Studies on synthesis of in-situ Al-TiC metal matrix composites

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Abstract. In the present research work, synthesis and characterization of in-situ Al-TiC composites reinforced with ceramic phases was carried out. The formation of undesirable TiAl3 particles could be avoided justifying the correct procedural requirement adopted while preparing Al-TiC composites. It was observed that distributions of reinforced particles were uniform along the grain boundaries. It was also observed that the average size of the TiC particles was of 0.5 µm. It was also noted that the presence of TiC particles in the composite enhances the yield strength and hardness substantially.

1. Introduction
Al-TiC belongs to the particulate type reinforced aluminium alloy based metal matrix composites. Aluminium based metal matrix composites have drawn the attention of many researchers due to their low density, excellent wear resistance, high specific strength and high specific modulus [1-2]. Particle reinforced metal matrix composites are likely to find high volume of commercial application due to their low cost, ease of fabrication and improved properties [1-5]. The practical applications of Al-TiC metal matrix composites are in the aerospace, automobile and structural industries [6-7]. Several processing techniques [4, 5] have been developed to disperse discontinuous (particulates, whiskers, platelets) reinforcements uniformly in the matrix. However, each fabrication technique has its own advantages and limitations. Some of the problems encountered relate to: uneven distribution of reinforcement, control of the matrix-reinforcement interface, scaling up of the process for industrial utilization and processing cost. To overcome some of the inherent problems that are associated with conventional methods, a new processing technique called, in-situ processing, has been chosen, which is cost effective and the interfaces produced are relatively stable and impurity-free [1, 6]. Interfacial bonding between the matrix and the reinforcement has been reported to be good [1].

The Al-TiC composite system has been studied by a number of researchers and it has been reported that during synthesis of Al-TiC composites using the Al-Ti-C system, fine TiC particulates are created in the Al matrix. However, the uniform distribution of the reinforcement may be hindered by the presence of TiAl3 (a brittle compound) that degrades the mechanical properties of the composite [6-10]. TiAl3 exhibits high strain-rate sensitivity and its flakes have been found to initiate and propagate cracks and low ductility in the composite.
Elimination of this compound is, therefore, a primary concern for successful synthesis of Al-TiC composites.

In the present work Al-TiC composites have been developed via in-situ route. The microstructure and mechanical properties have been studied and the results are presented.

2. Experimental procedure
The in-situ process involves introducing carbon bearing activated charcoal into an Al-Ti melt, thereby forming TiC particles in the melt. In these experiments master alloys of Al-10Ti were prepared in an induction furnace at a temperature of 1200°C and poured into graphite moulds to solidify. Thereafter, the same Al-10Ti master alloys were re-melted in a pit furnace at different temperatures such as 1200°C, 1250°C and 1300°C and activated charcoal was added into the melt to meet the stoichiometry of TiC (Ti:C) to complete the reaction for the formation of TiC particles inside the melt. The reaction time was varied from 20 min to 60 min. The degasser hexachloroethane was used to remove the dissolved hydrogen gas from the melt. A small amount of potassium fluoride and sodium fluoride was added as a flux cover to remove the oxide film from the molten metal surface and to act as a protective barrier to gas absorption and for facilitating spontaneous incorporation of the particles into the melt [10]. Afterwards the melt was cast into rod form (15 mm in diameter and 150 mm in length) in metallic moulds to complete the process. Table 1 gives the processing conditions used for the synthesis of Al-TiC metal matrix composites. Al-TiC composites were prepared with varying weight percentages of TiC reinforced particles such as Al-3TiC, Al-5TiC, and Al-10TiC. The experimental setup for fabricating in-situ Al-TiC composites is shown schematically in figure 1.

| Sl. No. | Nominal Composition | Processing condition |
|---------|---------------------|----------------------|
|         | Reaction Temp (°C)  | Reaction Time (Min)  |
| 1       | Al-TiC              | 1200                 | 45       |
| 2       | Al-TiC              | 1200                 | 60       |
| 3       | Al-TiC              | 1250                 | 20       |
| 4       | Al-TiC              | 1250                 | 30       |
| 5       | Al-TiC              | 1250                 | 45       |
| 6       | Al-TiC              | 1250                 | 60       |
| 7       | Al-TiC              | 1300                 | 20       |
| 8       | Al-TiC              | 1300                 | 30       |
| 9       | Al-TiC              | 1300                 | 45       |
| 10      | Al-TiC              | 1300                 | 60       |

