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Effect of compact density and preheating temperature of the Al–Ti–C preform on the fabrication of in situ Mg–TiC composites

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Abstract Magnesium reinforced in situ TiC particulates was successfully synthesized by utilizing the self-propagating high temperature synthesis (SHS) process. The result showed that preform temperature and compact density have effects on the SHS reaction. It is observed that when the compact density was below 68% of the theoretical density, no SHS reaction occurred. However, with an increase in density from 68 to 72%, the successful thermal explosion reaction was observed in the Mg melt. Besides this, the effect of preheat temperature on the fabrication of Mg/TiC composite was extensively studied and found that the preheat temperature below 300 °C failed to give rise to SHS reaction. However, the preheat temperature of 450, 500, and 550 °C favors the reaction inside the liquid melt, but the temperature of 600 °C leads to the ignition reaction in the preheating furnace itself. SEM and EDX study confirms fine distribution of TiC in the matrix.

Introduction

In recent years, magnesium alloys are becoming more important for the industrial applications due to their relatively low density, high-damping capacity, good castability, and machinability. However, the low strength, elastic modulus, and wear resistance at elevated temperature have restricted their applications as engineering materials [1]. Metal matrix composite (MMC) technology significantly improves the wear resistance, elastic modulus, and tensile strength of unreinforced metals and alloys. Among numerous MMC systems under development, composites with aluminum and magnesium matrices and ceramic particulate reinforcements are of commercial interests to the automotive and aerospace industries [2]. Because of the formation of clean, ultra fine, and stable ceramic reinforcements, the in situ MMCs exhibit excellent mechanical properties [3]. Karmer et al. have synthesize Schenfliesite-type $MgSn(OH)_6$ and found good coating material in the automotive and aerospace industries [4]. In recent different techniques and reinforcement (Al_2O_3, Y_2O_3, AlN, SiC etc.) have been used to produce nanocomposite and reported significant improvement in strength and wear resistance of the composites [5–7]. In magnesium matrix, TiC is particularly useful as reinforcement because of its hardness and stiffness, wettability, high-temperature stability, and low weight. Magnesium-based MMCs are currently being explored for a number of automotive and aerospace applications, such as automotive pulley, cog-tooth sprockets, oil-pump cover, cylinder liner, and aircraft engine casting [8–10].

Self-propagating high temperature synthesis (SHS) is drawing an increasing attention as a technique for synthesis of refractory materials due to its attractive advantages such as high purity of products, low processing cost, and energy and time efficiency [11, 12]. A wide variety of materials, such as carbides, borides, nitrides, intermetallics, and composites have been produced by this method. Recently, SHS reaction in the Al–Ti–C system has been widely investigated because of its lower ignition temperature, about 650–800 °C, which is approximately the same as the temperature of magnesium alloy [13–15]. Literature also reports that the particle size, density, and percentage

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aluminum content in the preform has a greater effect on ignition temperature of the preform [2, 3]. Many researchers have worked on Al–Ti–C system and demonstrated a significant effect of aluminum on ignition of SHS reaction [1, 10]. However, less work has been carried out on the effect of preheat temperature and compact density on the SHS reaction in molten magnesium.

In this study, an attempt is made to study the feasibility of the in situ synthesis of Mg–TiC and the impact of compact density and the preheat temperature on synthesis reaction of the preform of Al, Ti, and C powders in molten magnesium.

Experimental

Materials

In this study, magnesium ingot of commercial purity (99.5%) from China was used as a matrix material and for the reinforcement Al–Ti–C pellet was used. The pellet was made from Al powder of average size <40 μm (Himedia, India), Ti powder of average size <20 μm (Alfa Aesar, UK), and graphite powder of average size 8–10 μm (Himedia, India). The fine Al powder in the preform pellet melt at the ignition temperature and provide easier route for TiC formation reaction and also it acts as a reactant. Aluminum reacts with titanium to form Al_3Ti which is an exothermic reaction and provides heat for further reaction.

