



# Materials Science

An Indian Journal

Full Paper

MSAIJ, 12(12), 2015 [454-461]

## Study on in-situ synthesis of AL-TiC composite by self propagating high temperature synthesis process

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### ABSTRACT

Aluminum reinforced in-situ TiC particulate composites were successfully synthesized using mechanically milled Al-Ti-C powder by self-propagating high temperature synthesis (SHS) process. The reaction for the formation of TiC from the elemental Al, Ti & C was studied. The results show the compact density of the preform has a significant effect on the SHS reaction. No reaction was observed when the compact density falls below 68% of the theoretical density. However, with an increase in density from 68 to 80%, thermal explosion reaction was observed in the Al-melt. Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray analysis (EDX) confirmed the evolution and fine distribution of TiC in the matrix.

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### KEYWORDS

Composites;  
Al-TiC;  
SHS;  
Perform density.

### INTRODUCTION

High specific strength, stiffness and modulus, as well as high wear resistance, makes Al based metal matrix composites (MMCs) a potential material for advanced structural applications<sup>[1-5]</sup>. In particular, the particulate-reinforced MMCs are of interest due to the ease of fabrication, lower manufacturing cost with isotropic properties. The particulate reinforced composites are conventionally prepared, either by powder technology or by liquid metallurgy, where the ceramic particles are directly incorporated into solid or liquid matrices respectively. However, metal matrices reinforced with in-situ formed ceramic particles are emerging group of discontinuously reinforced composites that have distinct advantages over the conventional composites<sup>[6-12]</sup>. Both

liquid and solid state processes are being studied to produce in-situ particle composites based on metal matrices. In liquid state processes, solid / liquid / gaseous phases are introduced into a liquid metal/alloy to react with the base metal or its alloying elements to produce the reinforcement. In a solid-state process; elements /compounds are blended, compacted and heated at a selected temperature to form the desired reinforcement. Both techniques produce very fine reinforcements in the matrices. Mechanical properties of the in-situ composites are comparable with or better than the conventional composites<sup>[9]</sup>. Al-based MMCs with ceramics (SiC, Al<sub>2</sub>O<sub>3</sub>, TiC and TiB<sub>2</sub>)<sup>[5,6-12]</sup> as reinforcement have been widely studied. TiC is particularly attractive due to its high hardness, elastic modulus, low density, good wettability with molten aluminum and its low

chemical reactivity.

There are various in-situ production methods for TiC reinforced aluminum based composites. One of them is self-propagating high-temperature synthesis (SHS), which provides a number of advantages for making composites; such as low energy requirement, cost-effectiveness and high productivity. It produces high purity products and has the possibility to control their structure and properties<sup>[13-14]</sup>. Considerable work has been done to investigate SHS in aluminum melts for Al–Ti and Al–Ti–B grain refiner fabrication<sup>[15-16]</sup>. It was shown that microstructure and properties of the synthesized product could be controlled through SHS parameters, such as initial melt temperature, particle size of the powders, stoichiometric ratio, compact density and flux addition. Al–TiC composites are particularly adaptable to SHS process due to the highly exothermic reaction between Ti and C. Dong et al.<sup>[20]</sup> studied the effect of green compact density on SHS reaction in NiAl and reported that reaction mechanism depends on characteristics of Al particle size and is completely different in nano and micron size particles. He found the  $T_{ig}$  as 320°C for a compact density of 90% in 40 nm Al nanopowder, produced by wire electrical explosions. This work aims to in producing Al–TiC composites using SHS technique in liquid aluminum.

## EXPERIMENTAL DETAILS

### Materials

In present study, aluminium ingot of commercial purity (99.5%) from Hindalco (india) chemical composition of (0.40% Fe, 0.25% Si, 0.05% Mg, 0.05% Mn, 0.05% Cu, 0.05% Cu, 0.03% Ti, and balance Al) was used as a matrix material. Mechanically blended Al–Ti–C powder in the form of compact pellet was taken as reinforcement. The pellet was made from Al powder of average size  $\hat{A}40 \mu\text{m}$  (Himedia, India), Ti powder of average size  $\hat{A}20 \mu\text{m}$  (Alfa Aesar, UK), and graphite powder of average size 8–10  $\mu\text{m}$  (Himedia, India).

