Fabrication and Reaction Mechanism of *In-situ* TiC and TiB$_2$ Reinforced Mg Matrix Composites

Mohammed Shamekh[1, a], and Martin Pugh[1, b] and Mamoun Medraj[1, c]

[1]Concordia University, Department of Mechanical and Industrial Engineering, 1455 de Maisonneuve Blvd West, EV004.411, Montreal, Quebec, H3G 1M8, Canada

[a] shamekh_73@yahoo.com, [b] pugh@encs.concordia.ca and [c] mmedraj@encs.concordia.ca

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Abstract TiC and TiB$_2$ compounds in the form of interpenetrating network reinforced AZ91D magnesium matrix composites have been successfully synthesized by an *in-situ* reactive infiltration technique. In this process, the ceramic reinforcement phases, TiC and TiB$_2$, were synthesized *in-situ* from elemental powders of Ti and B$_4$C without any addition of a third metal powder such as Al. The molten Mg alloy infiltrates the preform of Ti$_p$ and B$_4$C$_p$ by capillary forces. The microstructure and reaction mechanism are investigated using SEM/EDS and XRD analysis. The results show that the processing parameters such as temperature, holding time and the green compact relative density have a significant influence on the reaction mechanism and the fabrication of the composite. In addition, the infiltrated Mg acts as an intermediary that makes the reaction possible at a lower temperature than that required for solid-state reaction between Ti and B$_4$C. Microstructural characterization reveals a relatively uniform distribution of the reinforcing phases, TiC and TiB$_2$ in the Mg matrix.

1. Introduction

The demand for Mg and Mg alloys is increasing due to their light weight especially for automotive applications. However, their application has been limited due to their rapid loss of strength with increasing temperature, low elastic modulus, low wear resistance and poor creep and corrosion resistance [1,2]. Mg matrix composites reinforced with suitable ceramic particles such as TiC and TiB$_2$ can compensate for some of these limitations and improve the properties of the Mg alloys.

There are several methods to fabricate the particulate reinforced Mg MMCs by ex-situ routes including powder metallurgy, preform infiltration, spray deposition, mechanical alloying and different casting technologies such as squeeze casting, rheocasting and compocasting [3].
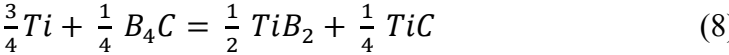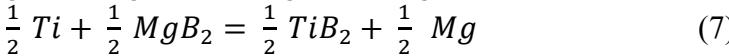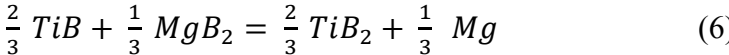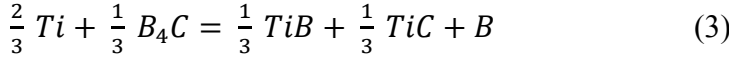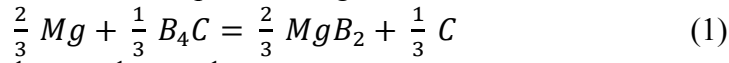
Compared to the conventional MMCs produced by *ex-situ* methods, the *in-situ* MMCs exhibit finer, homogeneously dispersed and thermodynamically stable reinforcements with stronger interfacial bonding due to clean reinforcement-matrix interface. Also, near-net-shape composites can be easily fabricated with a high volume percentage of the reinforcing ceramic phase and effective cost [1,4].

Mg matrix composites reinforced with *in-situ* TiC and TiB$_2$ particles have been fabricated using different techniques such as self-propagating high temperature synthesis (SHS) and remelting and dilution (RD). For example, Ma *et al.* [5] fabricated (TiB$_2$-TiC)/Mg matrix composites using the SHS technique via a master alloy route using a low cost Al-Ti-B$_4$C system. They are the first to use B$_4$C instead of B and/or C in the starting materials. On the other hand, Wang *et al.* [6] successfully fabricated (TiB$_2$-TiC)/Mg matrix composites using the RD technique and a preform of a sintered block of a mixture of Al-Ti-B$_4$C.

The main objective of this work is to fabricate Mg matrix composites reinforced with TiC and TiB$_2$ phases and to understand the *in-situ* reaction mechanism responsible for the formation of these phases in the Mg matrix. Although *in-situ* reactive infiltration technique has been used before to fabricate Mg matrix composites reinforced with TiC particles starting from Ti and C powders [7], this is the first time such Mg matrix composites are fabricated starting from Ti and B$_4$C materials without adding Al using a simple and cost effective technique.

