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Synthesis of TiC/Mg composites with interpenetrating networks by in situ reactive infiltration process

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Abstract

In this paper, a novel and cost-effective processing route, in situ reactive infiltration technique, was utilized to fabricate titanium carbide reinforced magnesium matrix composites (TiC/Mg) with interpenetrating networks. In this process, the ceramic reinforcement phase TiC was synthesized in situ from elemental powders of Ti and C without any addition of third phase metal powder, and the molten Mg can penetrate the preform of ($Ti_p + C_p$) by capillary force. By simply controlling the relative density of the predetermined preform, the volume fraction of the in situ synthesized reinforcement with interpenetrating network can be tailored, which was supported by experimental and theoretical comparison for the intrinsically volumetric shrinkage of the in situ formed TiC phase before and after the in situ reaction. Calculation of the lattice constant of the in situ formed TiC phase showed that TiC has a variable stoichiometry of C/Ti depending on the processing conditions and initial particle sizes of the elemental powders.

Keywords: Magnesium matrix composites; TiC; In situ reactive infiltration; Interpenetrating networks

1. Introduction

In traditional ceramic particulate- or fiber-reinforced metal matrix composites (MMCs), the microstructures consist of discrete, dispersed and isolated ceramic phases embedded in matrix metals. The properties of the composites depend mainly on those of the continuous matrix metals, while the contribution of the discrete ceramic phase is limited. In recent years, interpenetrating network or co-continuous metal/ceramic composites where both the ceramic and matrix metal are interpenetrated by each other in the composite microstructure have attained great attention (e.g. [1–10]), since they offer some distinctive mechanical and physical behaviors relative to the traditional MMCs, such as high modulus, low coefficient of thermal expansion, good thermal and electrical conductivities, advanced damage tolerance and wear resistance.

Till now, several processing techniques have been developed to fabricate interpenetrating network composites. For example, by gas pressure infiltration of molten metal into porous preforms, Al_2O_3/Al and Al_2O_3/Ni_3Al composites with microstructures of interpenetrating networks can be fabricated [2–4,11]. Using conventional powder metallurgy (PM) or that combined with squeeze casting [12–14], a processing route was proposed where a porous preform containing the reactive oxide can be first formed and the porous preform is then infiltrated with aluminum (alloys). Directed metal oxidation (DIMOX) process was successfully used in preparing ceramic/metal composites, where the surface of the molten Al is oxidized by oxygen in air and the Al_2O_3/Al composites layer grows up toward the air [5]. By immersing a silica preform into molten aluminum, another processing method was developed to fabricate Al_2O_3/Al composites [6], in which silica preform is reduced by the molten Al and transforms into a body consisting of continuous Al_2O_3 and continuous Al. Laterly, several researchers [15–18] adopted this approach to successfully fabricate alumina/aluminum

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composites. In addition to silica, dense ceramics such as mullite can also be used as preform to fabricate Al_2O_3/Al composites [19–21]. More recently, an alumina/aluminum structure was created with three-dimensional periodicity and submillimeter feature size by robotic deposition [9]. As could be found that these established processing routes for fabricating metal/ceramic composites with interpenetrating networks are generally restricted to the manufacture of Al-containing composites. Concerning the co-continuous ceramic/magnesium composites, however, there is little work appeared. Magnesium is the lightest metal of the industrial alloys, and environmentally benign. So, cost-effective process for producing Mg and Mg-based composites should be established.

Recently, an innovative process, in situ reactive infiltration, has been developed in which the reinforcement phases are in situ synthesized from elemental powders and the molten metal spontaneously infiltrates the preform of the formed reinforcement. By utilizing this processing technique, ceramic particles reinforced aluminum matrix composites have been successfully manufactured [22,23]. The advantages of the MMCs produced by this process can be ascribed to the follows: (1) thermodynamically stable and homogeneously dispersed fine reinforcement formed in situ within the matrix leads to an increase in their mechanical properties; (2) bonding strength is greatly improved due to existence of clean interface between reinforcement and matrix; and (3) the composites can be easily produced to a near-net shape with a high ceramic volume percentage (>50%) and effective cost. Since the reaction of Ti with C is controlled by diffusion process, the morphologies of the in situ formed reinforcement phase depend largely on the initial elemental powder sizes and processing conditions. The production cost is greatly reduced, which is resulted from the fact that for in situ reactive infiltration process in Mg–Ti–C system, the compacted elemental powders can react in situ by simply heating the entire preform together with Mg ingot on it. The porous preform can thus be densified by infiltration of the magnesium melt driven by capillary force, other than by any externally applied pressure.