### Composite preparation

The preforms were made from commercial powders as mentioned above. The reactants (powders) were mechanically blended using a ball mill. The resultant mixture was pressed into cylindrical compacts of 20

mm diameter and 15 mm length, using a stainless-steel die with two plungers and was pressed between 110–140 MPa. About 1 kg of aluminum (commercial ingot with ~ 99.6% purity) was melted in an electric resistance bottom-pouring furnace at 800°C under argon atmosphere. 60 g of the pellet of varying density was added to the melt. After 20 minutes, the melt was stirred at 600 rpm for 15 min using a stainless steel impeller to facilitate incorporation and uniform distribution of in-situ TiC in the Aluminum matrix. Subsequently, TiC particles were formed in the liquid aluminum because of SHS reaction. Aluminum matrix composites were prepared by melt stirring, followed by metal die-casting.

### Density measurements

The density of compacted pellet was measured using Archimedes' principle on three randomly selected polished samples of Al–TiC composites. Distilled water was used as the immersion fluid. The pellet samples were weighed in air and immersed in distilled water. A satorius electronic balance with an accuracy of 0.0001 g was used for recording the weights. Theoretical densities of the samples were calculated using rule-of-mixtures.

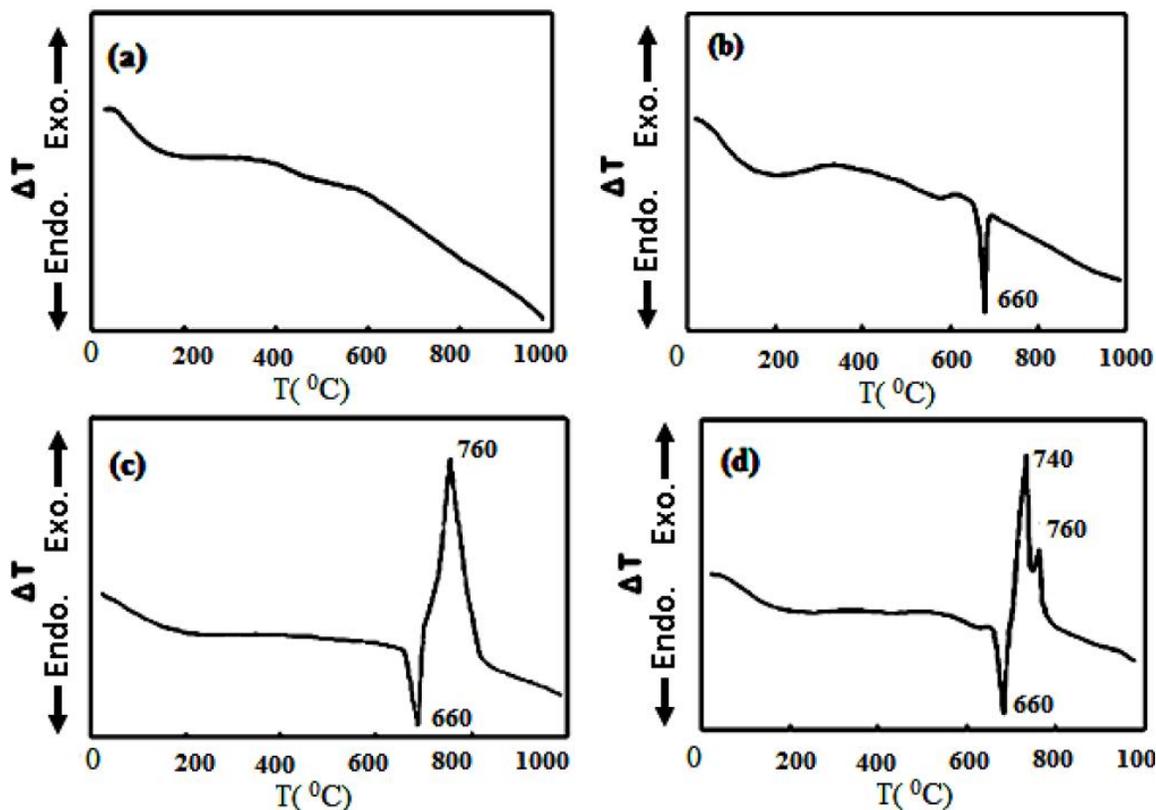
### Microstructural characterization

Microstructural characterization studies were conducted on metallographically polished samples to investigate morphological characteristics of grains and secondary phases and distribution of reinforcement. HITACHI-S-3400(SEM), Nikon LV-150Metallographic optical microscope and Scetist Image analyzer were used for this purpose. The etching solution was made using 95 mL water, 2.5 mL  $\text{HNO}_3$ , 1.5 mL  $\text{HCl}$ , 1.0 mL  $\text{HF}$  (Keller's reagent) to reveal the grain boundaries for microstructural analysis.

