Effect of Mg addition on the self-propagating high temperature synthesis reaction in Al-Ti-C system

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Self-propagating high temperature synthesis (SHS) reaction provides an attractive practical alternative to the conventional methods of producing advanced materials, such as ceramics, ceramic-composites and intermetallic compounds, since SHS offers advantages with respect to process economics and process simplicity [1, 2]. The main advantages of SHS reaction include the self-generation of energy required for the process, the high-purity products due to volatilization of low boiling point impurity at elevated temperature, and the high productivity due to such high reaction rates [3].

In the past years, Al-Ti-C as a typical system in the field of SHS reaction to synthesize TiC particulate has been extensively studied by a number of researchers [3–6], since titanium carbide possesses many desirable properties, such as high hardness, low density, high melting temperature, high modulus and high corrosion resistance [7]. These outstanding features portray it to be a good potential reinforcing candidate in aluminum and magnesium matrixes [8–12]. Choi and Rhee [4] studied the effect of aluminum addition on the SHS reaction of Ti and C to form TiC by using differential thermal analysis (DTA). They concluded that aluminum serves not only as a diluent, but also as a reactant and suggested that the Ti-C reaction in Al-Ti-C system is initiated by the heat of reaction between Ti and Al. Lee and Chung [6] investigated the effect of the amount of aluminum addition on the ignition phenomenon of the Al-Ti-C system. They concluded that Al affected ignition by providing an easier route for reactant mass transfer. Zhang *et al.* [10] studied the SHS reaction mechanism of Al-Ti-C system by using a water-quenched experiment and suggested that the synthesis of TiC is a solution-precipitation mechanism. However, research efforts on the effect of Mg addition on the SHS reaction in the Al-Ti-C system are rather limited [11, 12].

In the present study, the effect of Mg addition on the SHS reaction in Al-Ti-C system was investigated. The purpose was to *in situ* synthesize a reacted preform containing Al and Mg, as well as a large volume fraction of fine and spherical TiC particulates. The preform could, therefore, serve as an excellent master alloy for subsequent dilution in aluminum or magnesium melts and processing of TiC particulate reinforced metal matrix composites (MMCs), since the presence of a small amount of Mg in the master alloys can make the generated TiC particulates dispersion into the matrices easier [11, 12].

The characteristics of the reagents used in the present study are listed in Table I. The green preforms were made from commercial powders of 20 wt.% aluminum, 0, 5, 10, 15 wt.% magnesium, and titanium and graphite powders at a ratio corresponding to that of stoichiometric of TiC. The powder blends were mixed by ball milling at 100 r.p.m. for 8 hr and then pressed uniaxially into cylindrical performs (50 mm diameter and 70 mm length) by using a stainless die with two plungers at pressures about 100 MPa to obtain densities of (65 ± 5)% theoretical density. The perform was heated to 600 °C in an electric resistant furnace under an argon-protective atmosphere and then held at that temperature for 15 min. The bottom surface of the preform was ignited subsequently by applying a current of about 12A through a resistance wire. TiC particulates were *in situ* formed in the master alloy via the SHS reaction.

Microstructure and phase of the SHS reaction products were determined by using scanning electron microscope (SEM) (Model JSM-5310, Japan) equipped with energy-dispersive spectrum (EDS) (Model Link-Isis, Britain) and X-ray diffraction (XRD) (Model D/Max 2500PC Rigaku, Japan).

Figs 1 and 2 show the SEM micrographs and XRD patterns of the SHS reaction products synthesized by green preforms with a molar ratio of Ti:C = 1.0 mixed with 20 wt.% Al, and (a) 0, (b) 5, (c) 10 and (d) 15 wt.% Mg, respectively. According to the XRD patterns, when the Mg content is 0 or 5 wt.% in the green preforms, the master alloys only consist of TiC and Al, as shown in Fig. 2a and b. As the Mg content is further increased to 10 or 15 wt.%, however, in addition to TiC and Al phases, the $TiAl_3$, Mg, $Al_{12}Mg_{17}$ and residual C phases are also found in the final products, as shown in Fig. 2c and d.

Compared with Fig. 1a and b, it can be obviously seen that the sizes of spherical TiC particulates are decreased from ∼7.0 to ∼3.0 μm with the increasing of Mg content from 0 to 5 wt.% in the green preforms. The results reveal that the Mg addition has effectively hampered the growth of TiC particulates during the SHS reaction process. Furthermore, it is interesting to note that the Mg or $Al_{12}Mg_{17}$ cannot be detected by XRD in