2. Thermodynamic Analysis

For understanding the *in-situ* reaction mechanism, reaction thermodynamics is used to obtain the reaction direction and the expected stable phases and their compositions at elevated temperatures. The potential reactions that can take place in the (Mg-Ti–B_4C) system and between the reactants and some intermediate phases are given as follows:

$$\frac{2}{3} Mg + \frac{1}{3} B_4C = \frac{2}{3} MgB_2 + \frac{1}{3} C \tag{1}$$

$$\frac{1}{2} Ti + \frac{1}{2} C = \frac{1}{2} TiC \tag{2}$$

$$\frac{2}{3} Ti + \frac{1}{3} B_4C = \frac{1}{3} TiB + \frac{1}{3} TiC + B \tag{3}$$

$$\frac{1}{2} TiB + \frac{1}{2} B = \frac{1}{2} TiB_2 \tag{4}$$

$$\frac{1}{3} Mg + \frac{2}{3} B = \frac{1}{3} MgB_2 \tag{5}$$

$$\frac{2}{3} TiB + \frac{1}{3} MgB_2 = \frac{2}{3} TiB_2 + \frac{1}{3} Mg \tag{6}$$

$$\frac{1}{2} Ti + \frac{1}{2} MgB_2 = \frac{1}{2} TiB_2 + \frac{1}{2} Mg \tag{7}$$

$$\frac{3}{4} Ti + \frac{1}{4} B_4C = \frac{1}{2} TiB_2 + \frac{1}{4} TiC \tag{8}$$

To compare the feasibility and favorability of these reactions, the changes in the Gibbs free energy, *ΔG*, and the reaction enthalpy, *ΔH,* for one mole of the reactants were calculated as shown in Fig. 1. It can be observed from Fig. 1(b) that all reactions are exothermic reactions (-ve Δ*H*) and have negative standard Gibbs free energy that means all reactions are thermodynamically favorable as shown in   Fig. 1(a). It is worth noting that *ΔG₈* is more negative for the formation of TiB_2+TiC in the temperature range of interest and thus reaction (8) has a higher tendency for the formation of TiB_2 and TiC than the other reactions. Therefore, from the thermodynamic point of view, it can be deduced that the final equilibrium phases in the composite should be TiB_2, TiC and Mg.
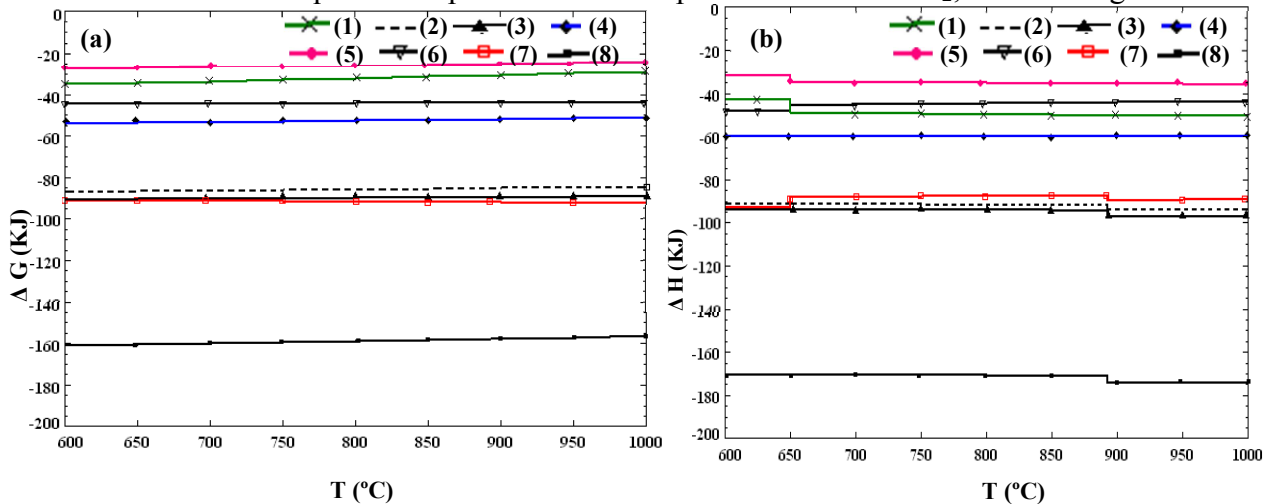

Fig. 1 Changes in (a) Gibbs free energy, ΔG, and (b) reaction enthalpy, ΔH, for reactions (1)-(8).

