Understanding the reaction mechanism of in-situ synthesized (TiC–TiB$_2$)/AZ91 magnesium matrix composites

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HIGHLIGHTS

- For the first time, MMC of Mg/(TiC–TiB$_2$ network) is fabricated without using Al.
- A practical and cost-effective in-situ reactive infiltration technique is developed.
- The effect of the infiltrated Mg on the reaction between Ti and B$_4$C is uncovered.
- The first attempt to study the effect of MgH$_2$ on the reaction mechanism.
- The formation of the Ti$_2$AlC ternary compound and its consequences are discussed.

ABSTRACT

Magnesium matrix composites reinforced with a network of TiC and TiB$_2$ compounds have been successfully synthesized via an in-situ reactive infiltration technique. In this process, the ceramic reinforcing phases, TiC and TiB$_2$, were synthesized in-situ from the starting powders of Ti and B$_4$C without any addition of a third metal powder such as Al. The molten AZ91 magnesium alloy infiltrates the preform of 3Ti–B$_4$C by capillary forces. Furthermore, adding different weight percentages of MgH$_2$ powder to the 3Ti–B$_4$C preforms was used in an attempt to increase the Mg content in the fabricated composites. The results reveal a relatively uniform distribution of the reinforcing phases in the magnesium matrix with very small amounts of residual Ti, boron carbide and intermediate phases when they are fabricated at 900 °C for 1.5 h using a 3Ti–B$_4$C preform with 70% relative density. On the other hand, after adding MgH$_2$ to the 3Ti–B$_4$C preform, TiC and TiB$_2$ formed completely without any residual intermediate phases with the formation of the ternary compound (Ti$_2$AlC) at the expense of TiC. The percentage of reinforcing phases can be tailored by controlling the weight percentages of MgH$_2$ powder added to the 3Ti–B$_4$C preform. The results of the in-situ reaction mechanism investigation of the Ti–B$_4$C and Mg–B$_4$C systems show that the molten magnesium not only infiltrates through the 3Ti–B$_4$C preform and thus densifies the fabricated composite as a matrix metal, but also acts as an intermediary making the reaction possible at a lower temperature than that required for solid-state reaction between Ti and B$_4$C and accelerates the reaction rate. The investigation of the in-situ reaction mechanism with or without the addition of MgH$_2$ powder to the 3Ti–B$_4$C preforms reveals similar mechanisms. However, the presence of the MgH$_2$ in the preform accelerates the reaction resulting in a shorter processing time for the same temperatures.

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1. Introduction

Magnesium matrix composites reinforced with suitable ceramic particles are attractive for different applications especially in automotive and aerospace industries due to their superior specific properties such as elastic modulus and strength, high wear resistance, and excellent thermal and electrical conductivities [1–3].

There are several methods to fabricate particulate reinforced Mg metal matrix composites (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 [4]. However, in-situ MMCs can exhibit excellent mechanical properties due to the formation of ultra-fine, homogeneously dispersed and thermodynamically stable ceramic reinforcements with clean reinforcement-
matrix interfaces. Also, near-net-shape composites can be fabricated with a high volume percentage of the reinforcing ceramic phase at an effective cost [5, 6].

Different techniques such as self-propagating high temperature synthesis (SHS) and remelting and dilution have been used to fabricate Mg matrix composites reinforced with in-situ TiC and TiB₂ particles. For example, Ma et al. [7] using the SHS technique via a master alloy route starting with a low cost Al–Ti–B₄C system succeeded in fabricating TiB₂–TiC/Mg matrix composites. They are considered the first to use B₄C instead of B and/or C in the starting materials. On the other hand, Zhang et al. [8] successfully fabricated TiB₂–TiC/Mg matrix composites via the remelting and dilution technique using a preform of a sintered block of a mixture of Al–Ti–B₄C.

The main objective of this work is to synthesize Mg matrix composites reinforced with TiC and TiB₂ and to understand the in-situ reaction mechanism responsible for the formation of these compounds in the Mg matrix. Although in-situ reactive infiltration has been used before to fabricate Mg matrix composites reinforced with TiC particles starting from Ti and C powders [9], this is the first time such Mg matrix composites are synthesized starting from Ti and B₄C materials without adding Al using a practical and low cost technique.

