Synthesis of TiCp reinforced magnesium matrix composites by in situ reactive infiltration process

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Abstract

Elemental powder in situ reaction combined with spontaneous infiltration of molten magnesium into compacted preform of titanium and carbon was utilized to synthesize TiCp reinforced magnesium matrix composites. Smaller elemental particle size and a processing temperature above 973 K are beneficial to synthesizing TiCp reinforced magnesium matrix composites for (Tip + Cp)/Mg system. © 2003 Elsevier B.V. All rights reserved.

Keywords: Spontaneous infiltration; Elemental powder; In situ reaction; TiCp; Magnesium; MMCs

1. Introduction

In recent years, ceramic particulate reinforced magnesium matrix composites have been receiving much attention, since they possess rather high specific strength and stiffness, wear-resistance, excellent thermal and electrical conductivities and can be an attractive candidate for structural and functional materials [1–3]. In industries, such as aeronautical, automobile, electronics, etc., this kind of material has shown potential applications.

A variety of fabricating routes, e.g. powder metallurgy, stir casting, pressure infiltration and in situ production method etc, have been developed for producing these kinds of light metal matrix composites (MMCs). Among those techniques, infiltration of molten metals into porous ceramic preform is the only one suitable for fabricating high volume percentage (>50%) MMCs and cost effectively. Depending on the source of driving force for infiltrating liquid metal into ceramic preform, molten metal infiltration can be classified into three categories, i.e. pressure assisted, vacuum driven and pressureless or capillarity driven [4].

In the absence of an external pressure (pressureless), spontaneous infiltration of a molten metal into a porous ceramic preform is particularly of interest in obtaining ceramic particles reinforced MMCs. As compared with other techniques mentioned above, it can be characterized by a significant inherent simplicity and hence, by a potential cost-effectiveness in scale-up manufacturing and its near-net shape processing capability [5–7].

Generally, MMCs are fabricated by non-reactive process in order to prevent the reaction between matrix and reinforcement. Now more and more reactive processes have been used to fabricate the MMCs. It is well known that PRIMEX process, VLS process and DIMOX process become wildly used, in which the reinforcing phase is obtained via the reaction between molten metal and reactive atmosphere [5,8]. Recently, the combustion reaction is enthusiastically applied for the synthesis of MMCs, which has the features that it is convenient and quick to fabricate. Although the material obtained may be porous, it can be soluted by the spontaneous infiltration simultaneously with the in situ reaction.

Without the aid of reactive atmosphere, in situ reactive pressureless infiltration is obviously novel and most viable, in which the preform contains two or several elemental powders and can react sufficiently and quickly with the infiltration metal to form one or several compounds during or immediately after infiltration. Recently, Omura et al. [9,10] fabricated TiC particles reinforced aluminum matrix composite by this technique and found that the addition of aluminum powder to (Tip + Cp) powder mixture is necessary for the in situ reaction of Ti and C. The optimal molar ratio of Ti to Al is about 1.0. Otherwise, there will be no TiC particles formed during this process.