Consequently, in this paper, we report the fabrication process of TiC/Mg composites with interpenetrating networks via in situ reactive infiltration technique, where no third phase metal powder such as Al is added to the preform. By choosing appropriate particle sizes of the initial elemental powders, the TiC/Mg composites with interpenetrating networks could be synthesized. The emphasis are put on: (1) processing the interpenetrating network TiC/Mg composites, (2) tayloring the volume percentage of the in situ formed reinforcement TiC through controlling the preform relative density and considering the intrinsic shrinkage resulted from the in situ reaction and infiltration process and (3) the lattice constant analysis of as in situ formed TiC_x phase associated with the processing conditions and further determining the appropriate C/Ti ratio in order to eliminate the residual carbon during in situ reactive infiltration and obtain high quality TiC/Mg composites with interpenetrating networks.

2. Experimental

In order to obtain TiC/Mg composites with interpenetrating networks, the coarse elemental powder Ti and rather fine C particles were deliberately chosen. The starting raw materials used for synthesizing TiC/Mg composites were Ti powder particles of 38 μm (>99.5% purity, General Research Institute for Nonferrous Metals, Beijing, PR China), C particles of 1.5 μm (>98.5% purity, Gel Chemicals, Shanghai, PR China) and AZ91D magnesium alloy casting ingot (99.5% purity, Mg–9.0Al–0.6Zn–0.2Mn, in wt.%, Yellow-river Magnesium Alloys Co. Ltd., Henan, PR China). After fully mechanical blending, the mixed Ti and C powders (molar ratio of Ti/C = 1:1) were firstly compacted into green body of cylindrical shape of 16.5 mm in diameter (height variable) with various relative densities of 72, 62, 58 and 51% in a steel mould. Assuming that all Ti and C powders will fully transform into TiC phases with the pre-designed molar ratio during in situ reactive infiltration process, TiC/Mg composites with different reinforcement contents could be obtained according to the product of TiC phases formed in situ in the magnesium matrix and by considering the intrinsic shrinkage of the reactants due to the in situ reaction. The preform together with a magnesium alloy ingot on it was then put into an alumina crucible. Several small holes were drilled at the bottom of alumina crucible in order to release the air during fabricating TiC/Mg composites. In situ reactive infiltration experiments were finally carried out in an electric furnace under a flowing argon (99.999% purity) atmosphere. The reaction chamber was degassed prior to heating and then backfilled with Ar. The heating temperature was set as 1073 K with holding time 1.5 h, and the heating rate was 10 K/min. Following these, the samples were cooled down to room temperature with the furnace.

The in situ reaction products and the microstructures for all as-fabricated composites were characterized by X-ray diffraction (XRD, D/max-2500PC, Rigaku, Japan) and a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. The apparent densities of the as-fabricated TiC/Mg composites were measured using Archimede’s principle.

3. Results and discussion

Fig. 1 shows the XRD profiles of the starting elemental powders of Ti and C, and the TiC/Mg composites of different ceramic contents fabricated at 1073 K/1.5 h. In Fig. 1(a), only diffraction peaks of Ti and C were detected and the cases differed for the as-fabricated composites. One can observe that under such synthesizing conditions the diffraction peaks