2. Thermodynamic analysis

For understanding the in-situ reaction mechanism, reaction thermodynamics are used to calculate the reaction direction and the expected stable phases and their compositions at elevated temperatures. The potential reactions that can occur in the Mg–Ti–B₄C system and between the reactants and some intermediate phases are as follows:

\[
\begin{align*}
\frac{2}{3}Mg + \frac{1}{3}B₄C &= \frac{2}{3}MgB₂ + \frac{1}{3}C \\
\frac{1}{2}Ti + \frac{1}{2}C &= \frac{1}{2}TiC \\
\frac{5}{6}Ti + \frac{1}{6}B₄C &= \frac{2}{3}TiB₂ + \frac{1}{6}TiC \\
\frac{16}{17}TiB₂ + \frac{1}{17}B₄C &= \frac{5}{17}Ti₃B₄ + \frac{1}{17}TiC \\
\frac{3}{4}Ti₃B₄ + \frac{1}{4}B₄C &= 2TiB₂ + \frac{1}{4}TiC \\
\frac{2}{3}TiB₂ + \frac{1}{3}MgB₂ &= \frac{2}{3}TiB₂ + \frac{1}{3}Mg \\
\frac{1}{2}Ti + \frac{1}{2}MgB₂ &= \frac{1}{2}TiB₂ + \frac{1}{2}Mg \\
\frac{2}{3}Ti + \frac{1}{3}MgB₂ &= \frac{2}{3}TiB₂ + \frac{1}{3}Mg \\
\frac{3}{4}Ti + \frac{1}{4}B₄C &= \frac{1}{2}TiB₂ + \frac{1}{4}TiC
\end{align*}
\]

(1)\( \cdots \) (9)

where \(\Delta H\) and \(\Delta G\) are the enthalpy and Gibbs free energy, respectively. All reactions are thermodynamically feasible as shown in Fig. 1(b).

It is worth noting that \(\Delta G_S\) and \(\Delta G_R\) are more negative for the formation of TiC–TiB₂ in the temperature range of interest and thus reactions (5) and (9) have a higher tendency for the formation of TiC–TiB₂ than the other reactions. However, reaction (5) is considered as an intermediate reaction to form TiC–TiB₂. Therefore, from the thermodynamics point of view, it can be deduced that the final equilibrium phases should be TiB₂, TiC and Mg in the composite.

3. Experimental work

3.1. Fabrication of the composites

In this work, two systems of starting powders were used for synthesizing the TiC–TiB₂/Mg composites: System I, Ti–B₄C, consists of 72.2 wt.% Ti (325 mesh, 99.61% purity, Alfa Aesar Co.) and 27.8 wt.% B₄C (99% purity, <10 μm particle size, Alfa Aesar Co.) powders. Titanium and boron carbide powders are at a molar ratio of 3:1 corresponding to that of stoichiometric TiC and TiB₂. System II, Ti–B₄C with MgH₂ powder, MgH₂ powder (98% purity, Alfa Aesar Co.) was added to the Ti–B₄C mixture at different weight percentages. The starting powders were mixed under Ar in a stainless steel jar with stainless steel balls inside a planetary ball mill, in which the ratio of the balls to the powder was 7:1 and the milling speed and time were 400 rpm and 5 h, respectively. In order to prevent oxidation, the mixtures were prepared in a glove box filled with Ar.

After full mechanical blending, the resulting mixture of Ti and B₄C powders was compacted at pressures ranging from 80 to 120 MPa into green compacts of cylindrical shape of 15 mm in diameter and variable heights with various relative densities of approximately 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 ≥ 99.9999%) as shown in Fig. 2(a). The heating cycle is shown in Fig. 2(b). The temperature was set in the range from 700 °C to 950 °C at 50 °C intervals, the holding time ranged from 1 to 6 h and the heating rate was 10 °C min⁻¹. The samples were naturally cooled down to room temperature.