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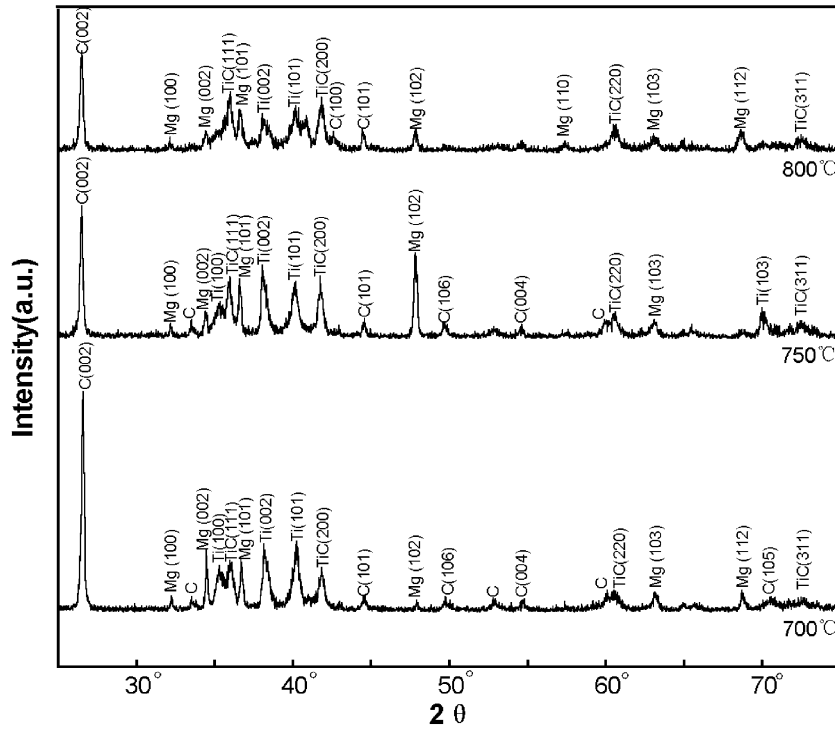*E-mail address:* lqchen@imr.ac.cn (L.Q. Chen).

Fig. 1. XRD patterns of as fabricated magnesium matrix composites for System I. Elemental particle size: Ti = ∼ 70 μm, C = ∼ 100 μm.

In the present study, the same processing technique as mentioned above was adopted to fabricate TiCp reinforced magnesium matrix composite and no aluminum powder was added to the mixture of Tip and Cp. Molten magnesium was spontaneously infiltrated, simultaneously the in situ reaction between titanium and carbon occurred and a dense composite material was obtained. The effects of primarily elemental powder (Ti and C) sizes on the in situ combustion
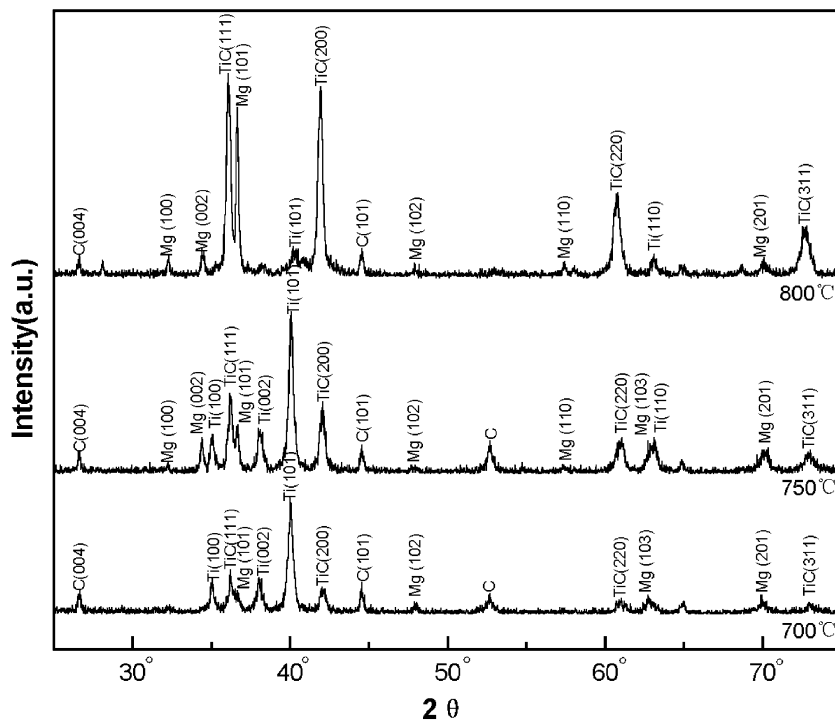

Fig. 2. XRD patterns of as fabricated magnesium matrix composites for System II. Elemental particle size: Ti = ∼ 44 μm, C = ∼ 30 μm.

reaction are taken into account at different fabricating temperatures. The processing mechanism for system (Ti + C) infiltrated with magnesium was also discussed.

