20 μ m thick) and ion-beam polishing to perforation in a GATAN PIPS. The foils were studied in a Philips CM200 TEM. An artificially produced model composite material, containing 10 vol% 10 μ m-TiC particles and supplied by A. Kennedy (Nottingham University) [7,13], was used to investigate the orientation relationship between the α -Al grains and the TiC particles in a casting using EBSD in the SEM [14]. This model material was used so that the particle size would be considerably larger than the diffracting volume.

3. RESULTS AND DISCUSSION

Figure 1: Grain sizes measured in the TP-1 test, as a function of time for commercial purity Al with additions of the developmental Al-3wt%Ti-0.15wt%C and a commercial Al-5wt%Ti-1wt%B master alloys, to give a Ti concentration of 0.005 wt%.



3.1 Comparison of the grain refining efficiency of Al-Ti-B and Al-Ti-C master alloys

Figure 1 shows the results of a modified TP-1 grain refining tests carried out in 99.7% Al for times of up to 2 hours. The melt was stirred once after the master alloy additions, before taking the first sample cone. The two grain refiners have been compared for equivalent Ti additions of 0.005wt%Ti. The Al-Ti-C refined samples had a slightly smaller grain size of approximately 160 μ m while the Al-Ti-B refined samples had a grain size of around 185 μ m. When the test is carried out with a more conventional addition rate of 0.01wt%Ti for the Al-5wt%Ti-1wt%B master alloy it is normally expected that the grain size would be of the order of 120 μ m. For both samples, at 0.005wt%Ti addition, there was only a very modest decrease in the grain refining efficiency with increasing holding time; i.e. only small levels of fade were detected. These findings are in contrast

to those presented by Cibula. [8] who noticed that grain refining efficiency of TiC particles decreased substantially over time in an Al-Ti alloy containing residual carbon. The observations were attributed to the TiC particles settling to the bottom of the melt. The fact that significant fade was not detected in these experiments is important, as in foundries the melts may be standing for long periods after the addition of the grain refiner and it is essential that the grain refining efficiency does not decrease with time.

3.2 Morphology of the extracted TiC and TiAl₃ particles

The TiC and TiAl₃ particles were isolated from the Al matrix, in cast samples of the experimental master alloy, using the anhydrous butanol extraction and filtration technique developed by Siemens [12]. The whole process was carried out in an autoclave under vacuum. Figure 2 shows typical examples of TiC particles that were extracted from the matrix and studied in the FEG high resolution SEM

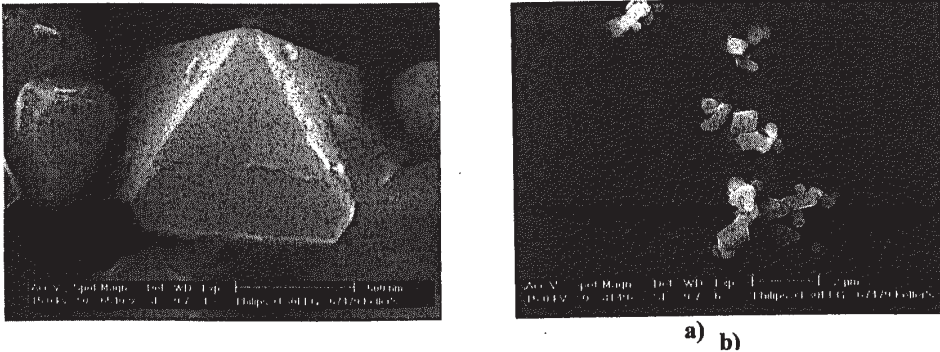
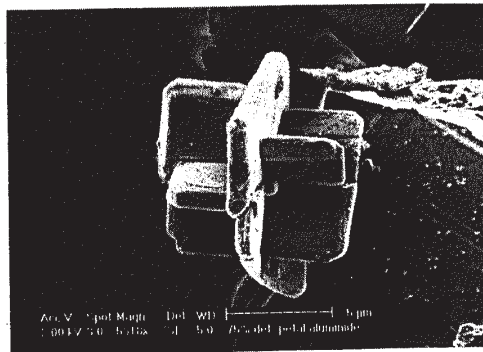


Figure 2: HRSEM micrographs of a) an individual TiC particle and b) polycrystalline chains of several TiC particles, found in the as-cast Al-Ti-C developmental master alloy.