3.2. Investigation of the reaction mechanism

3.2.1. Reaction mechanisms in the Mg–Ti–B₄C system

To understand the in-situ reaction mechanism for synthesizing TiC–TiB₂/AZ91D composites, the reaction mechanisms in the Ti–B₄C and Mg–B₄C systems have been investigated separately. For the Ti–B₄C system, 3Ti–B₄C green compacts with 70% relative density (RD) were heated to 900 °C and kept in the furnace at this temperature for different holding times (Δt) ranging from 1 to 10 h according to the heating cycle shown in Fig. 2(b). Also, to investigate the reaction sequence in the Ti–B₄C system experimentally, thin 3Ti–B₄C green compacts were prepared with 70% RD and placed in a quartz tube under Ar. The encapsulated samples were heat-treated at different temperatures from 600 to 900 °C for 1 h holding time and then quenched in water.

On the other hand, to investigate the effect of Mg melt during and after the spontaneous infiltration, two pure B₄C preforms were compacted at 70% RD. One of them was heated to 900 °C for 1 h and then naturally cooled down to room temperature while the other one was infiltrated by molten Mg at 900 °C for 1 h using the setup presented in Fig. 2(a). Also, the reaction sequence in the Mg–B₄C system was investigated in similar fashion to that of the Ti–B₄C
The molar ratio of Mg to B₄C in these preforms is (2.7:1) which matches with 25 wt.% Mg powder in the preform and higher than that required to complete the reaction between Mg and B₄C to form MgB₂.

3.2.2. Reaction mechanism of the infiltrated Mg in the (MgH₂–Ti–B₄C) preform

To understand the in-situ reaction mechanism of the infiltrated Mg in the MgH₂–Ti–B₄C preform, the reaction mechanism was divided into four subsystems; MgH₂–Ti, MgH₂–B₄C, MgH₂–Ti–B₄C and Mg–Ti–B₄C. The latter was discussed in section 3.2.1. It is very important to note that the molar ratio of these individual system matches with 25 wt.% MgH₂ powder added to Ti and B₄C powders with 3:1 molar ratio.

The reaction sequence in the MgH₂–Ti system was investigated as that of Ti–B₄C system but the temperatures in this case were from 400 to 800 °C. Also, a (MgH₂–Ti) compact heat-treated at 900 °C for 1.5 h according to the heating cycle shown in Fig. 2(b) was compared with the composite sample fabricated using the same green compact after the infiltration of molten AZ91D at the same processing parameters. The same was performed for the MgH₂–B₄C system. The molar ratio of MgH₂ to B₄C in these compacts is (2.52:1) which matches with 25 wt.% MgH₂ powder in the preform.

Finally, 25 wt.% MgH₂–(3Ti–B₄C) compact at 70% RD heat-treated at 900 °C for 1.5 h was compared with an AZ91D matrix composite sample fabricated at the same temperature and holding time using a similar preform.

The microstructure and the phase analysis of the heat-treated preforms and the fabricated composite samples were investigated using scanning electron microscope (SEM) (Model, Philips XL30 FEG) equipped with Energy Dispersive X-ray spectroscopy (EDS) and XRD using an X-ray diffractometer, (X’Pert PRO, manufactured by PANalytical Inc.). It is important to note that Si is added to all
particle size of B4C relative to that of Ti has been chosen to enhance milling of the mixture (time and speed) were kept constant. A small formed TiC and TiB2 particles is one of the main objectives of situ magnesium matrix composites reinforced with a network of the reinforcing phases without intermediate phases. However, the compositional mapping reveals that Al is distributed not only inside the Mg matrix but also in the Mg-free regions indicating that the ternary compound (Ti2AlC) is uniformly distributed in the network of the reinforcing phases making its detection by SEM very difficult. However, the compositional mapping reveals the existence of Al in some concentrated areas.

According to the compositional mapping of the composite sample fabricated at 1.5 h shown in Fig. 5, the observed overlap of the titanium, carbon and boron images indicates the existence of the network of TiC and TiB2 in the Mg matrix. Furthermore, the compositional mapping reveals that Al is distributed not only inside the Mg matrix but also in the Mg-free regions indicating that the ternary compound (Ti2AlC) is uniformly distributed in the network of the reinforcing phases making its detection by SEM very difficult. However, the compositional mapping reveals the existence of Al in some concentrated areas.