Processing

The synthesis process involved blending the reactants powders 40 wt% aluminum, 12 wt% graphite, and 48 wt% titanium in a dual drive planetary ball mill. Graphite and titanium powders were at a ratio corresponding to that of stoichiometric TiC. The resulting mixtures were pressed into cylindrical compacts of 20 mm in diameter and 15 mm in length using a stainless-steel die with two plungers. The compacts were pressed at pressures of 110–140 MPa to obtain density of 75 ± 2% theoretical density. About 1 kg of magnesium was melted in the electric resistance bottom pouring furnace at 800 °C under argon atmosphere. Sixty grams of the pellet of different density and preheat temperature were added to the melt. After about 20 min, 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 metallic matrix. Experiments were conducted under a protective atmosphere of argon. Subsequently, SHS reaction was observed to occur and TiC particles were formed in the liquid of magnesium alloy. Processing of the magnesium matrix composites was carried out by melt stirring and composite casting (metal die casting).

Density measurements

The density of compacted pellet was measured using Archimedes' principle. 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.

Recording of ignition temperature and transferring pellet into the melt

In order to study the ignition temperature 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° per min. The rise of the temperature of the pellet was measured by thermocouple just below the pellet. After certain time sudden rise in temperature of the pellet was observed followed by drop in temperature. The starting temperature of the sudden rise temperature was recorded as ignition temperature. The pellet from the preheating furnace was transferred in a pellet feeder system having argon gas purging arrangement and finally the pellet was put in the melting furnace by the opening of the valve.

Microstructural characterization

Microstructural characterization studies were conducted to determine grain size, grain morphology, and distribution of reinforcement. HITACHI-S-3400(SEM), Nickon LV-150 Metallographic optical microscope and Scetist Image analyzer were used for this purpose.

X-ray diffraction and Raman spectroscopy studies

X-ray diffraction analysis was carried out on the polished cast ingot of Mg–TiC composite samples using automated DMAX3C rotary-target X-ray diffractometer. The samples (20 × 15 × 2.5 mm) were exposed to CuKα radiation ($\lambda = 1.54056$ Å) 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 Mg–TiC and related phases. Raman spectra have also been recorded on the same polished surface using Micro-Raman Spectroscopy (Renishaw invia UK). The spectra were recorded in the range between −200 and 2,500 cm^{-1} with an acquisition time of 50 × 5 s and the spectra were taken from at least five different particles so as to examine the homogeneity of the composite.

Results and discussion

Effect of compact density

In this part of study, the effect of compact density on ignition temperature of preform and fabrication on Mg–TiC composites was carried out. Preform of densities of 68, 70, 75, 80, and 85% of theoretical density was used for study. Figure 1 shows that with the increase in compact density, ignition temperature of the SHS reaction decreases and it becomes optimum when the compact density is about 80% of the theoretical density.

In liquid-phase sintering, the predominant mechanism leading to densification involves fluid flow and particle rearrangement [13]. During this stage, the liquid wets the particles and flows among them. Thus, a more efficient packing occurs by the capillary forces acting on the particles. In the present study, aluminum added to titanium and graphite mixture is believed to give rise to a similar effect (i.e., particle rearrangement) on the reactant compact. However, the extent of the effect of capillary forces and subsequent particle rearrangement can be influenced by the density of the compact. If the density of the compact is low, capillary spreading and particle rearrangement are localized to where the liquid phase exists [13]. In contrast, if the density of the compact is high, capillary spreading and particle rearrangement are confined to close by among the particles. Therefore, an optimum compact density exists that allows the maximum extent of the capillary spreading and particle rearrangement to be achieved. Under such circumstances, the maximum interfacial area between the aluminum melt and the graphite particles is obtained, and, consequently, the ignition temperature is at its minimum at 450 °C.