### X-ray diffraction and raman spectroscopy studies

X-ray diffraction and Raman spectroscopy studies X-ray diffraction analysis was carried out on the polished cast ingot of Al–TiC composite samples using automated DMAX3C rotary-target X-ray diffractometer. The samples (20 x 15 x 2.5 mm) were exposed to  $\text{CuK}_\alpha$  radiation ( $k = 1.54056 \text{ \AA}$ ) at a scanning speed of 2°/min. The Bragg angle and the values of inter planar spacing ( $d$ ) obtained were subsequently matched with the standard values for Al–TiC and related phases. Raman spectra have also been recorded on the same polished

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**Figure 1 :** DTA curves for the mixtures (a) carbon- titanium (with a molar ratio of C/Ti=1.0) (b) aluminum–carbon (with a molar ratio of Al/C=4/3) (c) aluminum–titanium (with a molar ratio of Al/Ti=3.0) and (d) titanium–carbon–aluminum (with a molar ratio of Ti/C=1.0 mixed with 40%wt Al) heated at 20° C/min in nitrogen atmosphere.

surface using Micro-Raman Spectroscopy (Renishaw in via UK). The spectra were recorded in the range between 750 and 2000  $\text{cm}^{-1}$  with an acquisition time of 50 x 5s and the spectra were taken from at least five different particles so as to examine the homogeneity of the composite.

The preforms were made from commercial powders given in TABLE 1. The reactants (powders) were mechanically blended using a ball mill. The resultant mixture was pressed into cylindrical compacts of 20 mm diameter and 15 mm length, using a stainless-steel die with two plungers and was pressed between 110–140 MPa. About 1 kg of aluminum (commercial ingot with ~ 99.6% purity) was melted in an electric resistance bottom-pouring furnace at 800°C under argon atmosphere. 60 g of the pellet of varying density was added to the melt. After 20 minutes, the melt was stirred at 600 rpm for 15 min using a stainless steel impeller to facilitate incorporation and uniform distribution of in-situ TiC in the Aluminum matrix. Subsequently, TiC particles were formed in the liquid aluminum because of

SHS reaction. Aluminum matrix composites were prepared by melt stirring, followed by metal die-casting. The as-cast ingots were sectioned, polished, and examined using optical microscopy (OM) and field emission scanning electron microscopy (SEM) (Zeiss Supra-55). Phase identification was carried out using X-ray diffraction (XRD) - DMAX3C rotary-target X-ray diffractometer with Cu- $\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) and Micro-Raman Spectroscopy (Renishaw in via U.K.). The Raman spectra were recorded using a 514-nm radiation of an Ar laser excitation.

## RESULTS AND DISCUSSION

### Reaction mechanism and phase study

The interaction mechanism between the components of the Al-Ti-C system was studied using DTA analysis (Figure 1) in nitrogen atmosphere with a heating rate of 20°C/min. The samples were heated up to 1000°C. The samples used for DTA measurement were then subjected to XRD, in order to ascertain the phases formed