Figure 1. Schematic diagram of the apparatus for fabricating in-situ Al-TiC composites.
Microstructures of Al-TiC composites in the as-cast condition and of fractured surfaces of the tensile specimens were examined using a JEOL JSM-5800LV scanning electron microscope (SEM). Tensile tests were carried out at room temperature using an Instron 8516 machine with the loading speed controlled at 0.5 mm/min. The hardness of as-cast composites was measured on the HV scale using a Vicker’s hardness tester at an applied load of 5 kg. A X-ray diffractometer (PW 1840) operating at 40 kV and 20 mA was used to identify the various phases present in the specimens. In order to understand the mechanisms responsible for the formation of TiC via this process, a mixture of Al-10Ti (as-cast) alloy powders and high purity activated charcoal in an arbitrary weight ratio of 1:1 was prepared and analysed by differential thermal analysis (DTA). This analysis was carried out in an argon atmosphere from room temperature to 1300°C with incremental rate of 10°C/min in an alumina crucible.

3. Results and discussions

3.1 Microstructure analysis

The SEM micrographs of the Al-TiC composites are shown in figure 2 (a-h). It was observed that Al-TiC composites prepared at 1200°C with 45 min and 1200°C for 60 min of holding time have both TiAl₃ and TiC particles, which are shown in figure 2 (a-b). It is felt that the temperature was not sufficient to dissolve all the TiAl₃ particles inside the melt. In the next set of experiments, composites were prepared at 1250°C and 1300°C with 20 min holding time and it was observed that in this case also TiAl₃ and TiC particles were co-existing as shown in figure 2 (c-d). When the temperature was maintained at 1250°C and 1300°C but with higher holding time of 30 min, 45 min and 60 min, the composites, thus prepared, had only TiC reinforced particles and no TiAl₃ particles. This observation has been confirmed by EDX, XRD, DTA and SEM analysis. The SEM microstructure of Al-TiC composites prepared at 1250°C and 1300°C with 30 min holding time are shown in figure 2 (e-f). The figures show that at 1250°C with 30 min holding or higher temperature and holding time, all the TiAl₃ particles had been dissolved and formed stable TiC particles. The present results confirm the earlier reports of Rapp and Zhang [13] who reported that carbon normally reacts with titanium and aluminium to form titanium carbide (TiC) and aluminium carbide (Al₄C₃) and that at higher temperature TiC particles are more stable than Al₄C₃ particles. They suggested the following possible reactions and their accompanying free-energy changes:

Reaction 1 : Ti+3Al→ TiAl₃, ΔE₁ = -52503 + 21.483T

Reaction 2 : 3/4Al + C→ 1/3 Al₄C₃, ΔG₂ = -89611 + 32.841T

Reaction 3 : Ti+C→ TiC, ΔG₃ = -163382+80.347T+0.460x10⁻³T²+(3.094 x 10⁵)/T-0.962T ln T

where ΔG = Gibb’s free-energy (J mol⁻¹), T = Temperature (K). From reactions 2 and 3, it is revealed that the formation of TiC is more favorable than that of Al₄C₃. As Sahoo and Koczak [11] had presented the values ΔG for formation of TiC and Al₄C₃ are negative, indicating that the reactions can proceed spontaneously. In general, the more negative the standard free energy change of formation, the more stable the carbide is. They have showed that titanium is a very strong carbide former relative to Al₄C₃.

In the present experiments the average size of the TiC particles were observed to be 0.5 µm and those particles were found to be preferentially segregated at the grain boundaries. In addition, large clusters of carbides were also observed in the microstructure. Figure 2 (g-h), taken at higher magnifications, show clusters of TiC particles formed by the coalescence of several particles having faceted/polyhedral morphology. The particles observed in the microstructures were identified as TiC with the help of XRD and EDX analysis, the results of which are shown in figure 3 (a-b). figure 3 (a) represents the XRD of as-cast Al-TiC composite and extracted TiC particles. Figure 3 (b) represents the EDX of TiC particle.
Figure 2. SEM micrographs of Al-TiC composites: (a) 1200°C with 45 min, (b) 1200°C with 60 min, (c) 1250°C with 20 min, (d) 1300°C with 20 min, (e) 1250°C with 30 min, (f) 1300°C with 30 min and (g) 1250°C with 30 min, (h) 1300°C with 30 min reaction time at higher magnification.
Figure 3. XRD peak intensity of: (a) Extracted TiC particles and as-cast Al-TiC composites and (b) EDX of TiC particle.