2. Experimental

Two different sizes of elemental powders, Ti and C, were utilized to produce the magnesium matrix material (Hereafter denoted as System I and II). In System I, the particle size of the titanium and carbon is ~ 70 and ~ 100 μm, respectively. As for the System II, we chose relatively smaller titanium particles of about 44- and 30-μm carbon particles. The purities of these powders are all over 99.0%.

This fabrication process is accomplished in the following two main steps: (1) preparation of the preform (Tip + Cp) and (2) in situ reactive combustion processing of system (Ti + C) with spontaneous infiltration of molten magnesium into preforms simultaneously. However, during processing, there was no third phase metal powder, e.g. Al powder, to be added to the preforms. Also, there was no reactive atmosphere gas to be used in processing magnesium matrix composite in this experiment.

Firstly, the elemental powders of Ti and C (Ti/C = 1:1, in molar ratio) were uniformly mechanically mixed in the same way for these two systems. These powder mixtures were then uni-directionally dry-pressed into disks (dimension: $\phi 16 \times 12$ mm) at room temperature with an open porosity of about 25%. The compacted preform was placed at the bottom of an alumina crucible (inner diameter: 17 mm) with a magnesium ingot on it. Under the presence of flowing argon (99.999% pure), these systems together with magnesium ingots were finally heated in a electric furnace to 973, 1023, 1073 K, respectively, and the holding time is 1.5 h. After that, the samples were naturally cooled to the room temperature together with the furnace.

X-ray diffractometer (XRD) and Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray
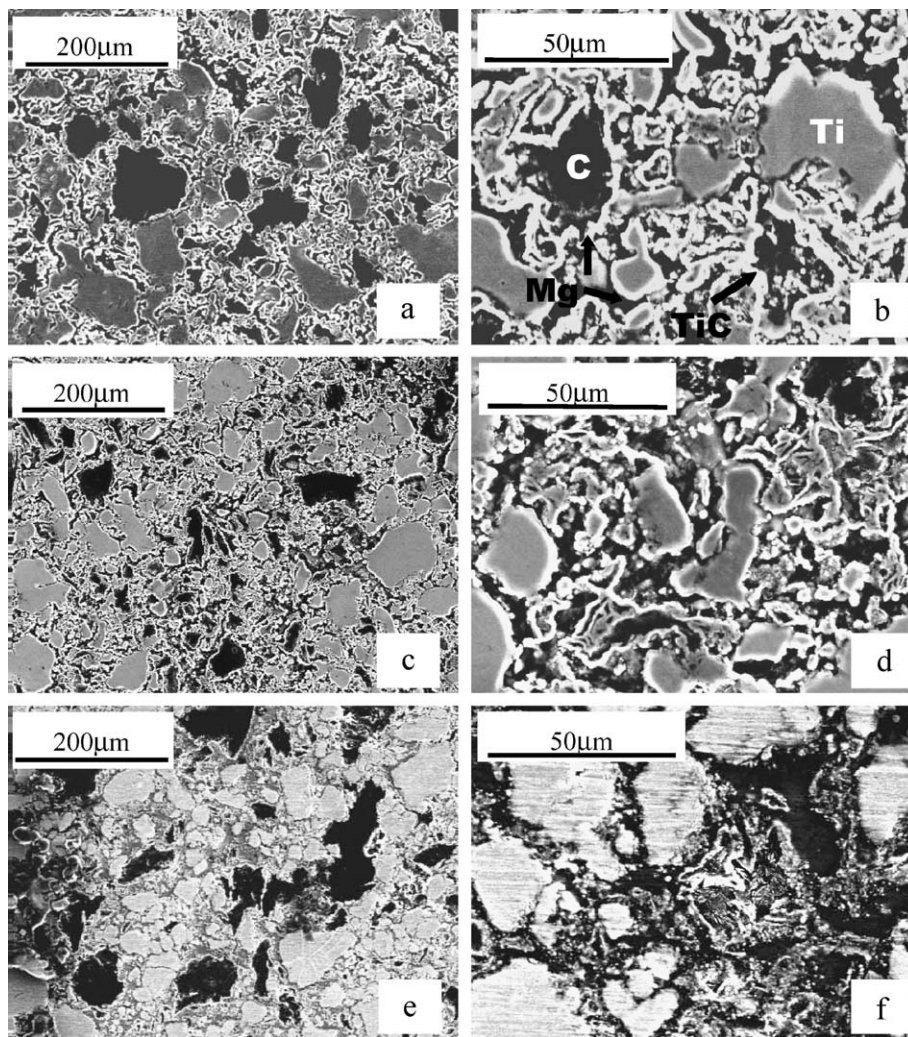