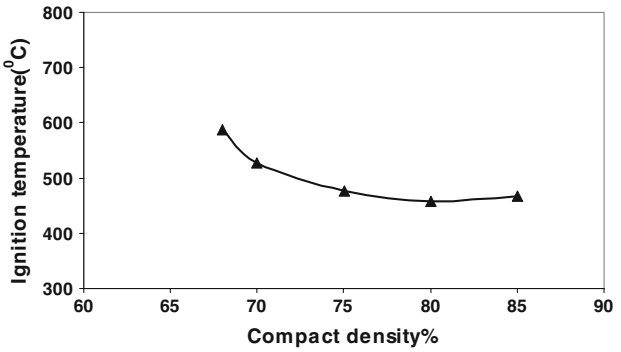

Fig. 1 Effect of compact density on the ignition temperature of SHS reaction

Figure 2 shows the XRD pattern of the Mg–TiC composite fabricated by using preform of different compact densities. From the XRD pattern it can be seen that when the compact density was 68% or below, no TiC peaks were observed. It means that the SHS reaction could not start in the magnesium melt. The reason may be the effect of magnesium as a diluent leading to the compact with 68% density dispersed into the molten magnesium before the initiation of the SHS reaction. As a result, the compact density with 68% failed to lead to SHS reaction in the liquid magnesium. With a compact density of 70%, the formation of TiC in the melt was observed which is supported by the XRD pattern as shown in Fig. 2. When density increased to 75% peaks corresponding to TiC become stronger, indicating more TiC formation in the magnesium matrix.

Effect of preheat temperature

When the preform preheat temperature was 450 °C, an exothermic reaction in the melt were immediately observed after the addition of the preforms to molten magnesium.

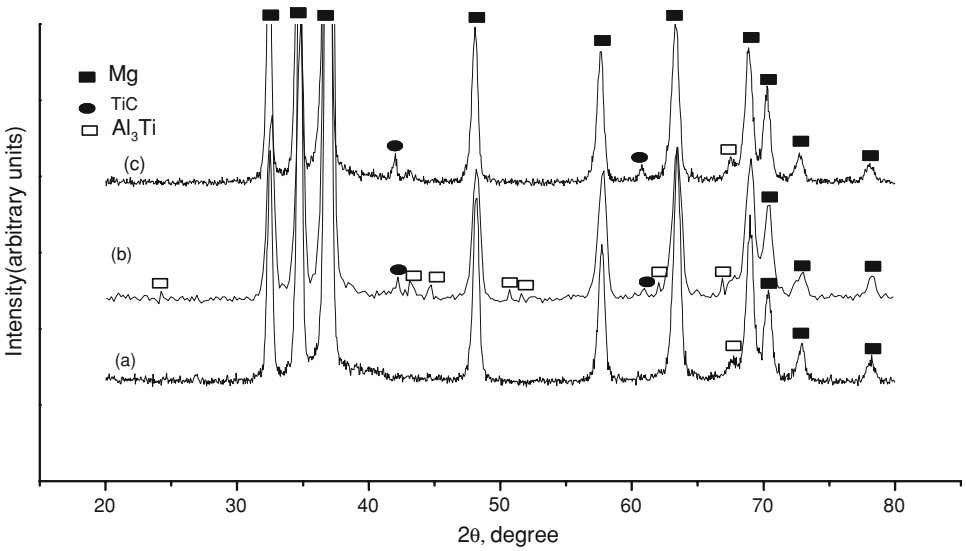

Fig. 2 XRD pattern of the Mg–TiC composite fabricated using preform compact density of (*a*) 68%, (*b*) 70%, and (*c*) 75% of theoretical density (CuKα radiation is used)

However, at temperature of 300 °C, the reaction in the melts could not occur, and there was a substantial amount of untreated graphite that floated on the surface of the melts during stirring. Furthermore, a large amount of residue was found in the bottom of the melts after stirring. XRD analysis (CuKα) showed the residue consisted of Ti and Mg when the preheat temperature was increased to 450, 500, and 550 °C, an exothermic reaction in the melt occurred immediately after the addition of the preform to the molten magnesium. In case of preheat temperature of 600 °C, the SHS reaction started in the preheating furnace and TiC was formed in the preform.