3. Experimental work

In this research, the starting powders for synthesizing the ceramic reinforcing phases were Ti (-325 mesh, 99.61% purity, Alfa Aesar Co.) and B_4C (99% purity, particle size <10 μm, Alfa Aesar Co.) powders at a molar ratio (3:1) corresponding to that of stoichiometric TiC and TiB_2. The starting powders were mixed under Ar in a stainless steel jar with stainless steel balls inside a planetary ball mill. After full mechanical blending, the resulting mixture of Ti and B_4C powders was compacted at pressures from 80 to 120 MPa into green compacts of cylindrical shape of 25 mm in diameter and variable heights with various relative densities of 55, 60, 65, and 70% ± 2% using a hardened steel die with two plungers. The *in-situ* reactive infiltration experiments were finally carried out in an electric furnace under the presence of flowing argon gas (purity ≥ 99.999%) as shown in Fig 2 (a). The heating cycle is shown in Fig. 2 (b). The temperature was set in the range from 700ºC to 950ºC at 50ºC intervals and the holding time ranged from 15 min to 6 h and the heating rate was 10ºC/min. The samples were naturally cooled down to room temperature.
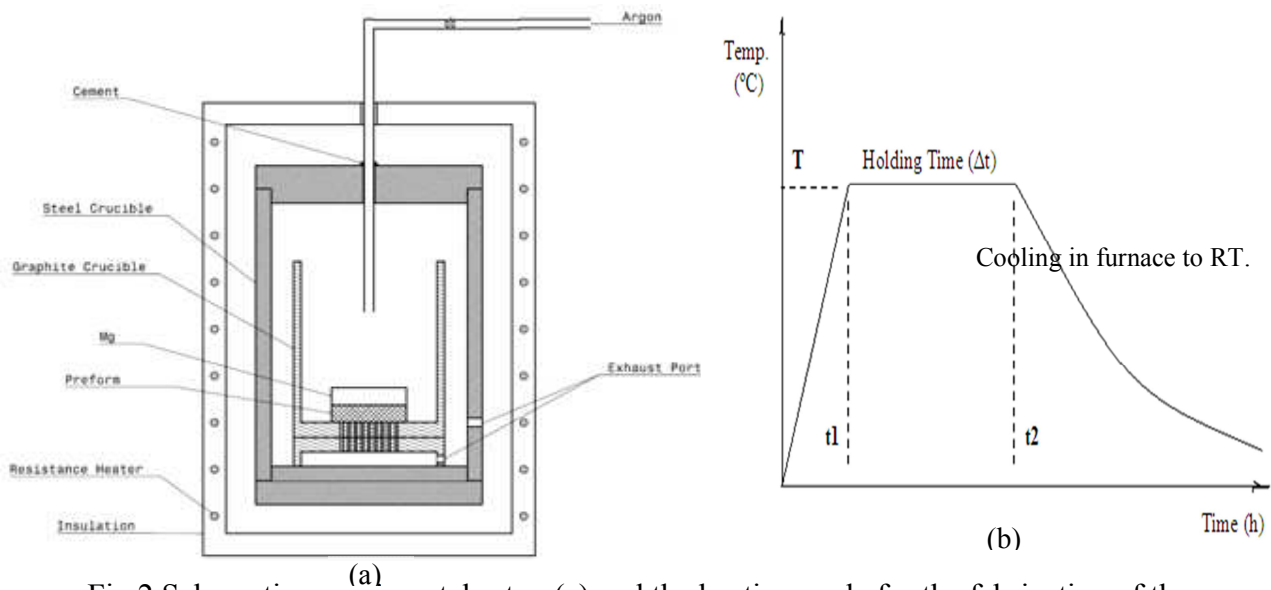
Fig.2 Schematic experimental setup (a) and the heating cycle for the fabricating of the composite samples (b).