Figure 3: HRSEM micrograph showing the morphology of the TiAl₃ particles



In figure 2a an individual TiC particle is shown displaying {111} facets. All the TiC particles studied were well-faceted with predominantly {111} facets, resulting in a tetrahedral morphology, or {100} facets, giving cubic shaped particles. Many particles exhibited mixtures of the two types of facets producing various shapes, such as truncated tetrahedra, and were often found to be in small clusters. Fig 2b shows a cluster of TiC particles that have clearly nucleated and grown off each other, forming a continuous chain, as opposed to agglomerates formed by particles adhering together in the melt. The clustered particles thus appear as polycrystalline chains that have grown during the reaction. The reaction process is thus autocatalytic, it being apparently easier for a new particle to nucleate on a pre-existing one, than on the graphite particles, or any other heterogeneous nucleation sites in the melt. The new TiC grains nucleate on the surface of previously formed particles and this process may be initiated by defects within the particles. In some of the chains low

angled boundaries, between adjoined crystals, and twinned particles were evident. These chains are subsequently broken up on extruding the master alloy rod. Most of the individual particles were between 200 and 600 nm in diameter, although sizes up to 1 μm were occasionally recorded. The extracted TiAl_3 particles were substantially larger, being between 1 μm and 10 μm in size. They were usually in the form of platelets and in some cases had grown around one another, and the TiC and Fe rich eutectic, to form interesting morphologies (an example of which is shown in Fig 3).

3.3 TEM studies of the TiC particles

Thin foils of the as-cast Al-Ti-C master alloy were prepared for examination in a Philips CM20 TEM, as detailed in section 2. In the cast material small chains of TiC particles could be seen (figure 4), although in some cases it did not look as if the particles were attached to each other, due to the sectioning of the sample. EDX analysis of the particles showed that the particles contained Ti and no other trace elements were detected, unfortunately, the carbon content could not be reliably determined with the equipment used. TEM investigation confirmed that the particles had simple crystallographic facets with predominantly $\{111\}$ and $\{100\}$ crystal planes exposed to the melt. It is on these crystal planes that the new aluminium grains must nucleate.

Figure 4: TEM micrograph of a TiC particle chain.

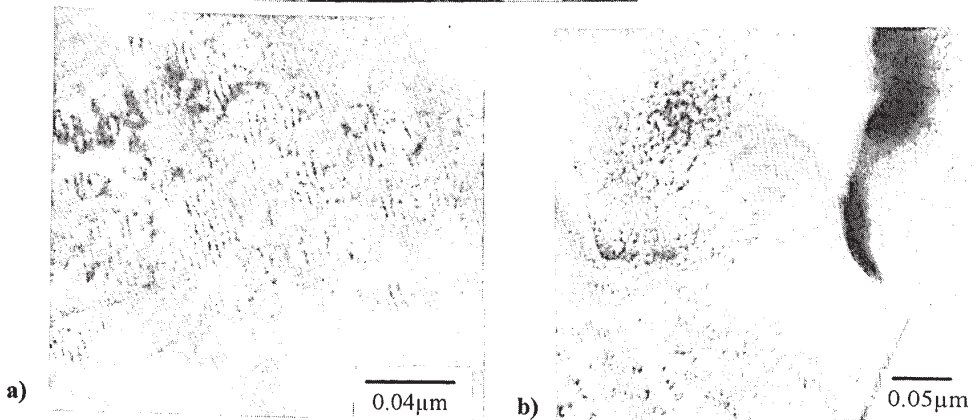
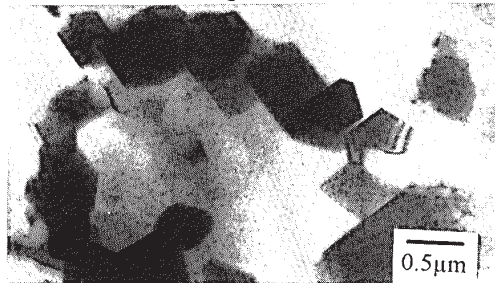


Figure 5: In (a) stacking faults are shown in a TiC particle using a two beam condition in the TEM and in (b) voids are visible due to Fresnel contrast in a slightly out of focus image, in a weakly diffracting orientation.

Figure 5 shows individual TiC particles at higher magnifications than used in figure 4. In figure 5 the high symmetry facet planes are easily visible. Interestingly, Moiré fringes could be seen within some of the particles (shown in figure 5a, imaged in a two-beam condition). This is indicative of the presence of stacking faults in TiC the particles, which presumably develop as growth defects. It has been suggested that such contrast may be due to Al precipitates within the TiC particles [15], however there is no evidence of an additional phase in the diffraction data. In some TiC particles when images were taken slightly out of focus and at weakly diffracting conditions, Fresnel contrast was also observed within the TiC particles (see for example figure 5b). The sense of the Fresnel fringes is consistent with the presence of voids in the sample [16]. The voids were generally less

than 10 nm in diameter and were found mainly in the centre of the sectioned particles. Due to the difficulties involved in preparing thin TEM foils from aluminium alloys containing hard second phase particles, one can never be entirely certain that such voids are not an artefact of the sample preparation process. However, the precision ion polishing system used for sample preparation is not normally expected to cause such substantial sample damage. The origin of the voids remains mysterious, but may be related to the entrapment of gas during the reaction process.