The SHS reaction of the Al–Ti–C system can be ignited by heating the top surface of the preform by passing an electric current through a resistance coil [16, 17]; however, the SHS reaction can also be ignited throughout the preform when it is heated to the ignition temperature by heating the entire preform at a constant rate [18]. In the present study, the exothermic reaction of the preform with a preheat temperature of 450 °C was initiated throughout the entire preform by the heat of molten magnesium, and the heat was liberated. Consequently it can further raise the temperature, facilitating a faster reaction. Thus, it can be considered to be SHS reaction with a simultaneous combustion mode.

Raman spectra analysis

Raman spectra were recorded by using the 514-nm radiation of an Ar laser excitation. The characteristic Raman spectra of the Mg–TiC composites fabricated using preheated preform at 300, 450, and 600 °C are shown in Fig. 3. From Fig. 3a it can be seen that when the preheat temperature was 300 °C only two peaks of carbon at 1,320 and 1,590 cm^{-1} was observed in the spectra. Since

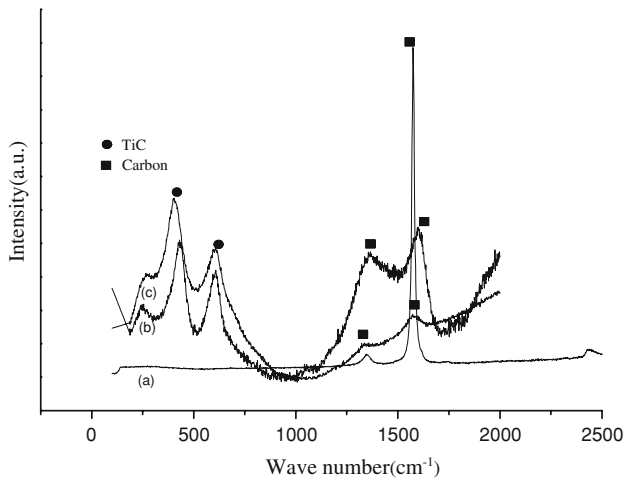

Fig. 3 Micro-Raman pattern of Mg–TiC composite by using preform preheated at (*a*) 300 °C, (*b*) 450 °C, and (*c*) 600 °C

titanium, aluminum, and magnesium do not have Raman active vibrational modes hence they do not produce a Raman spectrum. So it is believed that at 300 °C, the preform gets dissolved before the ignition of the SHS reaction in the Mg melt and as a result no TiC formation takes place. Figure 3b and c shows sharp TiC peaks with board peaks of carbon. The carbon peaks are strong in Fig. 3b as compared to Fig. 3c where it shows that some unreacted carbon is present with TiC. Unreacted carbon is more when the preheat temperature is low and it decreases at higher preheat temperature; this may be due to the incomplete formation of TiC.

X-ray diffraction analysis

Phase formation study in the preform was also studied by heating the preform at different temperature in the tube furnace having argon atmosphere. Three preform was heated at 300, 450, and 600 °C for 30 min, respectively, and cooled in the furnace. Phase identification in the preform was done by taking XRD spectra. From the XRD pattern (Fig. 4) it can be seen that when the preform heated at 300 °C Al_3Ti, Al, and residual C peaks are present and at 450 °C (Fig. 4b) Al_3Ti and TiC are only found. This shows that TiC formation reaction start at 450 °C. But the pellet preheated at 600 °C shows only TiC peaks, this indicate that Al_3Ti and residual carbon further reacted to form TiC and Al goes to the matrix. After 600 °C single phase indicate completion of the SHS reaction in the preform. The above results also support the mechanism of thermal explosion synthesis in Al–Ti–C system reported by Guan et al. [2] as below:

$$3Al + Ti \rightarrow TiAl_3 \quad (1)$$

$$TiAl_3 + C \rightarrow TiC + 3Al \quad (2)$$

$$Ti + C \rightarrow TiC. \quad (3)$$

Optical and scanning electron microscopy

Figure 5 shows optical micrographs of the in situ processed composites fabricated using preform of different preheat temperature. The microstructure shows agglomerates of residual carbon and titanium in the magnesium matrix (Fig. 5a) which was confirmed by XRD spectra, this indicates that preform does not take part in the reaction. Figure 5b shows blocky agglomerates of fine (5–6 μm) white particles imbedded in the matrix. Figure 5c and d reveals a relatively uniform distribution of TiC particulates of the size 1–2 μm in as cast composite samples. Because the reinforcement phases were in situ formed in the molten magnesium, the interface between TiC particulates was free from oxides.

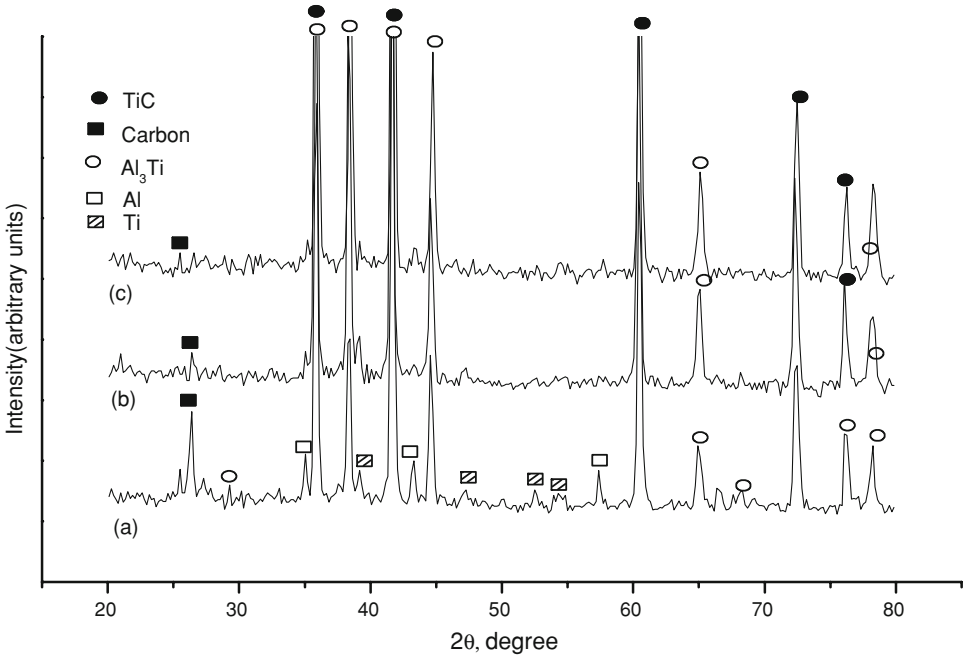

Fig. 4 XRD pattern of compact perform quenched from (*a*) 300 °C, (*b*) 450 °C, and (*c*) 600 °C

