Electron microscopy investigation of the TiBAl and TiCAl grain refiner master alloys

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Abstract. The present work brings a detailed statistical analysis of the microstructural characteristics and chemistry of the second phase particles present in the Al-5Ti-1B and Al-3Ti-0.15C (wt.%) commercial grain refiner rods used in the Al casting industry. The investigation was performed using the TEM, EDS, STEM and HREM techniques. Both refiner rods contained large, blocky Al₃Ti DOₒ₂ particles. Borides present in the TiBAl rod, known to be main α-Al nucleation substrates, exhibited a faceted, hexagonal platelet morphology and largely represented a mixed (Ti,Al)B₂ phase, with Ti and Al contents changing continuously across the particle dimensions. There were two distinct families of small particles observed in the TiCAl rod. The coarser, facetted particles corresponded to cubic TiC crystal structure and these are believed to be major α-Al nucleation sites. The family of finer, round particles appeared to correspond to orthorhombic Al₆Fe phase and their role in the nucleation process remains to be clarified. The results obtained may be used in optimising the grain refiner rod microstructures that would ensure improved refining performance during casting.

1. Introduction
In the Al casting industry, it is common practice to add grain refiner particles to the melt in order to promote heterogeneous nucleation of α-Al crystallites. Commercial grain refiner master alloys consist of Al matrix containing either stable TiB₂ or metastable TiC particles (and possibly other particles), which serve as potential nucleation substrates, as well as unstable Al₃Ti particles that dissolve in the melt providing excess Ti for constitutional undercooling [1,2]. There are stringent requirements on the characteristics of the nucleating particles in order to achieve optimum grain refining performance. Differing morphologies of the aluminide particles might also have a marked influence on the grain-refinement contact time during casting [1].

The aim of the present study was to undertake a detailed statistical analysis of the size, shape and chemistry of the second-phase particles in the TiBAl and TiCAl commercial grain refiner rods.

2. Experimental methods
Commercial Al-5Ti-1B and Al-3Ti-0.15C (wt.%) grain refiner rods (supplied by London & Scandinavian Metallurgical Co. Ltd.) were used as experimental material. Both the as-received grain refiner rods were examined using the TEM, EDS, HREM and STEM techniques. TEM thin foils were produced by electropolishing using a solution of 25% nitric acid and 75% methanol at a temperature of approximately –30 ºC at 20 V.
3. Results and discussion

3.1. TiBAl grain refiner rod

TEM examination of the Al matrix revealed small equiaxed Al grains with the mean diameter of approximately 3 µm, largely separated by high-angle boundaries, presumably resulting from recrystallisation of the as-solidified α-Al matrix occurring during the rod manufacture. Thus, as it was actually observed, any possible pre-existing orientation relationships between the Al matrix and second-phase particles established during solidification were effectively removed. Large aluminide particles (largely more than 10 µm in diameter) were also visible in each TEM foil. Corresponding diffraction patterns confirmed the equilibrium Al₃Ti DO22 crystal structure having the I4/mmm space group and lattice parameters $a = 0.385 \text{ nm}$ and $c = 0.861 \text{ nm}$ [1]. The aluminides frequently contained embedded boride particles and largely exhibited a block-like morphology. It has been suggested that different morphologies of aluminide particles (block, flake and petal) in the grain refiner master alloys might have a marked influence on the grain-refinement contact time during casting, as a result of differing dissolution times [1]. The boride particles exhibited a faceted, hexagonal platelet morphology with the {001} and {100} planes as their external faces (figures 1a, 1b). EDS analysis indicated that these particles generally contained, apart from Ti, significant amounts of Al and frequently consisted of Ti-rich shells and Al-rich cores (figures 1c, 1d). The boride particles thus largely represented mixed (Ti,Al)B₂ phase, with Ti and Al contents changing continuously across the particle dimensions. It is well known that TiB₂ and AlB₂ are isomorphous phases having a hexagonal crystal structure with the Pmmm space group and very similar lattice parameters (TiB₂: $a = 0.303 \text{ nm}$, $c = 0.323 \text{ nm}$; AlB₂: $a = 0.309 \text{ nm}$, $c = 0.326 \text{ nm}$ [1]). The preservation of Al-rich cores could be expected to increase the amount of Ti dissolved in the melt, for a given nominal Ti content in the grain refiner master alloy, thus increasing the nuclei growth restriction and aiding grain refinement.