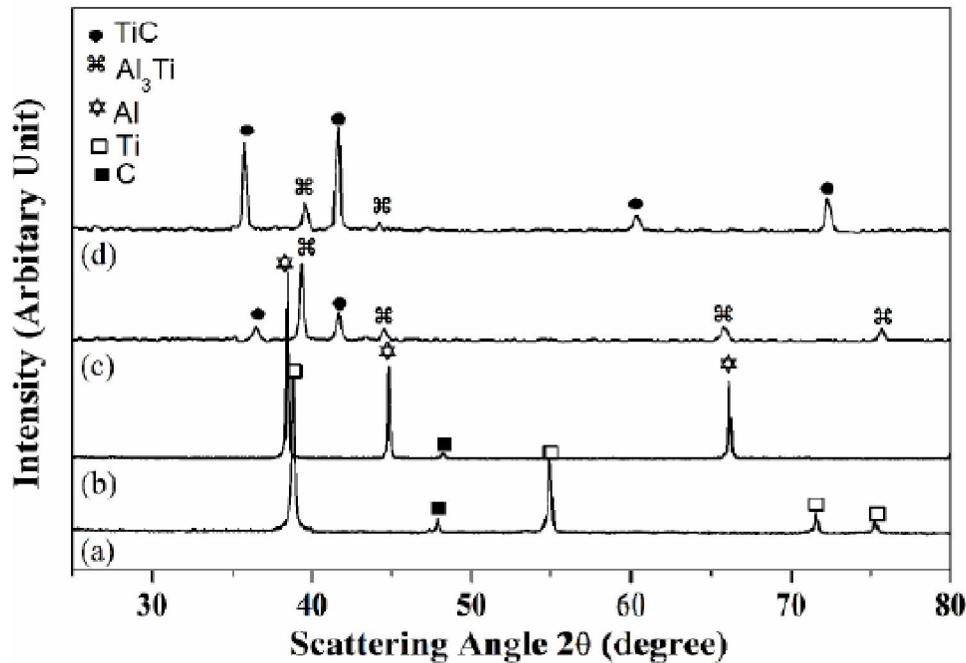


Figure 2 : XRD pattern of the mixture (a) carbon- titanium (with a molar ratio of C/Ti=1.0) (b) aluminum-carbon (with a molar ratio of Al/C =4/3) (c) aluminum-titanium (with a molar ratio of Al/Ti=3.0) and (d) titanium-carbon-aluminum (with a molar ratio of Ti/C=1.0 mixed with 40%wt Al) heated at 20°C/min in nitrogen atmosphere to 1000°C.

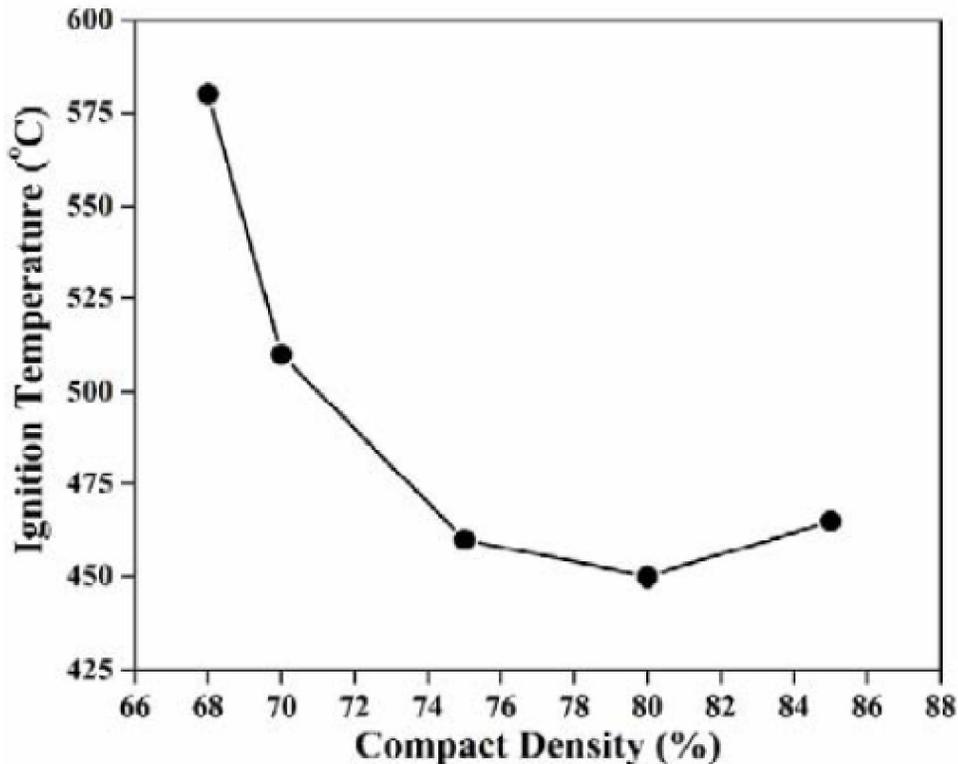


Figure 3 : Plot of preform compact density vs  $T_{ig}$  of SHS reaction

during the DTA measurements (Figure 2). The DTA curve in Figure 1(a) show no reaction between titanium and carbon, which is corroborated from the XRD pat-

tern (Figure 2) showing titanium and carbon peaks. Figure 1(b) shows an endothermic peak at 660°C, which corresponds to Al melting. The corresponding XRD