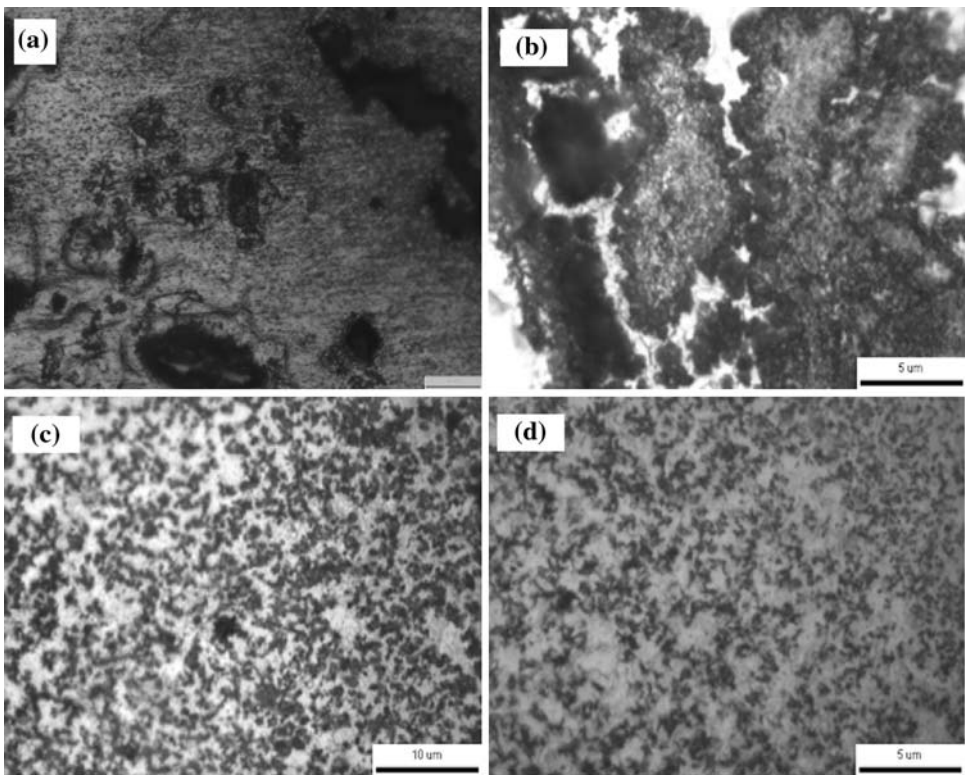

Fig. 5 Optical micrograph of Mg–TiC composite prepared by heating preform at **a** 300 °C, **b** 450 °C, **c** 550 °C, and **d** 600 °C

Figure 6a shows the SEM micrograph and EDX of the fabricated Mg–TiC composite using preform at 450 °C in which blocky Al_3Ti particles (3–4 μm) at some places and fine gray TiC particle (1–2 μm) are distributed in the magnesium matrix. Figure 6b SEM micrograph shows uniform distribution of fine gray particle of size (1–2 μm) in the matrix and the EDX of the particle confirms that gray particles are TiC particles. The EPMA result in Fig. 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. Figure 6b also shows that no other phases except TiC in the