Fig. 3. SEM micrographs of as fabricated Mg matrix composites synthesized by in situ reactive infiltration process for System I. Low magnification: (a) 1073 K; (c) 1023 K; (e) 973 K. High magnification: (b) 1073 K; (d) 1023 K; (f) 973 K.

spectroscopy (EDS) and X-ray electron probe microanalysis (EPMA) were used to investigate the in situ reaction products and the microstructures.

3. Results and discussion

XRD patterns (radiation source: CuKα) of the specimens for two systems after in situ reactive infiltration process at different fabricating temperatures are shown in Figs. 1 and 2. As the intensities agree with the theoretical values, the increase in the peak areas gives information about the kinetics of the in situ reaction process. This means that the product TiCp was formed via the in situ reaction within the systems.

From the XRD pattern in Fig. 1, one can see that the main diffraction peaks corresponding to the phases of Mg, Ti, C and TiC were detected. Undoubtedly, the product TiCp is formed via in situ reaction of elemental powder Ti with C and the peaks of Mg are produced by spontaneous infiltra-

tion process. However, there exist Ti and C within the System I, which remained as incomplete reaction product. For larger elemental particle size as that in System I, with increasing the processing temperature, there are more TiCp formed and more Mg spontaneously infiltrated during this process while the Ti and C were reduced due to the synthesizing of TiC particulate. At the processing temperatures of 1023 and 1073 K, there is no much difference quantitatively for the excessive products C and Ti. It can be notified that the reaction of Ti and C occurs and TiCp was obtained more or less without any addition of third metal powder Al. This differs from Omur et al.'s result [9,10], in which he emphasized the role of powder Al in infiltrating of Al into the preform of Ti and C.

It can be expected that the powder particle size can affect the in situ reaction process. Smaller sizes of elemental powder are more beneficial to the in situ reaction between Ti and C, as can be observed from the XRD pattern in Fig. 2. At the processing temperature up to 1073 K, it is evident that TiC is formed completely and a large quantity of molten magnesium
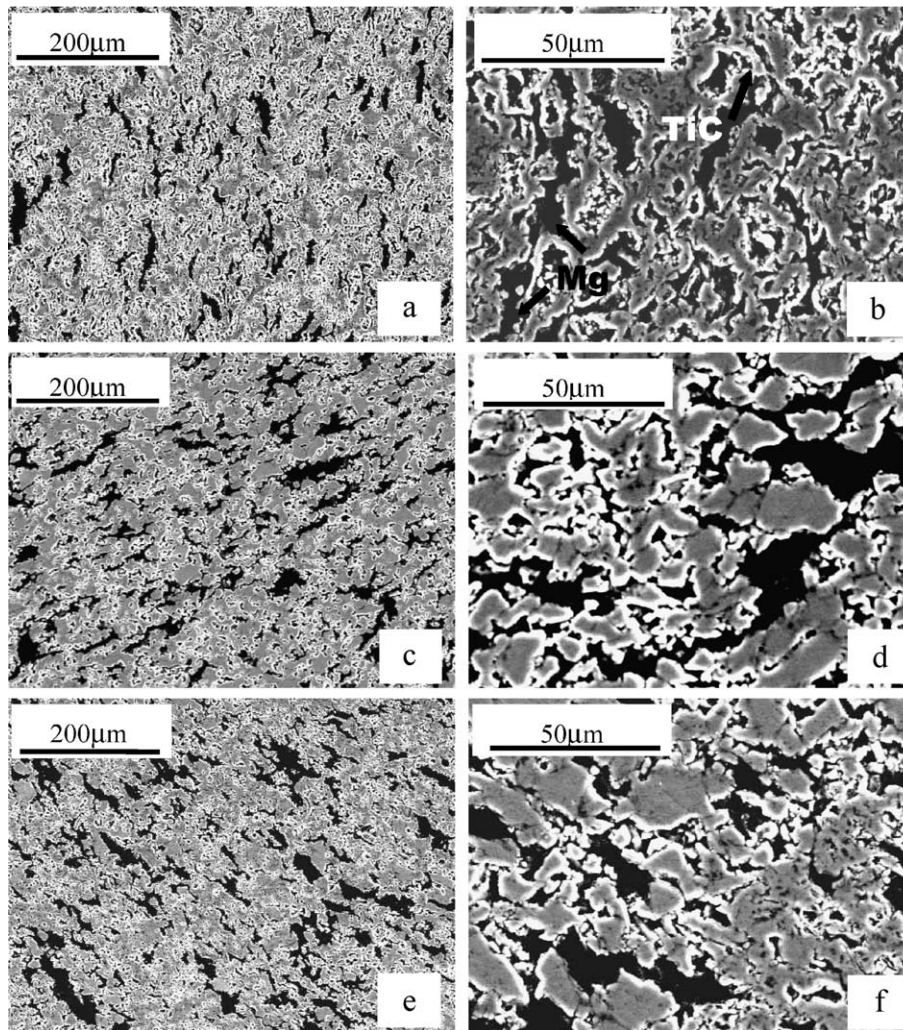