To show the influence of adding MgH2 powder to the 3Ti–B4C preform on the volume fractions of Mg and the reinforcing phases, XRD analysis for both scenarios was carried out. The XRD results, summarized in Fig. 6, reveal that the volume percentage of Mg in the fabricated composites increased after adding MgH2 powder to the 3Ti–B4C preform. However, more MgO was detected due to the decomposition of MgH2 at low temperature forming Mg with high affinity to oxygen due, in part, to its high surface area. Also, the presence of Mg with high reactivity in the preform enhanced the reaction between Mg, Ti and B4C and as a result, Mg composites were fabricated without any retained Ti, boron carbide or any intermediate phases such as TiB or MgB2.

As shown in Fig. 7, the XRD spectra of the composite sample fabricated using 10 wt.% MgH2–(3Ti–B4C) preform reveals the formation of the TiC and TiB2 reinforcing phases with very small residual intermediate phases such as TiB and MgB2. On the other hand, the XRD patterns of the composite samples fabricated using 25 or 40 wt.% MgH2 in the preform reveal the complete formation of the reinforcing phases without intermediate phases. However, the percentage of TiC in both cases is lower due to the formation of the ternary compound Ti2AlC at the expense of TiC.

4.2. Reaction mechanism of the infiltrated Mg in the (Ti–B4C) preform

4.2.1. The Ti–B4C system

Based on the thermodynamic considerations discussed earlier, the solid-state reaction between Ti and B4C to form TiC and TiB2 is...
the most favorable reaction but kinetically this reaction is very slow [10]. The XRD patterns of the two preforms heated to 900 °C for 1 h and 10 h compared with the starting powder mixture of 3Ti–B4C are shown in Fig. 8. The results reveal the formation of substoichiometric TiC\(_x\) prior to titanium borides with retained titanium and boron carbide (B13C2) after heat treatment for 1 h and 10 h. Also, it can be observed that TiB and Ti3B4 formed before TiB2. At 1 h, the peaks' area of the TiB2 phase is very small and increases with increasing the holding time to 10 h as shown in Fig. 8. There is still retained titanium and boron carbide indicating that the reaction is still incomplete even after 10 h holding time.

In the XRD analysis, the increase in the area under the peaks provides information about the kinetics of the reaction mechanism, as will be discussed below. It is also observed that the lattice constant of substoichiometric TiC\(_x\) increases with time due to the diffusion of C into TiC\(_x\). As the stoichiometry (x) increases, the lattice parameter of TiC\(_x\) increases. Hence, based on the values of the lattice constant of TiC\(_x\), the stoichiometry (x) in TiC\(_x\) at 10 h is consistent with that of TiC\(_{0.67}\) according to Pearson’s Handbook [11].

The results of the quenched (3Ti–B4C) preform at different temperatures for 1 h holding time are shown in Fig. 9. No reaction took place at 600 °C where only Ti and B4C peaks are observed, whereas, at 700 °C, Ti, boron carbide (B13C2) and TiC\(_x\) peaks are the main peaks in the XRD pattern. However, very low TiB and Ti3B4 peaks’ intensities can also be observed. This shows that the substoichiometric TiC\(_x\) formed prior to titanium borides. At 800 °C, it was found that the area under the peaks of TiB, Ti3B4 and TiC\(_x\) increased while those of Ti and boron carbide decreased with very low TiB2 peaks starting to appear. This shows that TiB and Ti3B4 phases formed prior to the TiB2 phase.

Monitoring the change of area under the peaks of the phases reveals that the amounts of TiC\(_x\) and TiB2 increased with increasing temperature to 900 °C while those of Ti, boron carbide, TiB and Ti3B4 decreased and it can be said that the retained Ti is very small and can be neglected at 900 °C. These results indicate that the reaction is still incomplete even at 900 °C for 1 h.

The variations of the lattice parameters of Ti and B4C formed after heat treatment of 3Ti–B4C samples at different temperatures after 1 h holding time are presented in Table 1. It can be observed that the lattice parameters of Ti increase with increasing temperature till 700 °C. This means that C-saturated Ti, TiC\(_{0.67}\), formed prior to titanium carbide due to the diffusion of C from B4C into Ti. With increasing temperature, the substoichiometric TiC\(_x\) forms while the lattice parameters of the retained Ti decreased again. However, the...
**Fig. 4.** XRD pattern of the AZ91D alloy MMCs fabricated using a 3Ti–B₄C preform with 70% RD at 900 °C for different holding times: (a) 1 h, (b) 1.5 h, (c) 3 h, and (c) 6 h.