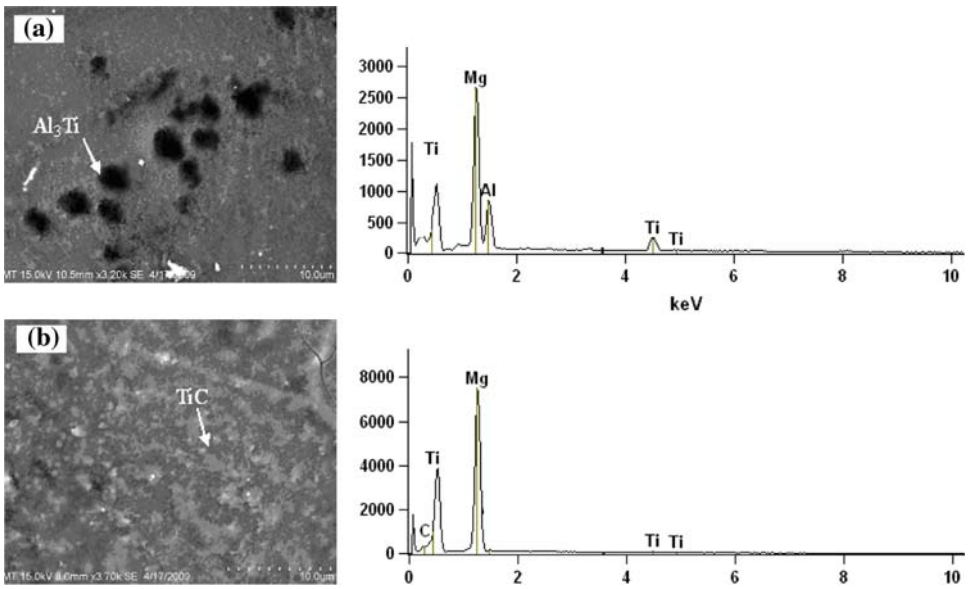

Fig. 6 SEM micrograph and EDX of Mg–TiC composites at different preheat temperature **a** 450 °C and **b** 550 °C

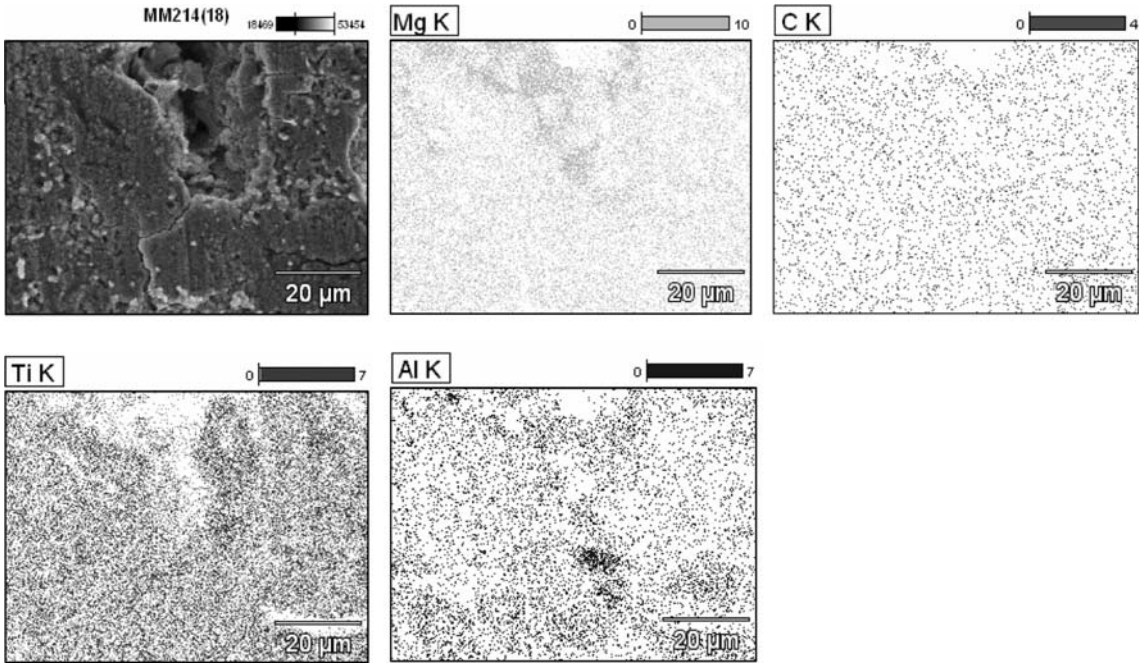

Fig. 7 EPMA map of the Mg–TiC composite showing distribution of the elements

matrix indicates the completion of the SHS reaction in the composite and also proves clean interface between the particulate and the matrix. The EDX of the particle confirms TiC.

Conclusions

The following conclusions can be drawn from the present study.

1. An in situ TiC particulate reinforced magnesium matrix composite has been successfully synthesized utilizing the exothermic reaction of the preform consisting of Al, Ti, and C powders.
2. SHS reaction does not take place in the magnesium melt when the preform temperature is below 450 °C.
3. Compact density below 68% of theoretical density fails to give rise to SHS reaction. Nearly 75% compact density is found to be optimum for SHS reaction and TiC particle distribution.

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