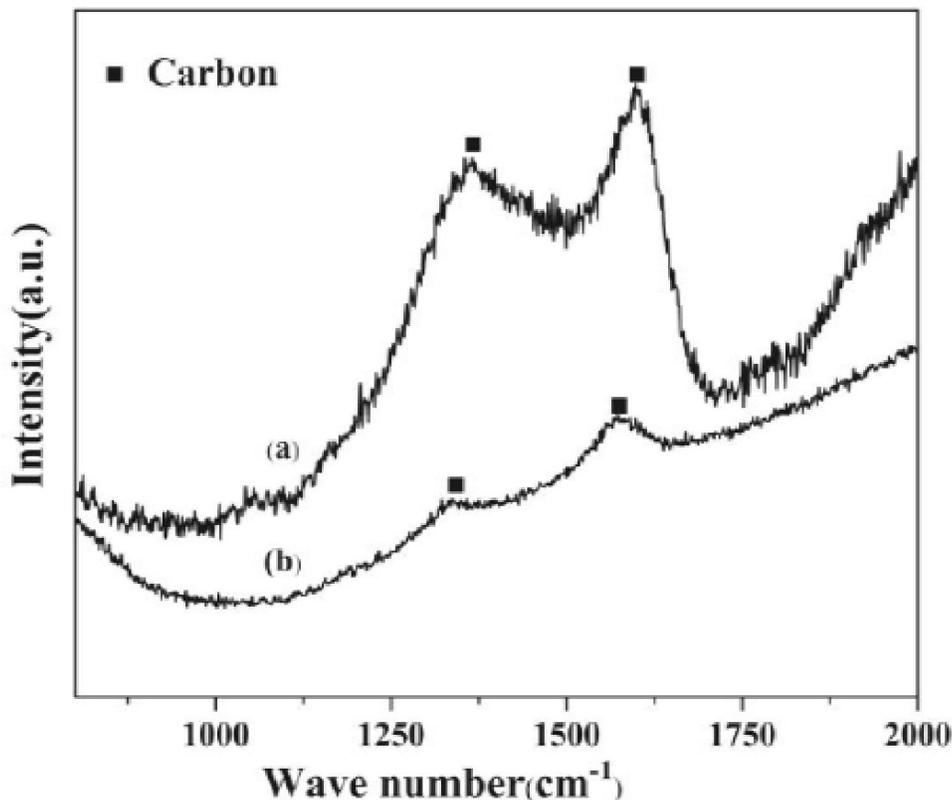


Figure 4 : Raman spectra of Al-TiC composite made using the Al-Ti-C preform of compact density (a) 70% (b) 75% of theoretical density (Compact preheat temperature = 450°C).

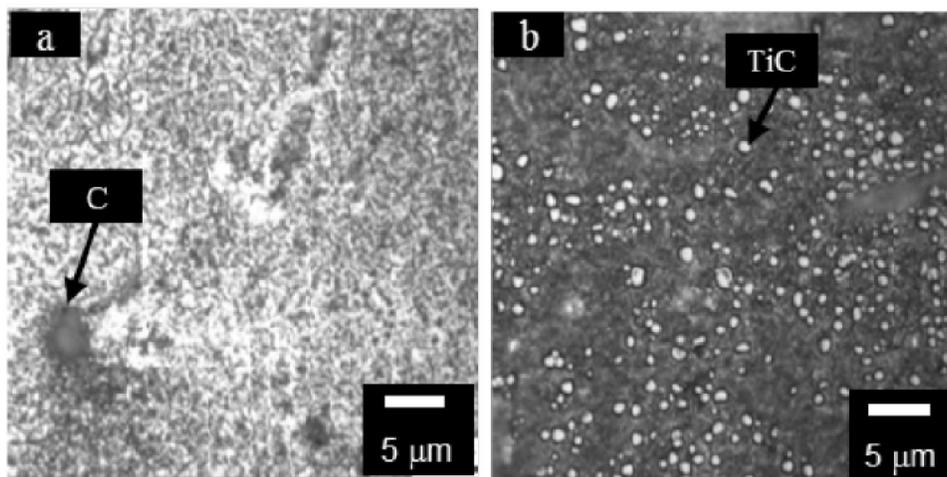


Figure 5 : Optical micrograph of Al-TiC composite prepared from the preform compacted density (a) 65% (b) 75% (Compact preheat temperature = 450°C).

