In-situ synthesis of Al/(TiC+α-Al_2O_3) and Al/($TiAl_3$+TiC+α-Al_2O_3) alloys by reactions between Al, TiO_2 and C in liquid aluminum

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Metal matrix composites (MMCs) refer to a kind of material in which rigid ceramic reinforcements are dispersed in a ductile metal or alloy matrix. Combining metallic properties with ceramic characteristics, MMCs possess attractive mechanical and physical properties such as high specific strength, modulus and good thermal stability. Both TiC and α-Al_2O_3 particles are widely used as reinforcements for MMCs [1] due to their high hardness, high melting points (3067 and 2040 °C respectively) as well as good thermal conductivity.

Grain refinement, achieved by addition of master alloy grain refiners containing particles acting as substrates for heterogeneous nucleation of α-Al, is of great importance in Al industry because it can bring many benefits such as improved mechanical properties and faster production rates. TiC has an excellent crystal lattice matching to α-Al and appears to act as a direct nucleant for α-Al during its solidification [2]. Aluminum master alloys containing TiC particles (e.g. Al-3.8%Ti-1.5%TiC [5], all compositions are in weight percent) have been found to be especially effective in refining Al grains when added into pure Al or aluminum alloys with a low addition level (only 0.2% for the Al-3.8%Ti-1.5%TiC) [2–5].

To produce either particulate reinforced metal matrix composites [1, 6–10] or master alloy grain refiners for Al and its alloys [2–5, 11, 12], the *in-situ* synthesis of TiC particles in aluminum matrices has been extensively investigated in the past several decades. Because it is especially difficult to add pure carbon directly into Al or Al-Ti melt, special techniques, e.g. compacting a mixture of carbon, titanium and aluminum powders into pellets [4, 6–8, 12], stirring carbon powders into Al-Ti melt [3, 10], infiltration of carbon-containing gases into Al-Ti melt [9], have been applied to form TiC in Al matrices.

Recently, the combustion reaction in the TiO_2-C-Al system has been examined as a means of synthesizing TiC-Al_2O_3 ceramic composites [13, 14] or aluminum matrix composites reinforced by TiC and Al_2O_3 [15, 16]. In these studies, a mix of TiO_2, carbon, and aluminum powders was pressed into a pellet and then heated in an argon atmosphere to the ignition temperature, Tig, when the exothermic reaction, $3TO_2 + 3C + (4 + x)\,Al = TiC + \alpha\text{-}Al_2O_3 + xAl$, takes place, transforming the reactants into products. Despite advantages such as being relatively pure, requiring short reaction time, products based on this approach are largely porous, subsequent consolidation is needed to obtain dense materials.

In a previous paper [17], we have studied the reaction process in an Al-24.1%TiO_2-3.6%C system by using DSC (differential scanning calorimeter), XRD (X-ray diffraction) and TEM (transmission electron microscope), and found that it comprises two steps as follows:

$$\text{(I)}\quad 3TiO_2 + 13Al \rightarrow 3TiAl_3 + 2\alpha{-}Al_2O_3 \quad (1)$$

$$4Al + 3C \rightarrow Al_4C_3 \quad (2)$$

$$\text{(II)}\quad 3TiAl_3 + Al_4C_3 \rightarrow 3TiC + 13Al \quad (3)$$

In the present work, the feasibility of synthesizing TiC and α-Al_2O_3 particles in Al matrix through above reactions in molten Al was investigated. To date, such an investigation has not been reported.

Al powder (200–300 mesh, 99.0%pure), graphite powder (600 mesh, 99.0% pure), TiO_2 powder (99.0% pure) and commercial pure Al ingot (99.7% pure) were used as raw materials. The three powders were milled for 8 hr in a ball mill under argon atmosphere. The Al ingot was heated to 1000–1150 °C in a clay-graphite crucible using an induction furnace, then the ball milled powder mixture was carefully added into it. After about 5 min of reaction, the Al melt was fully stirred and poured into a permanent iron mould. After solidification, Al alloys containing TiC, α-Al_2O_3, or $TiAl_3$ were obtained. The Al content in the powder mixture was 50%, the ratio of TiO_2 to C was varied to obtain alloys with different phase contents. According to reactions (1)–(3), only TiC and Al_2O_3 form in the Al matrix when the TiO_2/C (i.e. Ti/C) molar ratio equals the Ti/C ratio in TiC (1:1), whereas $TiAl_3$, in addition to TiC and α-Al_2O_3, will appear when the TiO_2/C ratio exceeds 1:1. Two alloys, A and B, with different Ti/C ratio, composition, and nominal phase content listed in Table I have been produced in this work.