Fig. 4. SEM micrographs of as fabricated Mg matrix composites synthesized by in situ reactive infiltration process for System II. Low magnification: (a) 1073 K; (c) 1023 K; (e) 973 K. High magnification: (b) 1073 K; (d) 1023 K; (f) 973 K.
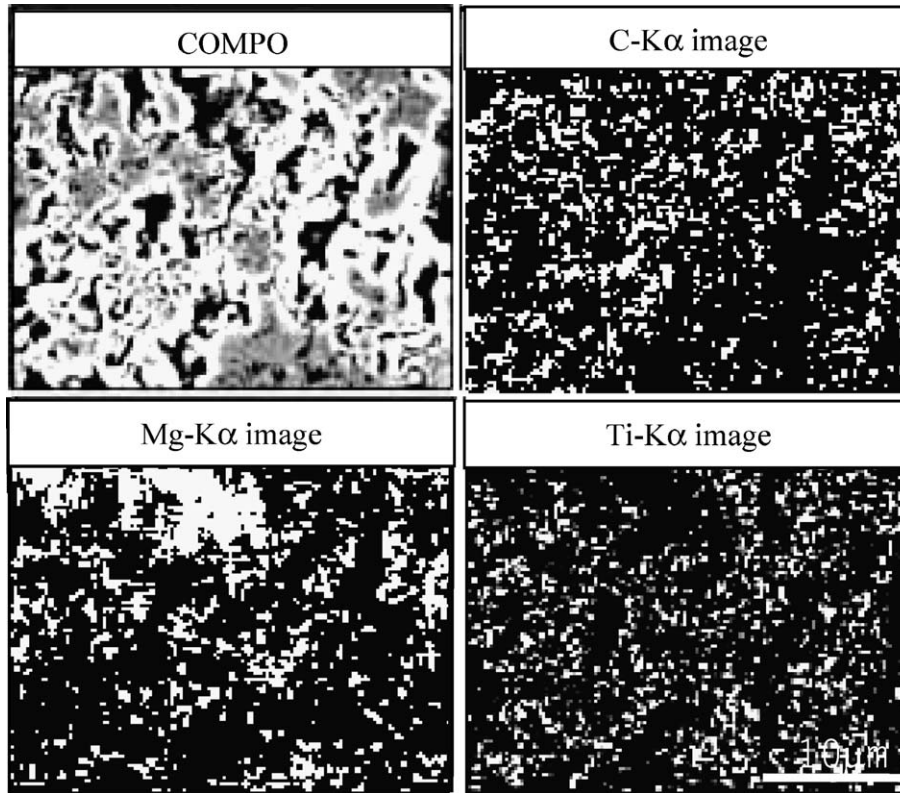
Fig. 5. EPMA analysis of the TiCp/Mg composites for System II synthesized at 1073 K.

fully infiltrates through the aperture gap of the in situ product TiCp. Lower processing temperature allows a little carbon and titanium remain, and therefore, the in situ reaction processed incompletely, which were characterized by intensities of the peaks of the corresponding X-ray patterns.