pattern show Al and carbon peaks. The results show that the exothermic reaction between Al and C and Ti and C to form  $Al_4C_3$  and TiC respectively has not taken place until 1000°C. The DTA measurement for Al-Ti, with a molar ratio of Al/Ti = 3 (Figure 1(c)) show two peaks; a endothermic peak at 660°C (Al melting) and an exothermic peak at 760°C. The XRD measurement

shows the presence of  $Al_3Ti$  peaks along with Ti peaks. Hence, the exothermic signal observed from the DTA measurement refers to the formation of  $Al_3Ti$ . The results suggest that  $Al_3Ti$  formation is more favorable in the Al-Ti-C system. Figure 1(d) show an endothermic at 660°C (Al melting) and two exothermic peaks at 740°C and 760°C, corresponding to  $Al_3Ti$  and TiC for-

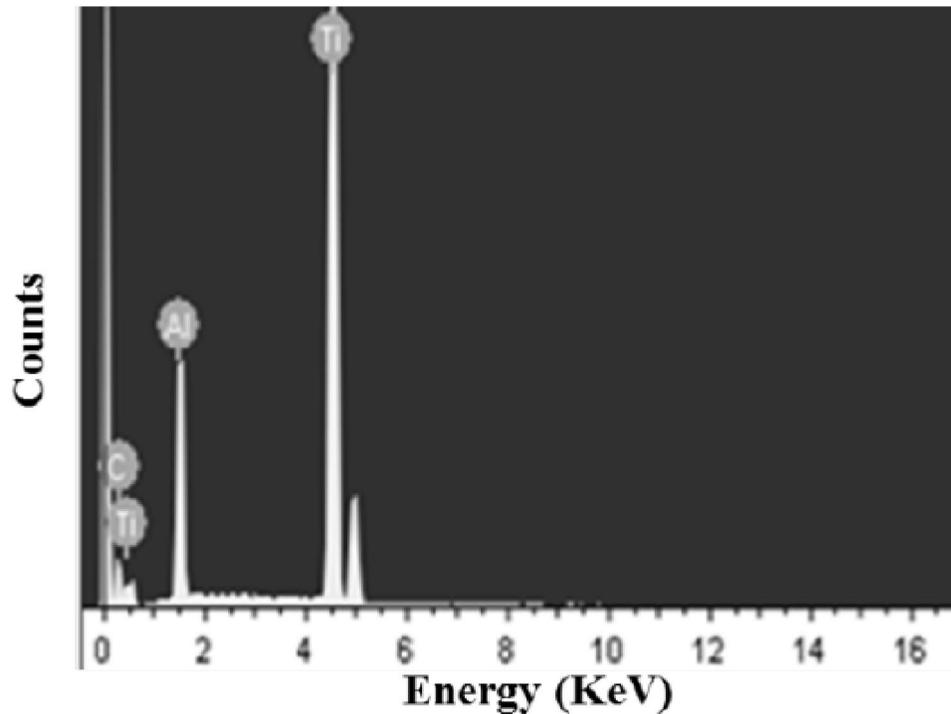


Figure 6 : EDX spectra of the TiC particle reinforced in Al matrix.

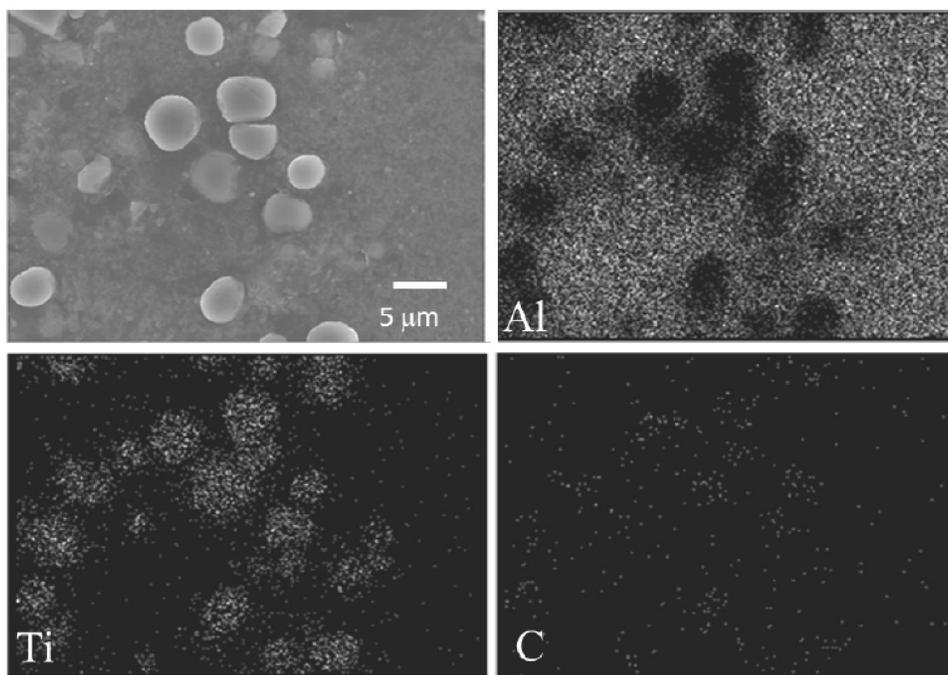
mation respectively. From DTA measurements, it can be suggested that aluminum serves not only as a diluent but also as an active reactant and participates in the SHS reaction<sup>[19]</sup>. The addition of aluminum kindles the TiC formation in Al–Ti–C system<sup>[20]</sup>.