Alloy A and B were subjected to X-ray diffraction for phase identification using a Rijaku D/max-rB X-ray diffractometer (XRD) with Cu Kα radiation. The microstructures were characterized by a JXA-8800R electron probe micro-analyzer (EPMA). For the purpose of evaluating refinement effectiveness, the two alloys

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TABLE I Nominal composition, Ti/C molar ratio and phase content of two alloys

	Composition (%)	Ti/C molar ratio	TiC (%)	α-Al_2O_3 (%)	$TiAl_3$ (%)
Alloy A	Al-5.6Ti-1.4C-3.7O	1:1	7	7.88	–
Alloy B	Al-5Ti-0.5C-3.3O	2.5:1	2.5	7.01	8

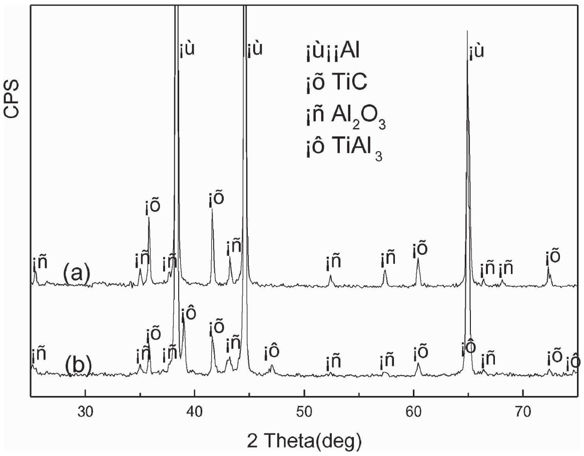


Figure 1 XRD patterns of alloy A (a) and alloy B (b).

were added, at a level of 0.2%, to commercial pure aluminum (99.7% purity) melt at 720 °C. The refinement procedure has been detailed in a previous paper [5].

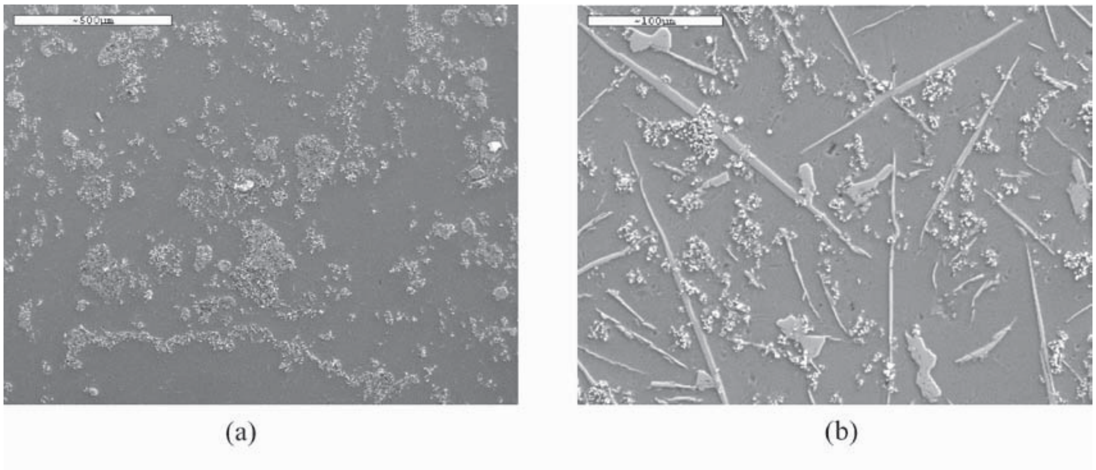
Fig. 1 shows the XRD patterns of alloy A and B. Peaks corresponding to Al, TiC and α-Al_2O_3 are detected in both alloys, the presence of $TiAl_3$ phase is also identified in alloy B, indicating that reactions between TiO_2, C and Al have taken place according to equations (1)–(3) to form $TiAl_3$, α-Al_2O_3 and TiC in liquid Al.