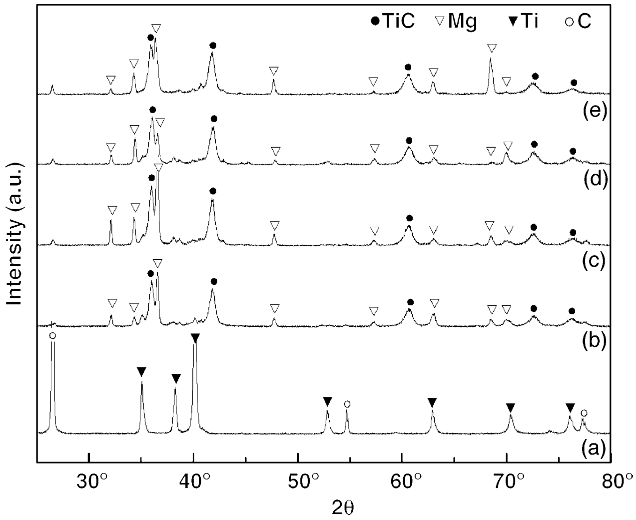


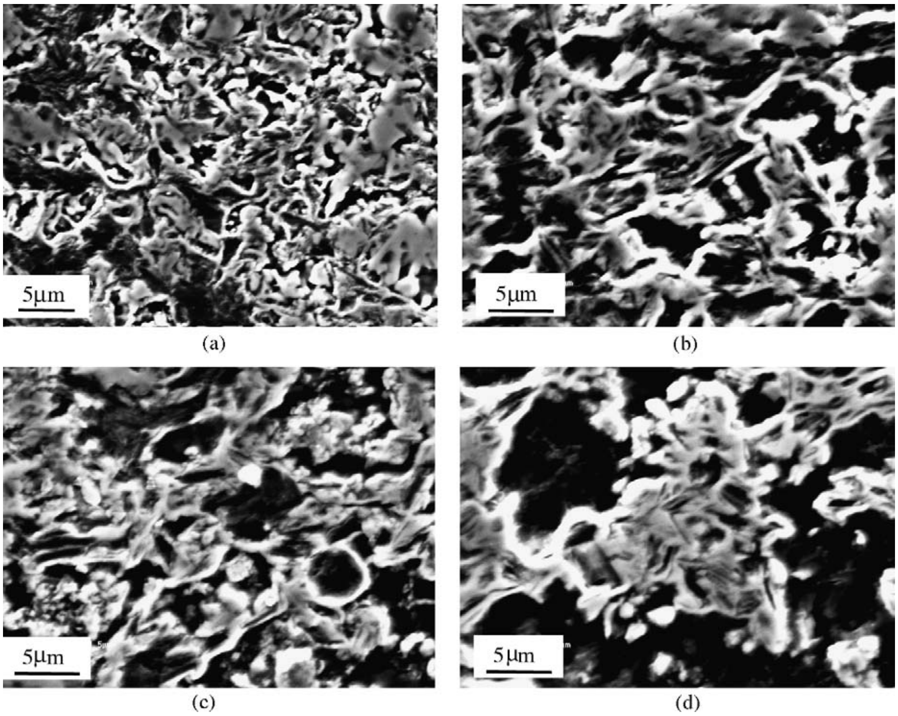
Fig. 1. XRD spectra of the starting elemental powder Ti and C (a) and as-fabricated interpenetrating network TiC/Mg composites with perform relative densities of 72% (b), 62% (c), 58% (d) and 51% (e).

of TiC and Mg appeared, which indicated that the in situ reaction between Ti and C occurred and molten Mg infiltrated the preform of Ti and C, as shown in Fig. 1(b–e).

Fig. 2 illustrates the SEM micrographs for the as-fabricated TiC/Mg composites with different initial relative densities of the preforms. They are all showing typical network microstructures interpenetrated by two phases of TiC and Mg in micron scale. SEM observations show that no voids are present in the microstructures of the as-fabricated TiC/Mg composites and this indicates that the composites are fully dense. Since the wettability between Mg and Ti or TiC is excellent under such processing conditions, the attainment of the fully dense composites can be attributed to the infiltration of Mg driven by strong capillary force. The EDS analysis shows that TiC phase appears as bright areas and Mg the dark region. The volume fraction of the in situ formed reinforcement TiC varies with the change of the relative density of the preform ($Ti_p + C_p$). One also can observe that the TiC network is not well interconnected and aggregated to some extent when the relative density of the preform is about or lower than 50%, which is due to the small volume fraction of the reinforcement TiC formed in situ.

As for the in situ formed TiC, we have calculated their lattice constants using Bragg's equation and least-square method. The calculated lattice constants together with the measured densities are presented in Table 1. As expected, the composite density decreases with lowering the relative density of the preform ($Ti_p + C_p$). One may also notice that the lattice constant of in situ formed TiC under such fabricating conditions remains almost the same, about 4.3156 ± 0.0004 Å, irrespective of the pre-designed relative density of the preform of Ti and C or ceramic content after in situ reaction. In other words, the lattice constant of the in situ formed TiC depends largely on the processing conditions (heating temperature and holding time) and characteristics of the starting elemental powders, such as particle size and its distribution.

In order to verify the deduction mentioned above, additional experiments were carried out for relatively large particle size of elemental powder C and for Ti of the same particle



(a) (b) (c) (d)

Fig. 2. SEM micrographs showing the interconnected microstructures of as-fabricated TiC/Mg composites with preform relative densities of 72% (a), 62% (b), 58% (c) and 51% (d).