Representative SEM micrographs of the samples under various processing conditions for the two systems are shown in Figs. 3 and 4. For System I, there still exist more titanium (gray part) and carbon (dark part), which remained as particulates at low temperature and are separated by magnesium emerging as pattern of reticulate structure. Fewer TiCp (bright part) was formed around the boundaries of titanium and carbon. As the synthesizing temperature was raised, more bright part appeared, which corresponds to product TiCp. However, it seems to be identical as compared the micrographs of 1023 K with that of 1073 K.

As for the System II at 973 K shown in Fig. 4, there is more brighter part formed by titanium and carbon. Magnesium was melted and spontaneously infiltrated into the gap of the reaction product driven by capillary force. Especially when the fabricating temperature was raised up to 1023 or 1073 K, the Ti and C in situ reaction processed fully and a dense microstructure of magnesium matrix composites was obtained. SEM micrographs of the MMCs with low and high magnifications were presented for comparison for the two reactive systems.

EPMA results for System II at 1073 K are more helpful to analyze the microstructure distribution of the in situ

reaction product TiCp and infiltrated magnesium, as shown in Fig. 5. According to the results obtained, the lack of the element magnesium image and the overlap of the element titanium and carbon images were clearly observed in the area of the brighter parts and some spherical particles existed. It can be deduced that the brighter parts were TiCp synthesized via in situ reaction. The morphology of the TiCp formed during the processing is shown in Fig. 6. One can observe that most of TiCp was formed as spherical
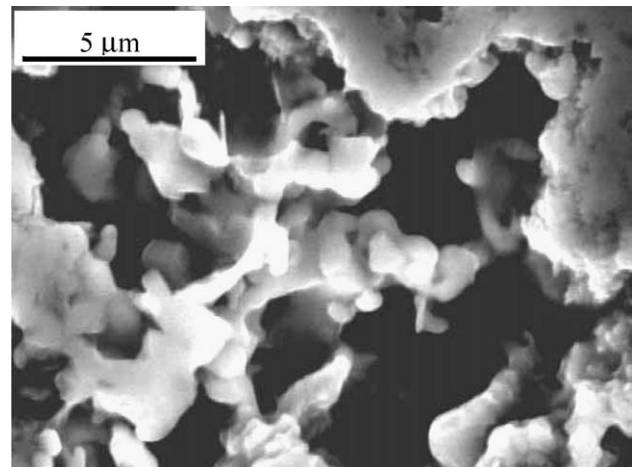

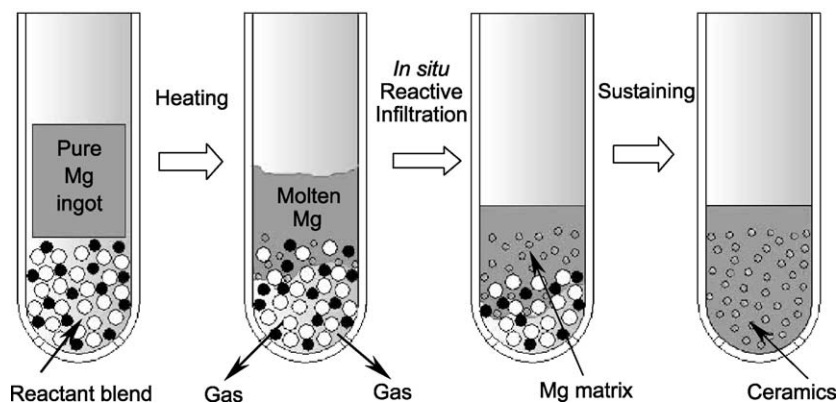Fig. 6. Morphology of the in situ formed TiC particles in System II at 1073 K.