![Figure 1](image-url)

**Figure 1.** (a) TEM bright-field image of a boride particle, composed of an Al-rich core and Ti-rich shell, found within the TiBAl grain refiner rod; (b) corresponding SAD pattern with a [100] zone axis; (c),(d) EDS spectra obtained from the particle core and shell respectively; (e),(f) histograms of boride width and thickness dimensions respectively obtained using TEM statistical analysis.
A detailed TEM statistical analysis (figures 1e, 1f) revealed that the mean width and thickness of the boride particles were approximately 0.29 \( \mu m \) and 0.12 \( \mu m \) respectively. The measured particle widths are directly related to the size of basal boride facets which are known to act as substrates for heterogeneous nucleation of \( \alpha \)-Al \([1,2]\). In order to achieve a small grain size in the as-cast product, it is necessary to produce boride particles with basal facets larger than the critical \( \alpha \)-Al nucleation size, for a given undercooling achieved during the casting process, but ideally being as small as possible and having a narrow spread of sizes \([2]\). It is also well known that the smaller the particles or the larger their aspect ratio the longer the sedimentation time in the melt, as these particles will take longer to settle, which facilitates a delay in the onset of fade during casting \([1,2]\). From a detailed analysis of the chemistry, crystallography and atomic structure of the boride/Al interfaces performed using the STEM, EDS and HREM techniques and reported in \([3]\) it appears to follow that boride particles within the grain refiner rod studied were not coated with thin aluminide layers suggested in \([1]\).

### 3.2. TiCAl grain refiner rod

TEM study of the matrix showed small equiaxed Al crystals being largely 1-2 \( \mu m \) in diameter. These crystals appeared to predominantly represent subgrains, separated by low-angle boundaries, resulting from recovery (rather than recrystallisation) of the as-solidified \( \alpha \)-Al matrix, which occurred during the manufacture of the refiner rod. Consequently, any orientation relations between phases, originally present within the as-cast grain refiner master alloy, could be expected to remain largely preserved in the final rod. Large particles, corresponding to the equilibrium Al\(_3\)Ti DO\(_{22}\) crystal structure \([1]\), were found embedded within the matrix. Both their blocky morphology and dimensions appeared to be very similar to those observed for the TiBAI refiner rod. These particles appeared to largely display a near-epitaxial, close to cube-to-cube, orientation relationship with respect to the neighbouring Al matrix. There were two distinct families of small particles observed within the TiCAl grain refiner rod. The family of coarser, faceted particles corresponded to carbides, present as separate particles as well as clusters containing several carbides (figure 2a). Diffraction study (figure 2b) revealed the cubic, NaCl-type ordered TiC crystal structure with a lattice parameter \( a = 0.436 \) nm \([4]\). As indicated by the TEM trace analysis, the TiC particles frequently appeared to display octahedron shapes bounded by \{111\} external facets, often truncated by \{100\} planes. These particles frequently appeared to have a near-epitaxial, cube-to-cube orientation relationship with the surrounding Al matrix. A preliminary statistical analysis indicated that the mean diameter of the carbide particles was around 0.5 \( \mu m \). EDS study revealed a rather complex chemical composition with varying Ti/C ratio. Although the above carbides are expected to be thermodynamically unstable in the Al melt under some industrial casting conditions \([4]\), they are believed to act as major \( \alpha \)-Al nucleation substrates. Requirements on the size distribution of TiC particles which would provide optimum grain refining performance are generally similar to those discussed for the TiBAI master alloy above \([2]\).

**Figure 2.** (a) TEM bright-field image of a cluster of TiC particles found in the TiCAl grain refiner rod; (b) micro-diffraction pattern from one of the particles displaying [112] zone axis.
The other family was represented by fine particles, displaying no pronounced faceting and being both roughly equiaxed and elongated in shape (figure 3a). These particles were present in clouds with a eutectic appearance and the observed roughly equiaxed shapes appeared to frequently result from sectioning of the elongated rod-like particles. Corresponding TEM diffraction patterns and EDS spectra (figures 3b, 3c) indicated the metastable orthorhombic Al₆Fe phase having lattice parameters a = 0.649 nm, b = 0.744 nm and c = 0.879 nm, and the Cmcm space group [5]. A detailed statistical analysis revealed that the mean diameter of the particles was approximately 0.22 µm (figure 3d). A possible role of these particles for the heterogeneous nucleation of α-Al remains to be clarified.

Figure 3. (a) TEM bright-field image of a cloud of Al₆Fe particles found in the TiCAl refiner rod; (b) corresponding micro-diffraction pattern with a [1-1 -1] zone axis; (c) typical EDS spectrum obtained from the particles; (d) histogram of the particle dimensions obtained using TEM statistical analysis.

4. Conclusions
A detailed statistical analysis of the size, shape and chemistry of the second-phase particles in the Al-5Ti-1B and Al-3Ti-0.15C (wt.%) commercial grain refiner rods was performed in the present work. Borides in the TiBAI rod exhibited a faceted, hexagonal platelet morphology of a mixed hexagonal (Ti,Al)B₂ phase. There were two families of small particles observed in the TiCAl rod. The coarser, faceted particles corresponded to cubic TiC crystal structure while the finer, elongated, non-faceted particles appeared to correspond to the orthorhombic Al₆Fe phase. The results obtained can be used in optimising the grain refiner rod microstructures and consequently their performance during casting.

References
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