To study the *in-situ* reaction mechanism for synthesizing $(TiC-TiB_2)$/AZ91D composites, the reaction mechanisms of the $Ti-B_4C$ and $Mg-B_4C$ systems have been investigated separately. For the $Ti-B_4C$ system, green compacts with 70% relative density were heated to 900ºC and kept in the furnace for different holding times from 1 to 10 h according to the heating cycle shown in Fig. 2(b). Also, thin $(Ti+B_4C)$ green compacts were prepared with 70% relative density and placed in a quartz tube under Ar, heat-treated at different temperatures from 600ºC to 900ºC for 1 h and then quenched in water. On the other hand, to investigate the effect of Mg melt during and after the spontaneous infiltration, the reaction mechanism of $Mg-B_4C$ system was investigated. For this purpose, two pure B_4C preforms were compacted at 70% relative density. One of them was heated to 900ºC for 1 h and then naturally cooled down to room temperature and for the other, molten Mg was infiltrated through at 900ºC for 1 h. The microstructure and phase analysis of the heat-treated preforms and fabricated composites are investigated using scanning electron microscope SEM/EDS and XRD.

4. Results and Discussions

4.1 Fabrication of $(TiC-TiB_2)$/AZ91D matrix composites

In this work, the influence of the processing temperature, holding time and the green compact relative density on the fabrication of $(TiC-TiB_2)$/AZ91D composites was studied. The small particle size of B_4C relative to that of Ti has been chosen to enhance the contact and the solid state reaction between them. Finding the optimal processing parameters for producing sound Mg matrix composites reinforced with interpenetrating networks of *in-situ* formed TiC and TiB_2 is one of the main objectives of this work. Results revealed that the composites can be fabricated at 900ºC for 1 h using a $Ti-B_4C$ preform of 70% relative density. A relatively uniform distribution of reinforcing phases as interpenetrating networks with very small retained titanium, boron carbide and intermediate phases was obtained as shown in the microstructure and elemental mapping in Fig. 3 and XRD pattern in Fig. 7(c).

According to the elemental mapping, the observed overlap of the titanium, carbon and boron images proves the existence of the interpenetrating network of TiC and TiB_2 in the Mg matrix. It is worth noting that it is difficult to distinguish between the TiB, TiC, and TiB_2 phases because the difference in their mean atomic numbers is insignificant making the discernment very difficult by SEM. On the other hand, Mg, $B_{13}C_2$ and MgB_2 phases can be detected easier due to the significant difference in their effective atomic numbers.
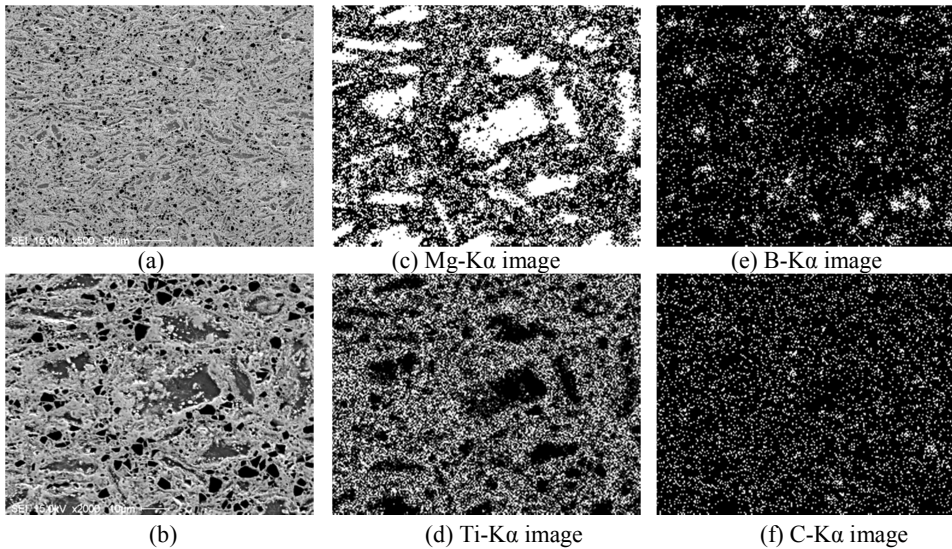
Fig. 3 Microstructure at (a) low magnification, (b) high magnification and elemental mapping micrographs for composites synthesized at 900ºC and 1h (c) to (f) at high magnification (b).

4.2 Reaction Mechanism of the Mg-Ti-B$_4$C System

The (Ti-B$_4$C) system:

The XRD patterns of the two preforms heat-treated at 900ºC for 1 h and 10 h and then naturally cooled down to room temperature are shown in Fig. 4. The results reveal the formation of substoichiometric TiC$_x$ prior to titanium borides with retained titanium and boron carbide in both cases. Also, it can be observed that TiB formed before TiB$_2$ in both cases. At 1 h, the peak area of TiB$_2$ phase is very small and increases with increasing the holding time to 10 h.