#### Effect of compact density on ignition temperature

The effect of compact density on ignition temperature ( $T_{ig}$ ) of the preform and the fabrication of Al-TiC composites were studied. In order to study the  $T_{ig}$  of the compact, the compact was kept in a tube furnace maintained under argon atmosphere. The heating of the preform was carried out at a very slow rate of 3–4 °C/min. The temperature of the pellet was measured by a thermocouple, placed just below the pellet. The  $T_{ig}$  was characterized by a sudden rise in temperature of the pellet, followed by temperature drop. Preform with theoretical densities of 68, 70, 75, 80, and 85%, were prepared by cold pressing and were used in this study.

A plot of preform density against ignition temperature is shown in Figure 3. It shows that with increase in compact density, the  $T_{ig}$  of the SHS reaction decreases and it becomes almost constant for compact densities between 75% to 80% of theoretical density. When the compact density is increased from 80%, the  $T_{ig}$  raises again. The curve also reveals that ignition does not oc-

cur, when the compact density falls below 68% of theoretical density and hence no SHS reaction. If the preform is porous with low density, the capillary spreading of the aluminum within the pores is localized, where the liquid phase exists and hence the particles are not completely covered by the liquid melt<sup>[20]</sup> and also less number of contact between the particles, less exothermic heat released<sup>[17]</sup>, which would not sufficient to start the SHS reaction. In the other case, when the preform is dense (high compact density) heat released is sufficient but the capillary spreading and the particle rearrangement is confined to closed pores among the particles and is not distributed throughout the pellet<sup>[17]</sup> the reaction does not propagate in the pellet. In both of the above conditions, the SHS reaction does not proceed throughout the compact and is localized. Therefore optimum compact density is essential to propagate the reaction throughout the compact for homogeneous distribution of the in-situ formed second phase particles (TiC). At the optimum compact density the heat released from the first step<sup>[18]</sup> of the combustion reaction  $[Al+3Ti \rightarrow Al_3Ti \dots \dots (1)]$  is enough to start the second step reaction  $[TiAl_3 + C \rightarrow TiC + 3Al \dots (2)]$  and capillary spreading throughout the preform provides the shortest diffusion path to propagate the reaction.



**Figure 7 :** EDX map of the Al-TiC composite showing distribution of the elements in the matrix. (Compact preheat temperature = 450°C and density = 80%).

The characteristic Raman spectra of the Al-TiC composites fabricated using pre-heated preform at 70% and 75% compact densities is shown in Figure 4. When the compact density is 70%, high intense peaks of unreacted carbon were observed at wave numbers 1320 and 1590  $\text{cm}^{-1}$ . The peaks reduce drastically in intensity, when the compact density is increased to 75%. Reduction of the peak intensity shows that concentration of free carbon decrease in the preform. Above observation demonstrate that second step of the combustion reaction  $[\text{TiAl}_3 + \text{C} \rightarrow \text{TiC} + 3\text{Al} \dots (1)]$  takes place at higher preform density, resulting in the formation of TiC. The spectra do not show any titanium and aluminium peaks because they do not have Raman active vibrational modes. It can be concluded that, at lower compact density, some part of the heat released from first step reaction may be dissipated in voids and pores and remaining heat is not sufficient to start the second steps of the reaction. As a result, the preform dissolves in the Al melt before TiC formation, which is not the case for preform with high compact density.