Secondary electron images of alloy A and B are shown in Fig. 2. Particle clusters can be observed in both alloys, whereas another needle-like or flaky phase $\sim$500 μm in length and $\sim$15 μm in width is also presented in alloy B. At higher magnification (Fig. 3a), it can be seen that particles in the clusters are discrete. Analyses through X-ray mappings (Fig. 3b–d) indicate that the white particle in Fig. 3a is TiC and the grey one α-Al_2O_3. TiC has a spherical or granular shape and ranges from 0.3 to 1.5 μm in diameter, and α-Al_2O_3 is polyhedral in shape and has a size of 1–3 μm. From a combination of analyses from Figs 1–3, it is clear that the needle-like phase in alloy B is $TiAl_3$.

$TiAl_3$ with flaky or needle-like morphology is brittle and has been found to initiate and propagate cracks, hence causing low ductility in MMCs [18]. Thus, its presence in the matrix should be avoided in a Al/(TiC + α-Al_2O_3) composite alloy. However, this phase is important for the alloy used as grain refiner to have better refinement efficiency, as suggested next.

Fig. 4 shows the macrographs of pure Al unrefined, refined through the addition of alloy A and B, respectively. It is clear that alloy B excellently refined Al grains. Alloy A produced some grain refinement too, but the refinement result is much less effective than that from alloy B. It should be noted that the TiC amount added into pure Al through alloy A is 2.8 times that through alloy B. After AlTiC master alloy containing $TiAl_3$ phase is added into Al melt to be refined at such low levels (usually 0.2% or so), the $TiAl_3$ phase in the matrix will dissolve into Ti and Al [2]. In Al grains refined by alloy A and B, TiC particles, instead of α-Al_2O_3, have been frequently observed at the centers, and these TiC particles at grain centers were found to be surrounded by Ti-rich structures (to be detailed in another paper), indicating that the refinement of Al grains is related to TiC and Ti, instead of α-Al_2O_3. The difference in the refinement abilities of alloy A and B is in accordance with the result of a recent paper wherein AlTiC master alloy containing both $TiAl_3$ and TiC exhibits much better effect in refining pure Al than that containing only TiC [5], revealing the importance of excess Ti (beyond that combined in TiC) in the refinement of Al by TiC-type Al master alloy.

In conclusion, Al alloys containing (TiC+α-Al_2O_3) or ($TiAl_3$ + TiC + α-Al_2O_3), i.e. Al/(TiC + α-Al_2O_3)



(a) (b)

Figure 2 Secondary electron image of alloy A (a) and alloy B (b).