Fig. 5 shows the XRD patterns of the quenched preforms. The results reveal that no reaction took place at 600ºC where only Ti and B$_4$C peaks are observed, whereas, at 700ºC, Ti, B$_{13}$C$_2$ and TiC peaks are the only peaks in the XRD pattern. This shows that at 700ºC, incomplete reaction occurred by the formation of substoichiometric TiC$_x$. At 800ºC and 900ºC, only TiC$_x$ and TiB$_2$ peaks are observed. This indicates that the reaction was complete resulting in the formation of TiC$_x$ and TiB$_2$. This also supports the idea that the substoichiometric TiC$_x$ forms prior to titanium borides with the conversion of B$_4$C to B$_{13}$C$_2$ which is consistent with Emin's suggestion [8].
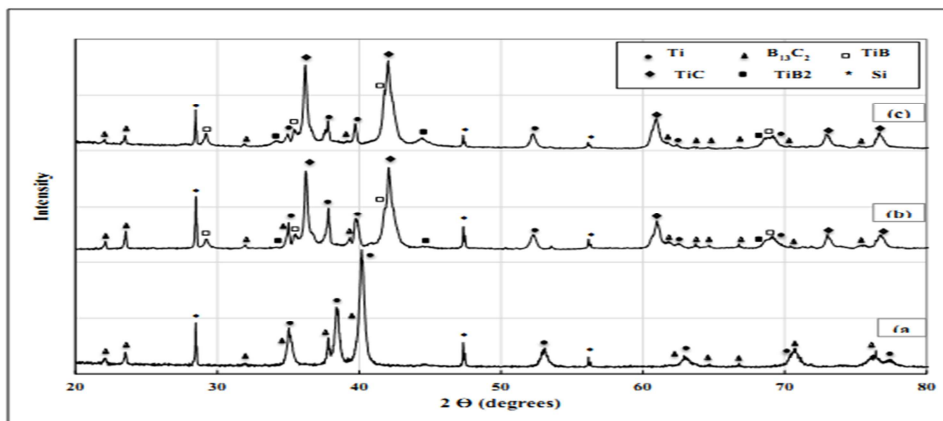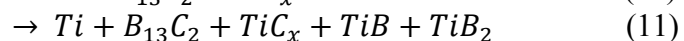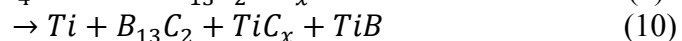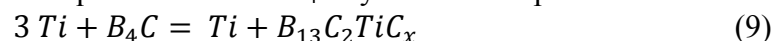

Fig. 4 XRD pattern of (a) as received Ti+B$_4$C mixture, (b) Ti+B$_4$C perform after heat-treating at 900ºC for 1 h and (c) Mg composite fabricated at 900ºC for 1 h

Based on these results, the reaction sequence in the Ti-B$_4$C system can be presented as follows:

$$3\,Ti + B_4C = \; Ti + B_{13}C_2 TiC_x \tag{9}$$
$$\rightarrow Ti + B_{13}C_2 + TiC_x + TiB \tag{10}$$
$$\rightarrow Ti + B_{13}C_2 + TiC_x + TiB + TiB_2 \tag{11}$$
$$\rightarrow TiC_x + TiB_2 \tag{12}$$

However, the complete formation of TiC$_x$ and TiB$_2$ will require very long time if the Ti-B$_4$C preform is heat-treated according to the heating cycle used for the fabrication of the composite.
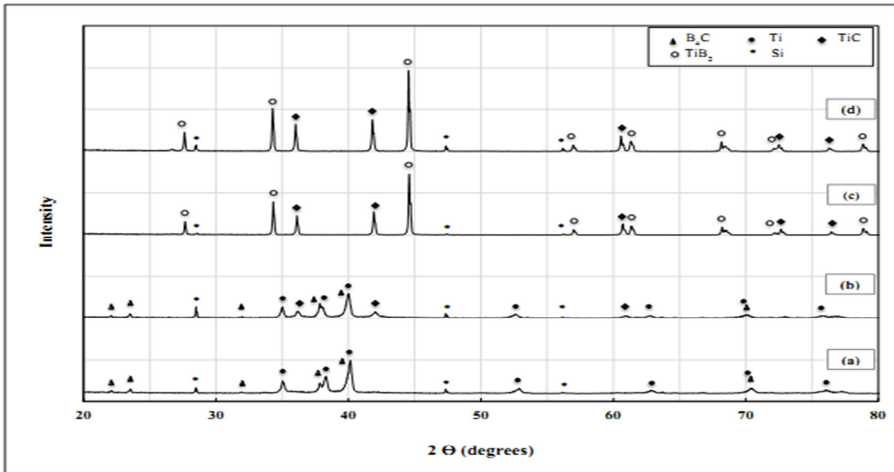
Fig. 5 XRD patterns of (Ti-B₄C) samples quenched from different temperatures after 1 h holding time (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C.