**Fig. 5.** SEM microstructure (a) and X-ray compositional mapping of the TiC–TiB₂/AZ91D composites synthesized at 900 °C for 1.5 h using a 25 wt.% MgH₂–(3Ti–B₄C) preform with 70% RD (b) to (f).
amount of the C-saturated Ti is very small and can be neglected after 700 °C. The range of the lattice parameters of the boron carbide is found to be consistent with that of the standard lattice constants of B13C2 reported in Pearson’s Handbook [11].

Thus, based on these results and the crystallographic data of the various phases in the system, the reaction sequence of the Ti–B4C system can be presented as follows:

\[
3\text{Ti} + \text{B}_4\text{C} \rightarrow \text{TiC}_{\text{sat}} + \text{B}_{13}\text{C}_2 + \text{TiC}_x + \text{TiB} \quad (10)
\]

\[
\rightarrow \text{Ti} + \text{B}_{13}\text{C}_2 = \text{TiC}_x + \text{TiB} \quad (11)
\]

\[
\rightarrow \text{Ti} + \text{B}_{13}\text{C}_2 + \text{TiC}_x + \text{TiB} + \text{Ti}_3\text{B}_4 \quad (12)
\]

\[
\rightarrow \text{B}_{13}\text{C}_2 = \text{TiC}_x + \text{TiB} + \text{Ti}_3\text{B}_4 + \text{TiB}_2 \rightarrow \text{TiC}_x + \text{TiB}_2 \quad (13)
\]

However, the complete formation of TiCx and TiB2 requires a very long time if the 3Ti–B4C preform is heat-treated according to the same heating cycle used for the fabrication of the composite (Fig. 2(b)). This reaction sequence is based on different partial reactions that involve Ti and B4C and/or the intermediate phases as follows:

\[
5/6\text{Ti} + 1/6\text{B}_4\text{C} = 2/3\text{TiB} + 1/6\text{TiC} \quad (14)
\]

\[
16/17\text{TiB} + 1/17\text{B}_4\text{C} = 5/17\text{Ti}_3\text{B}_4 + 1/17\text{TiC} \quad (15)
\]

\[
3/4\text{Ti}_3\text{B}_4 + 1/4\text{B}_4\text{C} = 2\text{TiB}_2 + 1/4\text{TiC} \quad (16)
\]

Zhao and Cheng [12] suggested that these reactions take place at relatively low temperatures (T ≤ 1300 °C) when they investigated the formation of TiC–TiB2 composites by reactive sintering of

![Graph](image1.png)

Fig. 6. Phase volume percentage of the AZ91D alloy MMCs fabricated at 900 °C for 1.5 h using different preforms (a) 3Ti–B4C and (b) 25 wt.% MgH2–(3Ti–B4C) preforms with 70 % RD.

![Graph](image2.png)

Fig. 7. XRD pattern of the AZ91D alloy MMCs fabricated at 900 °C for 1.5 h using MgH2–(3Ti–B4C) preforms with different MgH2 weight percentages (a) 10, (b) 25 and (c) 40 wt.%.
3Ti–B₄C compacts at temperatures between 950 and 1650 °C. The formation of substoichiometric TiCₓ prior to the titanium borides was also proposed by Zhao and Cheng [12]. This is attributed to the fact that the diffusivity of carbon in Ti is much greater than that of boron [13]. Despite the strong covalent bonds between the atoms in the boron carbide structure, carbon diffuses away from boron carbide faster than boron. Therefore, due to the reaction of Ti and B₄C, TiCₓ phase forms prior to titanium borides leaving a B-rich boron carbide core in the center of the particles as Shen et al. [13] observed.

The conversion of B₄C to B₁₃C₂ is consistent with Emin’s suggestion [14]. According to this suggestion, with decreasing carbon concentration in B₄C, boron substitutes for carbon in the intericosahedral chains converting the C–B–C chains to C–B–B chains (i.e., B₄C changes to B₁₃C₂). This also agrees with the work of Shen et al. [13].