Table 1
List of the parameters measured and calculated for in situ formed TiC/Mg composites

Sample no.	Relative density of perform (%)	Measured density (g/cm^3)	Ceramic content (vol.%)	Intrinsic shrinkage (vol.%)	Lattice constant (Å)
A-1	72	3.381	57.2	14.8	4.3160
A-2	62	3.110	47.5	14.5	4.3155
A-3	58	2.959	42.1	15.9	4.3152
A-4	51	2.798	36.2	14.8	4.3152

Table 2
List of lattice constants under different processing conditions

Sample no.	Relative density of perform (%)	Particle size (μm)	Processing condition	Lattice constant (Å)
B-1	70	Ti-38, C-30	1023 K/1.5 h	4.2930
B-2	70	Ti-38, C-30	1073 K/1.5 h	4.3067

size under different processing conditions, where the powders Ti and C have mean particle sizes of 38 and 30 μm, respectively. The relative densities of the preforms were all 70%. The processing conditions were set as 1023 K/1.5 h and 1073 K/1.5 h, respectively. Fig. 4 shows the XRD spectra of the TiC/Mg composites under such processing conditions. The same method was used to calculate the lattice constants of in situ formed TiC phases. The results are listed in Table 2 and it shows that the lattice constant changes with the processing condition and initial particle sizes of the elemental powders utilized. For the same sizes of elemental powders Ti and C, the lattice constant decreases with lowering processing temperature. Under the same processing condition, however, the lattice constant of TiC also changes with the elemental particle sizes. At elevated processing temperature up to 1023 K or above, the in situ reaction between Ti and C almost completely finished and rather little Ti and C were retained. In all cases, the in situ formed TiC has lattice constant smaller than that of standard value of 4.3274 Å as documented in JCPDS Card No. 32-1383, also depicted in Fig. 3 for comparison. Undoubtedly, the reason is due to the variation of stoichiometry of C/Ti in TiC.

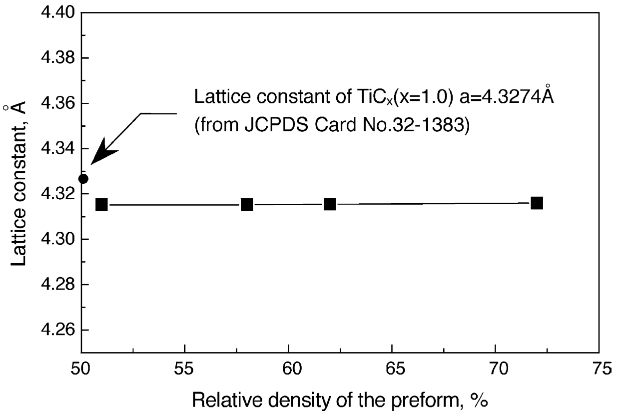


Fig. 3. Variation of the lattice constant of as in situ formed TiC at 1073 K/1.5 h with relative density of preform ($Ti_p + C_p$).

It is known that TiC phase, which has NaCl type crystalline structure, exists over a wide range of compositions, TiC_x, where x ranges from 1.0 to 0.5 [20] or to even lower value [24]. Consequently, the lattice constant of TiC deviating from the standard value is due to the slightly excess or unreacted C in the composites, which were also confirmed by XRD shown in Figs. 1 and 4 revealing that there was trace element C in the as-fabricated composites.

The above experimental fact could be interpreted in terms of diffusion capability of C in Ti or TiC_x. The self-diffusion coefficient of C in TiC is 10^4 times larger than that of Ti and this value will be much high with increasing processing temperature. The interface TiC_x and Ti moved to Ti side when TiC_x reacted with Ti, and a new TiC'_x layer was formed at the surface of former TiC_x. At a given temperature, this will reach to equilibrium. The nonstoichiometry of TiC is thus mainly caused by C vacancies and the lattice constant was accordingly changed.