The (Mg-B₄C) system:

Based on the XRD results of the pure B₄C preform and those after the infiltration of molten Mg at 900ºC for 1 h, shown in Fig. 6, it can be suggested that molten Mg reacts with boron carbide to form mainly MgB_2 liberating atomic C. Hence, the reaction mechanism is as follows:

$$2Mg + B_4C = 2\,MgB_2\,C \tag{13}$$
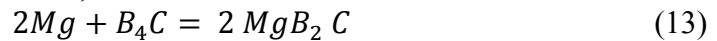
This result agrees with what is suggested by Kevorkijan and Skapin [9]. Also, the presence of MgB₄ peaks on the the XRD pattern proves that MgB₂ partially decomposes forming MgB₄ and Mg gas diffuses through the thin film of MgB₄ as follows: $MgB_2 = \frac{1}{2}MgB_4 + \frac{1}{2}Mg\,(g)$ (14)
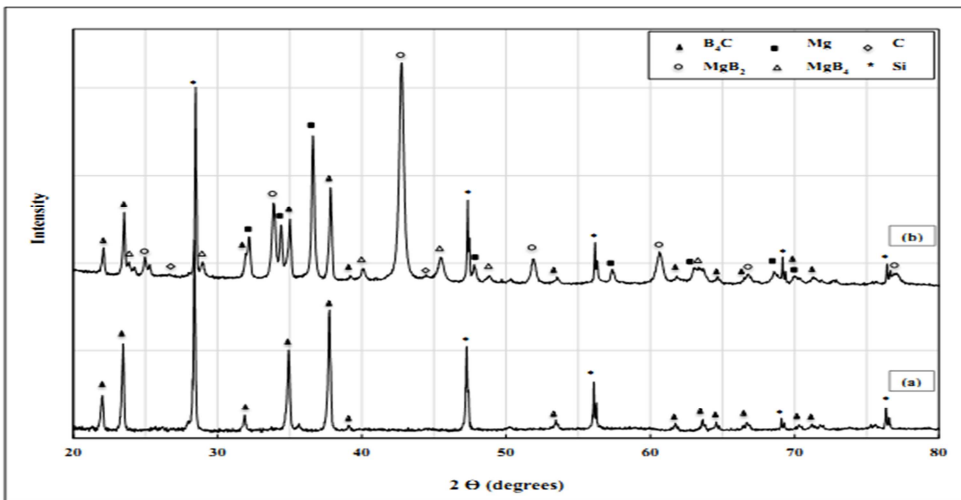This agrees with the results obtained by Brutti *et al.* [10].

Fig. 6 XRD pattern of (a) B₄C powder, (b) After infiltration of Mg into B₄C preform at 900ºC for 1 h.

The whole Mg-Ti-B₄C system:

Fig. 7 shows the XRD spectra of the Ti-B₄C preform (no Mg) compacted at 70% relative density after heat-treatment at 900ºC for 1 h and Mg matrix composite sample fabricated at the same temperature and holding time using a Ti-B₄C preform of the same relative density. It can be observed that substoichiometric TiC$_x$ formed in both of them while TiB₂ significantly formed only after infiltration of Mg even at this short time. The formed TiB₂ without Mg is very small and can be neglected. Based on these observations, it can be concluded that Mg does not only infiltrate through the Ti-B₄C preform and thus densify the fabricated composite as a matrix metal but also acts as an intermediary that makes the reaction possible at a lower temperature than that required for solid-state reaction between Ti and B₄C.