4.2.2. The Mg–B₄C system

It appears that without magnesium, the solid-state reaction between Ti and B₄C to form TiCₓ and TiB₂ is kinetically very slow during the heating cycle used for the fabrication of the composites especially in the temperature range used here. At 800 °C and below, it was found that no spontaneous infiltration could be attained without adding wetting agent such as Ti to the B₄C powder. Fig. 10 shows the XRD patterns of heat-treated B₄C and after infiltration of molten Mg to B₄C preform at 900 °C for 1 h.

However, the results at 900 °C revealed that magnesium infiltrated the preform and the main diffraction peaks corresponding to
Mg and MgB2 were detected but at the same time, there are MgB4 and retained boron carbide (B4C) phases in the sample as shown in the figure. This means that magnesium wets B4Ca through an interfacial reaction even without adding wetting agent as Ti. This is because the surface tension of liquid decreases with increasing temperature and this agrees with the results of Palmer [15].

Fig. 11 shows the XRD spectra of quenched Mg–B4C samples at different temperatures for 1 h. The results revealed that after heat treatment at 600 °C, the principal peaks are those of Mg and B4C. However, very small MgO particles have formed due to the partial reaction of Mg with oxygen. At 700 °C, the peaks of MgB2, MgB4 and MgC2 appeared beside those of Mg and retained B4C. MgC2 formed due to the reaction of the liberated carbon with Mg in the system but this phase is unstable and rapidly decomposes. With increasing temperature, the area under the peaks of MgB2 increased while those of Mg and retained B4C decreased till those of Mg disappeared at 900 °C.

It is worth noting that despite the fact that the molar ratio of Mg to B4C is higher than that required to complete the reaction between Mg and B4C to form MgB2, it was found that Mg disappeared while there was still retained B4C in the system. The reason is the partial reaction of Mg with oxygen as mentioned earlier.

Based on the XRD results, it can be suggested that molten magnesium reacts with B4C to form magnesium diboride liberating elemental carbon. This reaction is an exothermic reaction providing heat for further reaction to occur in the system. Hence, the reaction mechanism is as follows:

\[
2\text{Mg} + \text{B}_4\text{C} = 2\text{MgB}_2 + \text{C} \tag{17}
\]

This result agrees with what is suggested by Kevorkijan and Skapin [16]. Also, the presence of MgB4 peaks in the XRD pattern proves that MgB2 partially decomposes forming MgB4 and Mg gas that diffuses through the thin film of MgB4 as follows:

\[
\text{MgB}_2 = \frac{1}{2}\text{MgB}_4 + \frac{1}{2}\text{Mg(g)} \tag{18}
\]

This agrees with the results obtained by Brutti et al. [17].

4.2.3. Infiltrating Mg in the (Ti–B4C) preform

Fig. 12 shows the XRD patterns of the 3Ti–B4C preform (no Mg) compacted at 70% RD after heat treatment at 900 °C for 1 h in relation to the Mg matrix composite sample fabricated at the same temperature and holding time using a 3Ti–B4C preform of the same relative density.

It can be observed that substoichiometric TiC, formed in both cases while significant amounts of TiB2 formed after infiltration of Mg even at this short time. This reveals the role of infiltrated molten Mg or Mg alloy in the reaction which was very important especially because no other metal powder, such as Al, was added to the Ti–B4C system.

Based on the reaction sequences of the individual systems, Ti–B4C and Mg–B4C, the reaction mechanism of the complete infiltrated Mg–(Ti–B4C) system after the infiltration of molten Mg alloy through the 3Ti–B4C preform can be presented as follows:

\[
3\text{Ti} + \text{B}_4\text{C} + \text{Mg} = \text{Ti} + \text{B}_{13}\text{C}_2 + \text{TiC}_x + \text{TiB} + \text{MgB}_2 \tag{19}
\]

TiC, formed due to the reaction between Ti and B4C (Eq. 10) and also the diffusion of atomic C liberated by the reaction between Mg and B4C (Eq. 17) into Ti according to the following equation:

\[
\text{Ti} + \text{C} = \text{TiC}_x \tag{20}
\]

MgB2 partially decomposes forming MgB4 and Mg gas that diffuses through the thin film of MgB4 according to Eq. 18. On the