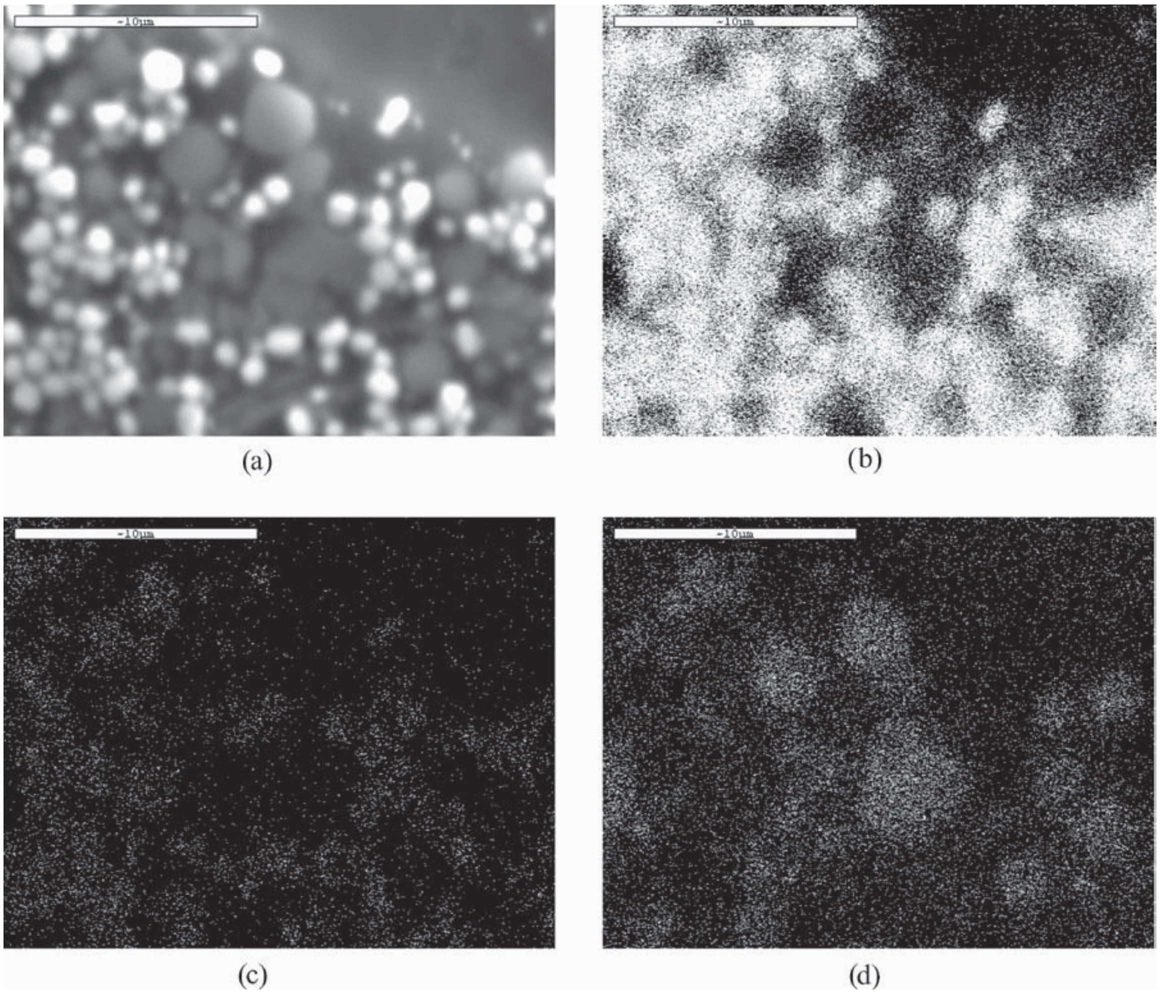


Figure 3 EPMA analysis of TiC and Al_2O_3 particles: (a) secondary electron image; (b) Ti X-ray mapping; (c) C X-ray mapping; (d) O X-ray mapping.

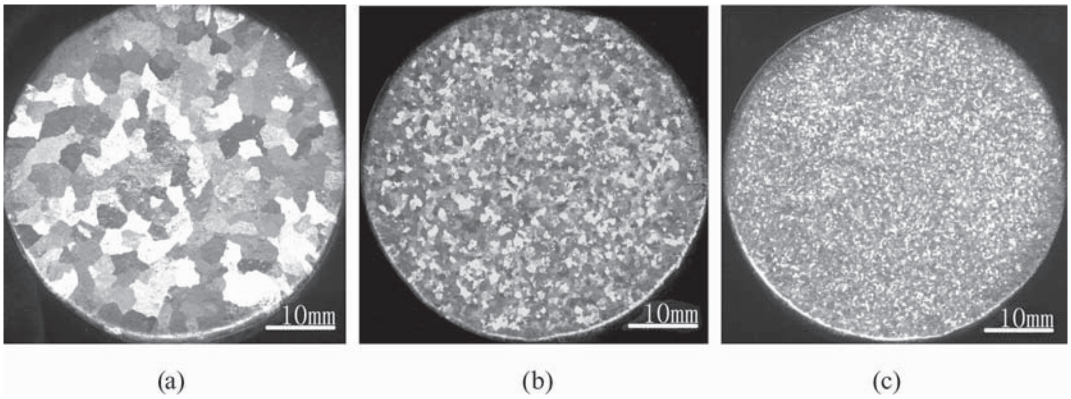


Figure 4 Macro grain sizes of pure Al (99.7%) unrefined (a), refined by the addition of alloy A (b) and alloy B (c) at a level of 0.2%. The two alloys have been held in the pure Al melt for 5 min before pouring.

or Al/($TiAl_3$ + TiC + α-Al_2O_3), have been successfully synthesized by reactions between Al, TiO_2, and C in liquid aluminum. The TiC particle generated is spherical in shape, has a size of 0.3–1.5 μm; α-Al_2O_3 has the polyhedral shape and is 1–3 μm in size. The Al/($TiAl_3$ + TiC + α-Al_2O_3) alloy is excellent in refining pure Al, whereas the refinement efficiency of the Al/(TiC + α-Al_2O_3) alloy is inferior. Work is in progress to study the relationships between the reaction parameters, microstructures, and mechanical properties of the produced alloys.

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