The role of TiB₂ in strengthening TiB₂ reinforced aluminium casting composites

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Abstract. With an aim of developing high quality in situ TiB₂ reinforced aluminium foundry alloy based composites, the conventional direct synthesis method was modified into a two-step route. In step one we optimized the halide salt route to fabricate in situ TiB₂ particulate reinforced aluminium matrix composites and in step two we investigated the effects of the Al−5wt.% TiB₂ composite, as a “master composite”, on strengthening the practical foundry alloys. The in situ formed TiB₂ particles play two roles while strengthening the composites: (1) The grain refinement effect that improves the quality of the alloy matrix; and (2) The interactions between the hard particulates and the matrix add extra increment to the material strength. In different alloy systems, TiB₂ may play distinct roles in these two aspects (figure 1). Further analysis of the strengthening mechanisms shows that particle agglomeration behaviour during solidification is responsible for the latter one. The present work details the role of TiB₂ in strengthening TiB₂ reinforced aluminium casting composites.

1. Introduction

The use of K₂TiF₆ and KBF₄ salts, in the halide salt route to produce aluminum matrix composites (AMCs), suffers from two predominant drawbacks. One is that a substantial portion of the charge is of no use, giving rise to detrimental fluoride-bearing emissions and troublesome decanting operation. The other, more intractable, is that the unclear reaction mechanism adds extra difficulties to eliminating unwanted salt compounds, oxides, metastable intermetallic compounds, etc. and composition adjustment owing to the loss of raw materials. These drawbacks can be resolved well if we adopt a remelting and diluting (RD) process using master composites that have been pre-fabricated.

In the literature regarding in situ aluminum alloy composites, efforts were made either on composites with pure Al matrix [1-7] or on those with alloy matrix [4, 5, 8-13] through direct synthesis with reactants. In Part I and II of our previous work we described an improved halide salt route to produce in situ TiB₂ reinforced aluminum foundry alloy based composite with enhanced mechanical properties [14,15].

While it seems the RD approach is generally suitable to prepare high quality aluminum foundry alloy based composites, the reinforcing efficiencies may vary because of different agglomeration behaviors of TiB₂ in different alloy systems. Yet the key question that needs to be answered is: What roles does the TiB₂ play in reinforcing the matrix?

This work was undertaken to discuss this question.
2. Experimental
99.85 wt.% Al, 99.7 wt.% Si, 99.8 wt.% Mg, 99.97 wt.% Cu and 99.8 wt.% Zn were used as the starting materials. Al−5wt.% TiB$_2$ master composite was prepared via the improved halide salt route described in Ref. [14]. The Ti and B recoveries in the as-received composites were measured using an inductive coupled plasma (ICP) emission spectrometer calibrated for Ti and B. The materials were cut, weighted and melted in an electric resistance furnace to produce a series of AlSi7Mg0.3, AlCu4.5Si1.1 and AlZn6Mg0.5 alloy matrix composites with 0, 1, 2, 3 and 4 wt.% TiB$_2$.

Mechanical stirring was made 2 min before casting to bring back the settled particles from the lower part of the melt. The pouring temperature was 720 ºC. X-ray diffraction (XRD) analysis was conducted to confirm the presence of TiB$_2$.

The etched specimens were observed using field emission secondary electron microscope (FESEM). Tensile tests (0.2% offset yield strength ($\sigma_{0.2}$), ultimate tensile strength (UTS) and elongation ($\delta$)) were conducted on a computerized universal testing machine.

3. Results and discussion
A 98.6% Ti recovery and 90.8% B recovery were obtained in the final composite using the improved halide salt method. Figure 1 shows the microstructures of the in situ composite. It can be seen that the TiB$_2$ particles in sample 1 and 2 were formed in agglomerates, most of which segregated at the $\alpha$-Al grain boundaries (figure 1a). In the inset of figure 1a we can see that the TiB$_2$ existed in near-equiaxed shape with two shrunk (0001) planes.

![Figure 1. SEM micrographs of the in situ Al−5TiB$_2$ master composite at a (a) lower magnification and (b) higher magnification. Shown in the inset is the morphology of in situ TiB$_2$ particles.](image)

Equiaxed particles, profiting from desired symmetry and shape, are most desirable. The composite recorded a 140% improvement in UTS compared to the matrix (from 43.2 to 103 MPa) without compromising its elongation (from 37.1% to 36.2%).