Fig. 7. Schematic illustration of the mechanism of in situ reactive infiltration process.

shape particles with a diameter of about 1 μm. Besides, there exist irregular TiC particles within the microstructures of in situ reactive infiltrated magnesium matrix materials.

Concerning the mechanism of in situ reaction or self-sustaining process between Ti and C, we can thermodynamically analyze as follows. From the results of XRD, SEM, and EPMA, it can be found that titanium and carbon powders have the combustion reaction at about 973 K or above to form TiC particles. There is no reaction between titanium and magnesium or between carbon and magnesium, because there will be no intermetallic compounds to appear according to the Ti–Mg binary phase diagram. Magnesium carbide can form at about 953 K and is not stable above this temperature. So, the only reaction among Ti, Mg and C during the processing can be expressed by the following reaction mode:

$$Ti(s) + C(s) \rightarrow TiC(s) \tag{1}$$

Variation of free energy change ΔG and enthalpy change ΔH with temperature for this reaction is given by the following equations ($T < 1000$ K) [11]:

$$\Delta H = -184571.8 + 5.042T - 2.425 \times 10^{-3}T^2$$
$$- 1.958 \times 10^6/T \tag{2}$$

$$\Delta G = -184571.8 + 41.382T - 5.042T\ln T + 2.425$$
$$\times 10^{-3}T^2 - 9.79 \times 10^5/T \tag{3}$$

It indicates that reaction (1) is exothermic, $\Delta H_f = -185.03$ kJ/mol at 973 K. It can be calculated by program that adiabatic temperature of this reaction is nearly equal to 3210 K in accordance with empirical law $T_{ad} > 2500$ K propounded by Merzhanov [12]. Therefore, it can become self-sustaining and will propagate through the reactant blend in the form of a combustion wave [13].

Analyzing Figs. 3 and 4 revealed that the product microstructures and in situ reaction process mostly depend on: (1) reactant particle size and its distribution, their morphology

and purity; (2) initial temperature (processing temperature) of the reacting system. As the particle size of reactant blend is large as that in System I, the surface area in contact was so small that reaction could proceed partially and could not sustain by itself. On the contrary, as reducing the particle size in the System II, the combustion synthesized fully and more TiC formed. Simultaneously, the magnesium infiltrated the zone containing TiC and pores by the capillary force to obtain magnesium matrix composite with dense microstructure. Schematic illustration of the in situ reactive infiltration is shown in Fig. 7. The capillarity is the result that additional pressure is engendered by curvature of liquid level. The capillary pressure of a pore with a radius of r is produced by the pressure difference between upper and lower level. The capillary force can be formulated by Eq. (4) while the molten magnesium infiltrate porous performs [14]:

$$\Delta P = \frac{6\rho\gamma\cos\theta}{D(1-\rho)} \tag{4}$$

where D, ρ, γ and θ represent average particle size of reactant, relative density of the preform, surface tension of magnesium with TiC and its contact angle, respectively. Surface free energy of molten magnesium is about 6×10^3 kJ/m². Its contact angle with the solid substrate (entryway diameter: ~ 1 μm) is characterized by $\theta < 45°$. The capillary force produced under such conditions will reach about two hundred atm pressure, which could sufficiently impel molten magnesium to penetrate the entire bulk preform and a dense composite microstructures would be obtained.

4. Conclusions

A combined processing route, in situ reaction of elemental Ti and C powders and spontaneous infiltration of molten magnesium into the (Tip + Cp) perform, was successfully utilized to fabricate TiC particulate reinforced magnesium matrix composites. In (Tip + Cp)/Mg system, in situ formed TiC particle size is about 1 μm at the

temperature of 973 K or above and magnesium is then spontaneously infiltrated along the interfacial region containing TiCp driven by capillary force. Unlike (Ti + C)/Al system, there is no need to add third phase metal powder or use reactive atmosphere gas for (Ti + C)/Mg system. Smaller elemental particle size and an elevated temperature up to 1073 K are beneficial to synthesizing TiCp reinforced magnesium matrix composites.

Acknowledgements

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