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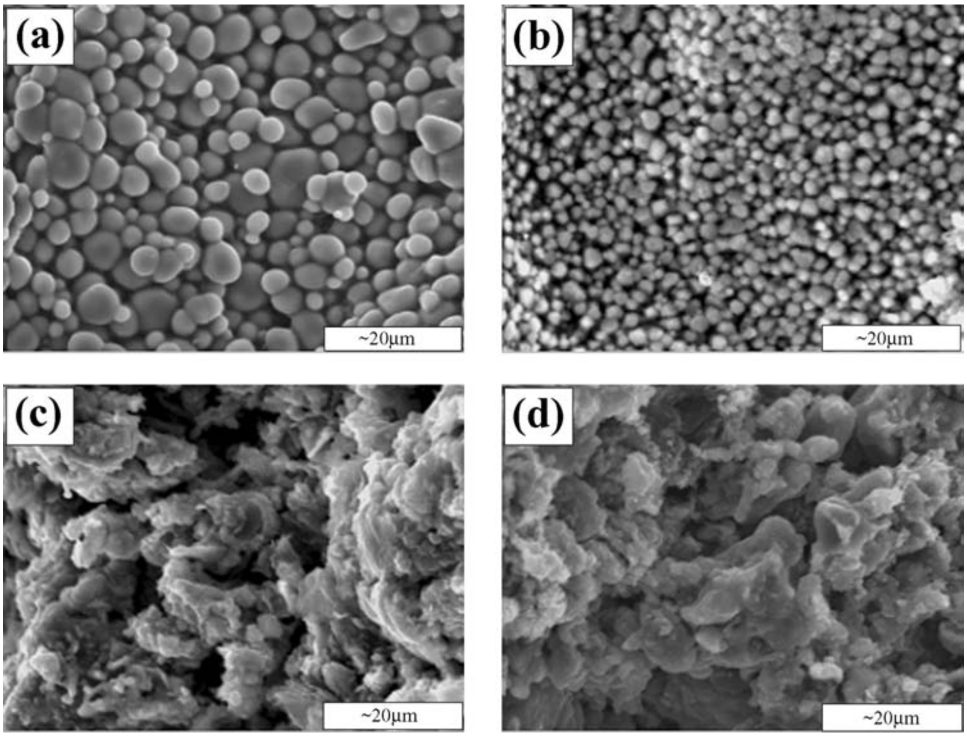

Figure 1 SEM microstructures of the SHS reaction products synthesized by green preforms with a molar ratio of Ti:C = 1.0 mixed with 20 wt.% Al, and (a) 0, (b) 5, (c) 10 and (d) 15 wt.% Mg.

the master alloy with 5 wt.% Mg, as shown in Fig. 2b. It may be the reason that some Mg evaporated in the high temperature of the SHS reaction. However, the trace of Mg in the final products can be identified by the EDS result. At the same time, much of heat dissipates into the surroundings owing to the Mg evaporation; therefore, it is difficult that TiC particulates grow up sufficiently, since the grain growth of TiC is an exponential function of the combustion temperature [4].

As the Mg content is further increased to 10 or 15 wt.%, it is difficult to distinguish TiC particulate from the SEM micrographs in the master alloys due to its fine size (see Fig. 1c and d). In this case, the full conversion of Ti and C to TiC is not achieved, since a large amount of $TiAl_3$ and residual C are also found in the final products. It could be explained that under the condition of a propagating combustion wave, the dwell time of the material in the combustion zone is not long enough to achieve the equilibrium compositions, since the combustion temperature is reduced as the increasing of Mg content. It should be mentioned that the $Al_{12}Mg_{17}$ phase is found in the final products synthesized by green preforms with 10 and 15 wt.% Mg, indicating that Mg also participates in the SHS reaction process.

The addition of aluminum provides an easier route for the TiC formation during the SHS reaction process in Al-Ti-C system, because the reaction between Al and Ti to form $TiAl_x$ occurs initially, which further reacts with C to form a more thermodynamically stable TiC [6, 10–12]. In the present study, the Al content is only 20 wt.% and Mg content ranges from 0 to 15 wt.%; therefore, the addition of Mg may dilute Al and influence its function to provide an easier route. It is believed that the increase of Mg content would reduce the mass transfer function of Al [6] in the Al-Ti-C-Mg system. During the SHS reaction, the solid-state reaction between Al and Mg to form $Al_{12}Mg_{17}$ occurs initially; with the increasing of temperature, the $Al_{12}Mg_{17}$ phase, and the unreacted Al and Mg phases will melt to form the Mg containing Al melts, and therefore, the reactions between Al and Ti to form $TiAl_x$, and $TiAl_x$ and C to form TiC are relatively weakened by the presence of Mg atoms in the melts; furthermore, the growth of TiC is also suppressed by the dilution of Mg, resulting in the fine size of TiC particulates.

TABLE I The characteristics of the reagents

Reagent	Size (μm)	Purity (wt.%)
Aluminum	~29	98.00
Titanium	~15	99.50
Graphite	~38	99.99
Magnesium	~106	98.00

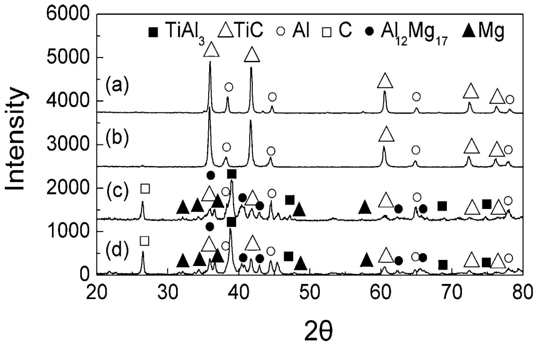

Figure 2 XRD patterns of the SHS reaction products synthesized by green preforms with a molar ratio of Ti:C = 1.0 mixed with 20 wt.% Al, and (a) 0, (b) 5, (c) 10 and (d) 15 wt.% Mg.

In conclusion, the result reveals that besides serving as a diluent, the addition of Mg also participates in the SHS reaction and reacts with Al to form $Al_{12}Mg_{17}$ phase. As the Mg content is increased from 0 to 5 wt.%, the TiC particulate is decreased from $\sim$7.0 to $\sim$3.0 μm in the SHS reaction products. The *in situ* formed master alloy containing Al and Mg, as well as a large volume fraction of fine and spherical TiC particulates is successfully synthesized.

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