![Fig. 10. XRD pattern of (a) heat-treated B4C preform and (b) after infiltration of molten Mg into B4C preform at 900 °C for 1 h.](image)
other hand, TiB reacts with B₄C forming Ti₃B₄ and TiC according to Eq. 15 then:

$$3\text{Ti} + \text{B}_4\text{C} + \text{Mg} = \text{Ti} + \text{Ti}_3\text{B}_4 + \text{TiC} + \text{MgB}_2 + \text{MgB}_4$$  (21)

Considering that:

$$\text{Ti} + \frac{1}{2}\text{MgB}_4 = 2\text{TiB}_2 + \frac{3}{2}\text{Mg}$$  (22)

Reaction 21 leads to:

$$\text{B}_3\text{C}_2 + \text{TiC} + \text{TiB} + \text{Ti}_3\text{B}_4 + \text{TiB}_2 + \text{MgB}_2$$  (23)

Since MgB₂ reacts with TiB forming TiB₂ and titanium borides, TiB and Ti₃B₄ react with the retained boron carbide as presented earlier in the reaction mechanism of the Ti–B₄C system, the reaction between Ti, B₄C and infiltrated molten Mg alloy is finally obtained as follows:

$$3\text{Ti} + \text{B}_4\text{C} + \text{Mg} = \text{TiC}_x + 2\text{TiB}_2 + \text{Mg}$$  (24)

Based on these observations, it can be concluded that Mg not only infiltrates through the 3Ti–B₄C 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 that required for solid-state reaction between Ti and B₄C.

Finally, the study of the in-situ reaction mechanism is very important to understand and interpret the microstructure of the produced composites and their properties. The infiltration of Mg melt through the preform of (3Ti–B₄C) basically depends on its viscosity and the wettability between Ti, B₄C and/or the in-situ formed TiC. Mg infiltrated the preform through the pores by the capillary force resulting in dense microstructure of magnesium matrix composites.

Fig. 11. XRD patterns of heat-treated Mg–B₄C samples quenched from different temperatures (a) 600, (b) 700, (c) 800 and (d) 900 °C after 1 h holding time.

Fig. 12. XRD pattern of (a) the starting 3Ti–B₄C powder mixture, (b) heat-treated 3Ti–B₄C preform at 900 °C for 1 h and (c) Mg composite fabricated at 900 °C for 1 h.
4.3. Reaction mechanism of the infiltrated Mg in the (MgH₂–Ti–B₄C) preform

4.3.1. The MgH₂–Ti system

The XRD patterns of heat-treated MgH₂–Ti compacts at different temperatures from 400 to 800 °C for 1 h followed by quenching in water are shown in Fig. 13. The results reveal that at 400 °C, Mg, MgH₂, Ti and TiH₂ are present in the sample. However, the only main peaks at 600 °C are those of Mg and TiH₂ while with increasing temperature, Ti appeared again along with Mg and TiH₂ at 700 and 800 °C. The change in the lattice constant of TiH₂ as shown in Table 2 reveals that the highest value is for 600 °C which decreases with increasing temperature. Based on this, TiH₂ that formed at the beginning has a high content of hydrogen stemming from the decomposition of MgH₂. With increasing temperature, the rate of hydrogen release increased due to the decomposition of TiH₂.

Also, the XRD patterns of the MgH₂–Ti preform and the sample after infiltration of the molten AZ91D alloy into this preform heated to 900 °C for 1.5 h are shown in Fig. 14. Based on the XRD results, it can be observed that MgH₂ decomposed at low temperature (around 400 °C) forming Mg and releasing hydrogen according to the following equation:

\[ \text{MgH}_2 \xrightarrow{\text{600 °C}} \text{Mg} + \text{H}_2 \]  

Then Ti reacts with H₂ to form TiH₂ which decomposes with increasing temperature forming more reactive Ti due to an increase in its surface area and releasing hydrogen as follows:

\[ \text{Ti + H}_2 \xrightarrow{\text{700 °C}} \text{TiH}_2 \]  

\[ \text{TiH}_2 \xrightarrow{\text{700 °C}} \text{Ti} + \text{H}_2 \]  

4.3.2. The MgH₂–B₄C system

The XRD patterns of the MgH₂–B₄C preform with 70% RD and the sample after infiltration with molten AZ91D alloy processed at 900 °C for 1.5 h are shown in Fig. 15. Based on the XRD results, it is found that the reaction mechanism of the MgH₂–B₄C system is similar to that of the Mg–B₄C system. The difference between the two cases is that Mg formed by the decomposition of MgH₂ is more chemically reactive due to its higher surface area than Mg in the Mg–B₄C system. By comparing the MgH₂–B₄C with the Mg–B₄C system, it is found that the magnesium formed by the decomposition of MgH₂ is more reactive than Mg powder in the Mg–B₄C system. This can be proved by its high affinity for oxygen and forming MgO as shown in Fig. 15.