#### Optical and scanning electron microscopy

As-cast optical micrographs of the composites fabricated using preform of two different compact densities are shown in Figure 5(a) & (b), where Figure 5(a)

shows the microstructure of the composite prepared using the preform of 65% compact density. The microstructure shows carbon patches along with some titanium segregation, which suggests no reaction has taken place in the melt. The preform dissolves in the melt and remains in its elemental form. The density of the compact (65%) was not sufficient for the ignition of the SHS reaction to takes place as described in section 3.2. When the density is increased to 75%, fine distribution of TiC was observed in the matrix as shown in the Figure 5(b). Apart from TiC no other phases were observed in the matrix, indicating the completion of SHS reaction. The EDX of the composite sample shown in Figure 6 confirms TiC particle in the matrix. The EDX map in Figure 7 of the composite shows the distribution of the different element in the composite, which further strength the claims for the fine distribution of TiC particles in the matrix.

#### CONCLUSIONS

In-situ TiC particulate reinforced aluminium matrix composite was successfully synthesized using SHS process. The reaction mechanism between elemental Al-Ti-C powder shows, that Al acts as diluent as well as active reactant and participates in the SHS reaction.

Further experimental result shows that compact density has significant role on the  $T_{ig}$  of the preform. Preform with compact densities between 75% - 80% of theoretical density was found to be optimum for successful SHS reaction and to have uniform TiC particle distribution in Al matrix.

### ACKNOWLEDGEMENTS

The authors are grateful to the Department of Science and Technology New Delhi, India for providing the financial support and also to the Institute of Minerals and Materials Technology, Bhubaneswar for providing necessary facility to carry out the work.

### REFERENCES

- [1] A.C.Albiter, C.A.Leon, R.A.L.Drew, E.Bedolla; Mater. Sci. Eng. A, **289**,109 (2000).
- [2] W.H.Jiang, G.H.Song, X.L.Han, C.L.He, H.C.Ru; Mater. Lett., **32**, 63 (1997).
- [3] C.Selcuk, A.R.Kennedy; Mater. Lett., **60**, 3364 (2006).
- [4] I.H.Song, D.K.Kim, Y.D.Hahn, H.D.Kim; Mater. Lett., **58**, 593 (2004).
- [5] Q.C.Jiang, H.Y.Wang, Y.G.Zhao, X.L.Li; Mater., Res. Bull., **40**, 521 (2005).
- [6] S.Scudino, G.Liu, K.G.Prashanth, B.Bartusch, K.B.Surreddi, B.S.Murty, J.Eckert; Acta Mater, **57**, 2029 (2009).
- [7] A.K.Chaubey, B.K.Mishra, N.K.Mukhopadhyay, P.S.Mukherjee; J. Mater. Sci., **45**, 1507 (2010).
- [8] A.B.Padney, R.S.Mishra, Y.R.Mahajan; Mater. Sci. Eng. A, **206**, 270 (1996).
- [9] K.G.Prashanth, B.S.Murty, Mater. Manuf. Proc., **25**, 592 (2010).
- [10] K.G.Prashanth, S.Scudino, K.B.Surreddi, M.Sakaliyska, B.S.Murty, J.Eckert; Mater. Sci. Eng. A, **513**, 279 (2009).
- [11] R.Ayers, D.Burkes, G.Gottoli, H.C.Yi, J.J.Moore; Mater. Manuf. Proc., **22**, 481 (2007).
- [12] K.G.Prashanth S.Kumar, S.Scudino, B.S.Murty, J.Eckert; Mater. Manuf. Proc., **26**, 1242 (2011).
- [13] P.Li, E.G.Kandalova, V.I.Nikitin, A.G.Makarenko, A.R.Luts, Y.Zhang; Scripta Mater., **49**, 699 (2003).
- [14] G.Xiao, G.Zhang, Q.Fan; J. Ceramic Proc. Res., **10**, 609 (2009).
- [15] V.I.Nikitin, J.I.E.Wanqi, E.G.Kandalova, A.G.Makarenko L.Yong; Scripta Mater, **42** 561 (2000).
- [16] E.G.Kandalova, V.I.Nikitin, J.Wanqi, A.G.Makarenko; Mater. Lett., **54**,131 (2002).
- [17] S.Dong, P.Hou, H.Cheng, H.Yang, G.Zou; J. Physics Cond. Matter, **14**, 11023 (2002).
- [18] S.K.Roy, A.Biswas; Mineral Proc. Extractive Metallurgy Rev., **22**, 567 (2002).
- [19] H.Y., Wang, Q.C., Jiang, X.L. Li, F.Zhao; J. Alloys Comp., **366**, L9 (2004).
- [20] W.C.Lee, S.L.Chung; J. American Ceramic Soc., **80**,53 (1997).