The XRD spectra for the alloys and experimental composites, as given in figure 2, reveals only TiB$_2$ reflections besides those of the matrix alloys. This is taken to indicate that TiB$_2$, once formed, is not to react with the solute elements, including Si, Mg, Cu, and Zn, in Al. The increasing intensity of TiB$_2$ signals suggests a higher weight percentage of TiB$_2$ in the composite.
Figure 2. XRD spectra of the experimental (a) AlSi7Mg0.3−xTiB2, (b) AlCu4.5Si1.1−xTiB2 and AlZn6Mg0.5−xTiB2 (x = 0, 1, 2, 3, 4) composites prepared by remelting and diluting approach.

Figure 3 shows the microstructure changes of the alloys incorporated with TiB2 particles in different addition levels. It is expected that different reinforcing efficiencies may be owing to different roles the TiB2 plays in two aspects upon solidification: (1) The grain refinement effect that improves the quality of the alloy matrix; and (2) The interactions between the hard particulates and the matrix add extra increment to the material strength.
Figure 3. The as-cast microstructures of (a), (d) and (g) the unreinforced matrix and (b) AlSi7Mg0.3−2TiB₂, (c) AlSi7Mg0.3−4TiB₂, (e) AlCu4.5Si1.1−2TiB₂, (f) AlCu4.5Si1.1−3TiB₂, (h) AlZn6Mg0.5−1TiB₂, (i) AlZn6Mg0.5−2TiB₂, respectively.

Figure 4 shows the grain boundary spacing, including grain size and SDAS, versus Vp for the three systems. TiB₂ is but less efficient in reducing the SDAS of AlSi7Mg0.3, despite its evident efficiency in refining the primary grain structure confirmed by microstructural analysis.

Figure 4. Average grain size versus TiB₂ content (vol.%) for the three systems. p was obtained by fitting the experimental data with $d = d_0 \cdot (1 + pV_p)^{-1/3}$.
The tensile properties, i.e. $\sigma_{0.2}$, UTS and $\delta$ of the composites with different alloy systems in as-cast state are shown in figure 5. From figure 5a–c we can see that all three systems can be successfully strengthened, but the reinforcing efficiency was rather discrepant for each alloy system.

Figure 5. As-cast tensile properties of the (a) AlSi7Mg0.3, (b) AlCu4.5Si1.1 and (c) AlZn6Mg0.5 samples as a function of the TiB$_2$ content. Dashed lines represent the UTS and $\delta$ of the unreinforced matrix and shaded areas depict those of the diluted composites. (d) is an overview of the reinforcements by taking $\delta$ as the x axis and UTS as the y axis.

In figure 6, the predicted yield strength of the composites are higher than the measured values. This is not surprising since practically the TiB$_2$ particles are distributed unevenly in the matrix. Considering clustering of TiB$_2$, we can replace $Vp$ by $Vp^* = \varepsilon Vp$ and then adjust $\varepsilon$ to fit the curve with the experimental data using the following equation [15].

$$\Delta \sigma_{total} = \Delta \sigma_{gf} + ((\Delta \sigma_{Orowan})^2 + (\Delta \sigma_{CTE})^2)^{1/2}$$

where $\Delta \sigma_{total}$ is the total increment of yield strength owing to the grain refinement, Orowan and CTE strengthening mechanisms. $\varepsilon$ were estimated to be 0.14, 0.56, and 0.35 for the AlSi7Mg0.3, AlCu4.5Si1.1 and AlZn6Mg0.5, respectively, indicating that ~35%, 56%, and 14% of the added TiB$_2$ particles can be uniformly distributed to participate in strengthening. Compared with the microstructural features shown in figure 3, these values were found quite reasonable.
Figure 6. Comparison of the theoretically predicted yield strength (a) before and after adjusting $V_p$ with the experimental data from tensile tests.

We now compare the estimated $\varepsilon$ values with the measured percentage of dispersed TiB$_2$ particles analyzed from the microstructural features in figure 7. It can be seen that the measured TiB$_2$ percentages dispersed near the estimated $\varepsilon$ values well, indicating that these values were quite reasonable.

Figure 7. Comparison of the theoretically fitted $\varepsilon$ values with the measured percentage of dispersed TiB$_2$ particles analyzed from the microstructural features.

4. Conclusions

The homogeneity of TiB$_2$ is strongly dependent on the alloy system. By way of incorporating pre-fabricated Al-TiB$_2$ master composite in different alloy systems, improved mechanical properties can be obtained in all three series of composites. But for different alloy systems, the strengthening efficiency may vary, owing to the different agglomeration behaviour of TiB$_2$ particles. In AlSi7Mg0.3–xTiB$_2$, the predominant mechanisms are Orowan and CTE strengthening. In AlCu4.5Si1.1–xTiB$_2$, all the three mechanisms contribute to the final yield strength. In AlZn6Mg0.5–xTiB$_2$, the main mechanism is grain refinement and the contribution of Orowan and CTE strengthening is very little.
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