During and after complete infiltration of liquid magnesium through the MgH₂–B₄C preform, some of the molten magnesium reacts with some of the remaining boron carbide, as mentioned earlier during the discussion of the reaction mechanism of the Mg–Ti–B₄C system, while the remaining molten magnesium just fills the pores in the preform.

4.3.3. Infiltrating Mg in the (MgH₂–Ti–B₄C) preform

Fig. 16 shows the XRD spectra of the 25 wt.% MgH₂–(3Ti–B₄C) preform mixture, that was compacted at 70% RD and heat-treated at 900 °C for 1.5 h, and an AZ91D matrix composite sample fabricated at the same temperature and holding time using the same preform.

It can be observed that substoichiometric TiCₓ formed in both cases while TiB₂ formed significantly after infiltration of molten magnesium through the preform. The peaks of the formed TiB₂ before Mg infiltration are very small. Also, there are still peaks of retained Ti and boron carbide and those of the intermediate phases MgB₂ and TiB in the case of the heat-treated preform before infiltration of molten AZ91D alloy. This proves that the reaction is...
incomplete. The complete reaction after infiltration of molten magnesium without retained Ti and boron carbide and intermediate phases reveals the role of MgH$_2$ in this reaction mechanism. The MgH$_2$ plays a similar role as the infiltrated magnesium before and during the infiltration process.

Based on these results, the in-situ reaction mechanism of the infiltrated Mg–(MgH$_2$–Ti–B$_4$C) system was investigated based on the reaction mechanism of MgH$_2$–Ti–B$_4$C and that of the infiltrated Mg–(3Ti–B$_4$C) which was discussed earlier.

It was found that the reaction mechanism of the whole infiltrated Mg–(MgH$_2$–Ti–B$_4$C) system is similar to that of the infiltrated Mg–(Ti–B$_4$C) system. The difference between the two cases is that the Mg that formed by the decomposition of MgH$_2$ is more chemically reactive due to its higher surface area than Mg in the Mg–Ti–B$_4$C system. Also, Ti that formed after the decomposition of TiH$_2$ is more chemically reactive due to its higher surface area than Ti in the Mg–Ti–B$_4$C system making the reaction between Ti and B$_4$C much faster and the same applies for the case of Mg with B$_4$C.

Also, it is observed that the ternary Ti$_2$AlC compound formed when AZ91D is used. Ti$_2$AlC forms by the diffusion of Al into sub-stoichiometric TiC$_x$ at high temperature. The amount of Ti$_2$AlC is higher if compared with that formed without MgH$_2$ in the preform. The reason behind this is that the reaction is faster by the presence of MgH$_2$ in the preform and then the formation of
substoichiometric TiC$_x$ is very fast allowing more formation of this ternary compound compared with the case without MgH$_2$ in the preform within the same holding time. It can be concluded that MgH$_2$ after decomposition plays the role of magnesium to react with B$_4$C before and during the infiltration of molten magnesium or magnesium alloy into the preform.

5. Conclusions

(1) AZ91D magnesium matrix composites reinforced with a network of TiC$_x$ and TiB$_2$ particles were successfully synthesized using a practical and low cost in-situ reactive infiltration technique.

(2) The microstructure of TiC$_x$–TiB$_2$/AZ91D composites is essentially evolved from the reaction between Ti, B$_4$C and the 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 in-situ reaction mechanism revealed the role of the Mg melt in the system where it not only infiltrates through the 3Ti–B$_4$C preform and thus densifies the fabricated composites as a matrix metal but also acts as an intermediary that makes the reaction possible at a lower temperature than that required in the case of the solid-state reaction between Ti and B$_4$C.

(4) The addition of MgH$_2$ powder to the 3Ti–B$_4$C preform significantly accelerates the reaction between Ti and B$_4$C and raises the Mg content in the fabricated composites.

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