It was reported that lattice constant of TiC_x decreases as x is lowered [24]. The lattice constant 4.3156 Å in these experiments corresponds to a value of x, ~0.65 in TiC_x [25] and the resultant TiC_x has a determined density of about 4.58 g/cm^3 [26]. For simplicity, the excess C was not taken into consideration in calculating the intrinsic shrinkage of the composites preform before and after the in situ reaction between Ti and C due to its very small amount existing in the as-fabricated

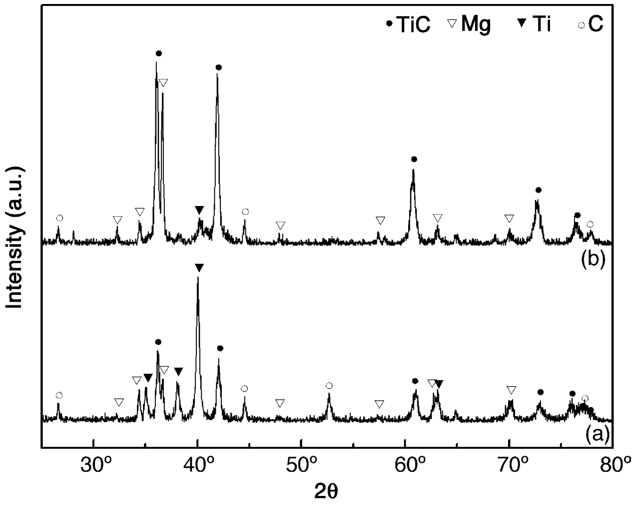


Fig. 4. XRD spectra of TiC/Mg composites fabricated at 1023 K/1.5 h (a) and 1073 K/1.5 h (b) with initial Ti and C powder particle sizes of 38 and 30 μm, respectively.

composites. The overall reaction of Ti and C can be described as follows:

$$\mathrm{Ti} + x\mathrm{C} + (1 - x)\mathrm{C} \rightarrow \mathrm{TiC}_x + (1 - x)\mathrm{C} \quad (1)$$

According to the above reaction, we may theoretically calculate the intrinsic or volumetric shrinkage induced by the in situ reaction from the elemental powders of Ti and C to TiC_x phase. The calculated intrinsic shrinkage is about 13 vol.%, which is close to the measured values of 14.5–15.9 vol.% listed in Table 1.

It is known that the residual carbon present in TiC/AZ91D magnesium alloy matrix composites after the in situ reaction and infiltration process has a detrimental effect on the mechanical properties of the composites. How to eliminate the residual carbon in as-synthesized composites becomes a critical issue in controlling the mechanical behavior of the composites. From the above experimental fact that the in situ formed TiC_x phase has a variable stoichiometry of C/Ti, it suggests that by lowering the content of elemental carbon powder to some extent such as higher than ∼0.65 and lower than 1.0, we may still obtain the TiC/Mg composites with interpenetrating networks under such processing conditions while the TiC remains NaCl crystalline structure. The molten Mg could carry some carbon particles with it while infiltration process proceeds. However, this effect is limited, since the two processes, in situ reaction between Ti and C and infiltration of molten Mg, occurred simultaneously [27].

From above analysis, we may conclude that the volume percentage of the in situ formed ceramic reinforcement can be controlled by deliberately designing the preform relative density, just considering the intrinsic shrinkage of the reinforcement phases from initial elemental powders resulted from in situ reaction.

It should be pointed out that TiC is a refractory compound and it is generally synthesized at rather high temperature approaching to 1273 K. The in situ reaction between Ti and C will not take place under such lower processing temperature without Mg. The most interesting is that it does occur with the existence of molten Mg. The detailed mechanism and its formation process were discussed in a recent work associating with the two-fold roles of Mg [27], which differs from the case of Al. For the later one, intermetallic compounds TiAl and $\mathrm{TiAl_3}$ always formed at first and Al can then be reduced by C from TiAl and $\mathrm{TiAl_3}$, and TiC finally formed [28].

4. Conclusions

(1) The TiC/Mg composites with interpenetrating networks were successfully synthesized by in situ reactive infiltration process.
(2) By simply controlling the relative density of the preform ($\mathrm{Ti_p} + \mathrm{C_p}$) and considering the intrinsic shrinkage of the reaction product resulted from the in situ reaction, the volume percentage of the ceramic reinforcement formed in situ could be predetermined, and tailoring its mechanical and physical behavior is possible.
(3) The in situ formed reinforcement phase TiC_x in as-fabricated magnesium matrix composites has a variable stoichiometry of C/Ti, where x depends on both the processing conditions and initial particle sizes of the elemental powders utilized. To eliminate the residual carbon in as-fabricated TiC/Mg composites, the C/Ti molar ratio lower than 1 in initial elemental powders is recommended during this process.

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