3.2 Thermal analysis
The DTA analysis of Al-TiC composite helps to understand the possible mechanism for the formation of TiC during the in-situ process. DTA results during heating and cooling are presented in figure 4. Three reaction peaks were found at 673°C, 1046°C and 1250°C, during the heating cycle. The reaction peak at 673°C represents the melting of aluminium and the peak at 1046°C represents formation of TiAl\textsubscript{3} particles. The third peak at 1250°C appears to be an exothermic reaction indicating the formation of TiC particles. There are two peaks occurring during cooling. The first peak at 1250°C represents the solidification of TiC particles and another at 647°C represents the freezing point of pure aluminium. This shows that all the Ti in the (Al-Ti) alloy melt had completely reacted with the carbon dispersed in the melt during heating. Microstructures of samples reveal many interesting results. Firstly, TiC particles within the matrix are finer than the activated charcoal powders used in the melt. Secondly and most importantly, the fine TiC particles are not only polyhedral in shape but also uniform in size. This strongly suggests that the formation of TiC is achieved via a mechanism of nucleation and growth during isothermal holding. Nucleation would require the dissolution and rapid diffusion of carbon from the large size (20 µm) of the activated charcoal powders into the melt, while the growth of the carbides would be controlled by the diffusion of the lower diffusivity element, Ti. Diffusion of carbon in molten aluminium is sufficiently fast for
nucleation of TiC. The present results also confirm the findings of Nukami and Flemings [14] who had suggested the following in-situ reactions for synthesizing the TiC particulates reinforcement in the Al-Ti-C system based on DTA and XRD analysis:

Reaction 4: Ti +3Al→ TiAl₃
Reaction 5: 3TiAl₃+ Al₄C₃→ 3TiC+ 13Al
Reaction 6: TiAl₃+ C→ TiC+ 3Al

Table 2. Tensile results and hardness of pure Al and the Al-TiC composites.

| Sl. No. | Material     | Yield Strength (MPa) | % Elongation | Hardness (HV₅) |
|---------|--------------|----------------------|--------------|---------------|
| 1       | Al           | 80                   | 30           | 18.13         |
| 2       | Al-3TiC      | 123                  | 16           | 32.92         |
| 3       | Al-5TiC      | 142                  | 12           | 37.83         |
| 4       | Al-10TiC     | 189                  | 5            | 44.17         |

3.3 Tensile properties
The results of the tensile tests are presented in table 2. The effect of the TiC particles in increasing the yield strength of the Al-TiC composites is illustrated by comparing properties with those of commercially pure Al. The composites containing TiC particles have higher yield strength. The fine submicron TiC particles that are present in these composites are believed to contribute to strengthening. From table 2 it is observed that with increases in the amount of TiC particles in the Al-TiC composites the tensile strength increases whereas the elongation decreases. The increasing amount of TiC reduces the grain size of α-Al (because the α-Al nucleates on the surfaces of TiC particles) and hence there is a possibility of improving strength. According to Sahoo et al [11], a decrease in grain size from 300 to 60 µm would result in an improvement in yield strength of approximately 13 MPa. The improvement in the proof stress corresponding to this grain size reduction (for 18 vol. % particle additions) was about 50 MPa, indicating that the TiC particles contribute strengthening to the composite. As compared with pure Al, the Al-3TiC composite contains a small amount of TiC particles leading to increasing yield strength by 1.5 times, i.e. from 80 MPa to 123 MPa; and in the Al-5TiC and Al-10TiC composites the yield strengths increased by 1.75 and 2.3 times respectively. The hardness values of pure Al and the Al-TiC composites are also shown in table 3. The hardness of Al-TiC improved due to the formation of reinforcement particles. From the table 2 it can be concluded that with increases in the amount of TiC particles, the hardness increased substantially. It can thus be said that with the increase in the value of hardness there is a corresponding increase in tensile strength. Fractured surfaces of tensile specimens are shown in figure 5 (a-b), which reveals that the Al-3TiC composites had ductile fractures. The Al-10TiC (figure 5 (b)) composite exhibited smaller fracture dimples compared with those of Al-3TiC (figure 5 (a)). It can be said that materials having dimples of smaller sizes require more force for deformation/failure, which indicates that the Al-10TiC composite has still better strength.

Figure 5. Fracture surface of: (a) Al-3TiC and (b) Al-10TiC composite.
4. Conclusions

Al-TiC metal matrix composites have been prepared successfully at a processing temperature of 1250°C and holding time of 30 minutes by an in-situ route which eliminates the incidence of unwanted brittle TiAl3 particles and the average size of the TiC particles was observed to be about 0.5 µm. Microstructures of the composites showed uniform distributions of TiC particles along the grain boundaries. These particles have a polyhedral shape and are uniform in size. The presence of TiC particles in the composite increased the yield strength and hardness with substantial decrease in elongation.

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