Based on the reaction sequences of the individual systems, Ti-B₄C and Mg-B₄C, the reaction mechanism of the whole Mg-Ti-B₄C system after the infiltration of molten Mg through the Ti+B₄C preform can be presented as follows:

$$3\,Ti + B_4C + Mg = Ti + B_{13}C_2 + TiC_x + TiB + MgB_2 \tag{15}$$
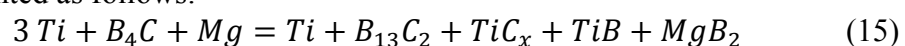
TiC_x formed due to the reaction between Ti and B_4C (Eq. 9) and also the diffusion of atomic C liberated by the reaction between Mg and B_4C (Eq. 13) into Ti according to the following equation:

$$Ti + C = TiC_x \qquad\qquad (16)$$

MgB_2 partially decomposes to form MgB_4 (Eq. 14) and B from $B_{13}C_2$ diffuses into TiB as follows:

$$TiB + B = TiB_2 \qquad\qquad (17)$$

Hence,
$$3Ti + B_4C + Mg = Ti + B_{13}C_2 + TiC_x + TiB + TiB_2 + MgB_2 + MgB_4 \quad (18)$$

$$2Ti + MgB_2 + \frac{1}{2}MgB_4 = 2TiB_2 + \frac{3}{2}Mg \qquad\qquad (19)$$
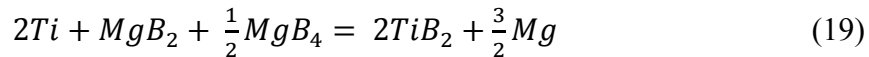
Finally the reaction between Ti, B_4C and infiltrated molten Mg alloy is obtained as follows:

$$\boldsymbol{Ti + B_4C + Mg \rightarrow TiC_x + 2TiB_2 + Mg} \qquad\qquad (20)$$
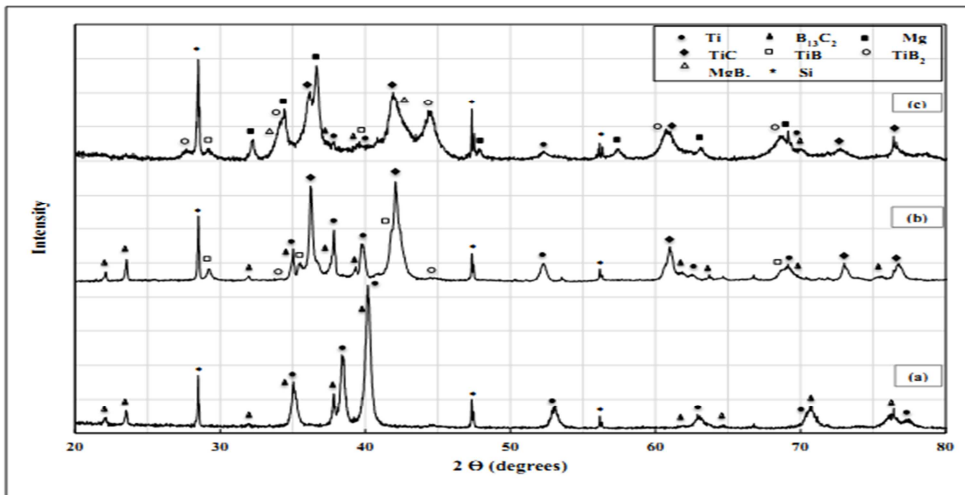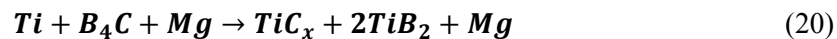
Fig. 7 XRD pattern of (a) as received Ti+B_4C mixture, (b) Ti+B_4C perform after heating at 900ºC for 1 h and (c) Mg composite fabricated at 900ºC for 1 h.

5. Conclusions

(1) AZ91 magnesium matrix composites reinforced with TiC and TiB_2 phases have been successfully synthesized by an *in-situ* reactive infiltration technique.

(2) The microstructure of (TiC_x-TiB_2)/AZ91D composites is essentially evolved from the reaction between Ti, B_4C and Mg melt. The substoichiometric TiC_x forms prior to TiB_2 because the diffusion of carbon in Ti is much faster than that of boron.

(3) Studying the reaction mechanism revealed the role of Mg melt in the system where it not only infiltrates through the Ti-B_4C preform and thus densifies the fabricated composite as a matrix metal but also acts as an intermediary that makes the reaction possible at a lower temperature than what is required in the case of the solid-state reaction between Ti and B_4C.

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