3.4 EBSD analysis of Al-10vol%TiC

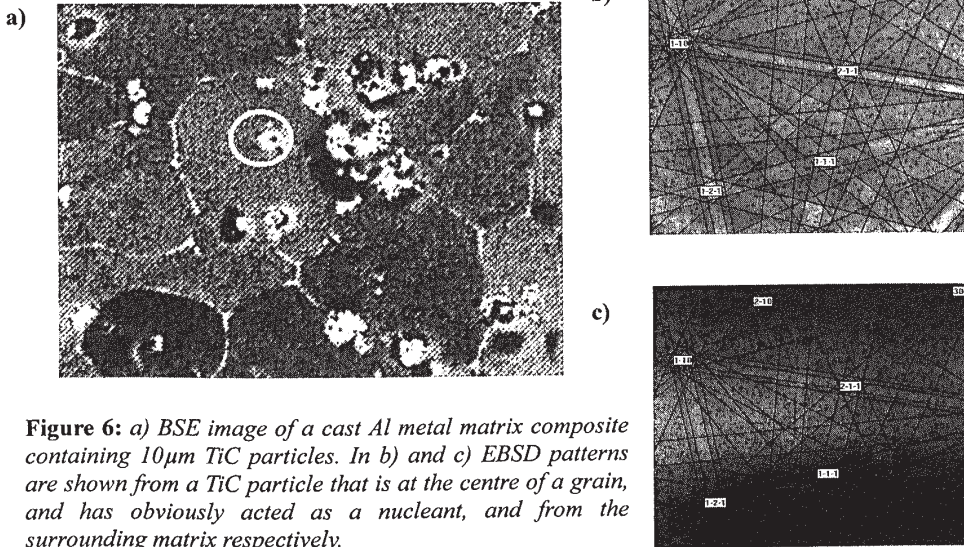


Figure 6: a) BSE image of a cast Al metal matrix composite containing 10µm TiC particles. In b) and c) EBSD patterns are shown from a TiC particle that is at the centre of a grain, and has obviously acted as a nucleant, and from the surrounding matrix respectively.

A cast metal matrix composite sample containing a 10% volume fraction of TiC particles in a commercial purity Al matrix Al-10vol%TiC [7] was studied by electron back-scattered diffraction (EBSD) analysis using a JEOL JSM-6300 Scanning Microscope. The sample contained TiC particles up to 10µm in diameter, and so was an ideal material for this type of analysis, as the size of the particles was substantially larger than the diffracting volume. The material was used as a model system because the TiC particles in the grain refining alloys were submicron, and consequently smaller than the SEM beam size. From the BSE image of the sample, shown in figure 6a, it can be seen that not all of the grains appear to contain a TiC particle. However this is probably due to sectioning effects. A considerable proportion of the TiC particles were not just at the centres of Al grains. Many of the particles were found at grain boundaries, where they have been pushed by the solid-liquid interface during solidification. This means that only a minority of the TiC particles have participated in the nucleation process, which could be interpreted as meaning that individual particles have a range of heterogeneous nucleation potency. It may therefore be possible to decrease the number of TiC particles required in the casting, to achieve a given grain refinement, by selectively removing the ineffective nucleants from the distribution. However, nucleation is a random process and site saturation may not always occur if the nucleation rate is low relative to the growth rate.

In figure 6 electron back scattered diffraction (EBSD) patterns are shown that were obtained from a TiC particle (figure 6a), that has clearly acted as a nucleant, and the surrounding grain (figure 6b) that has grown from the particle. It can be seen that the patterns from the surrounding Al grain and the TiC particle match very closely. This suggests that, for the example shown, there is an epitaxial orientation relationship between the TiC particle and the Al matrix. A similar relationship was found for several particles studied, however, other particles were also observed where no obvious relationship existed. The epitaxial growth of aluminium grains has also been noted by Cissé and Bolling in a study of the solidification of aluminium on a polycrystalline TiC surface [17].

4. CONCLUSIONS

1. When the grain refining efficiency in 99.7% Al of the Al-3wt%Ti-0.15wt%C developmental alloy investigated was compared to a commercial Al-5wt%Ti-1wt%B grain refiner, on the basis of additions to give equivalent Ti concentrations in the melt, it was found to have an efficiency very slightly better than that of the conventional Al-5wt%Ti-1wt%B master alloy, under these test conditions.
2. After the reaction process, the as-cast Al-Ti-C master alloy was found to contain many, very small TiC particles, in the size range 200 - 500nm. These particles appear to grow in polycrystalline chains consisting of several individual particles, each new particle nucleating on one previously formed. The TiC particles are highly-faceted and have relatively simple cubic or tetrahedral morphologies, resulting in {111} and {001} type crystal planes being exposed to the melt. These chains break up on subsequent processing.
3. TEM studies have revealed the presence of growth defects within the individual particles, consisting of stacking faults and voids.
4. A substantial proportion of the TiC the particles within an Al-10vol%TiC, cast, model, composite material were found not to have acted as heterogeneous nucleation sites for the α -Al grains, and were pushed into the inter-dendritic regions during freezing. Some of the particles within the model sample, that were identified as acting as nucleation sites, were found to have an epitaxial relationship with the Al matrix.

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