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Scripta Materialia 48 (2003) 1349–1354

In situ synthesis of TiC/Mg composites in molten magnesium

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Received 16 August 2002; received in revised form 20 December 2002; accepted 31 December 2002

Abstract

Magnesium reinforced by in situ particulates was synthesized utilizing the self-propagating high-temperature synthesis (SHS) reaction of Al–Ti–C preforms in molten magnesium. The result showed that the preform preheat temperature has a great effect on the SHS reaction. For a preheat temperature of 450 °C, in situ TiC/Mg composite was fabricated successfully.

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Keywords: In situ; Magnesium; Self-propagating high-temperature synthesis reaction; Composites; Temperature

1. Introduction

Recently, a large number of metal matrix composites (MMCs) have been developed for high-performance applications in automotive and aerospace industries [1–6]. For the conventional MMCs, the reinforcing phases were prepared separately prior to the composite fabrication. Thus, the scale of the reinforcing phase is limited by the starting powder size, which is typically of the order of microns to tens of microns and rarely below 1 μm. Other main drawbacks that have to be overcome are the interfacial reactions between the reinforcements and the matrix, and poor wettability between the reinforcements and the matrix due to surface contamination of the reinforcements [1,2,7]. To overcome the inherent problems

that are associated with conventionally processed MMCs, new in situ processing techniques have been developed, in which the reinforcements are synthesized in a metallic matrix by chemical reactions between elements or between element and compound during the composite fabrication [1,6]. Compared to the conventional MMCs produced by ex situ methods, the in situ MMCs exhibit the following advantages: (a) the in situ formed reinforcements are thermodynamically stable at the matrix, leading to less degradation in elevated-temperature service; (b) the reinforcement-matrix interfaces are clean, resulting in a strong interfacial bonding; and (c) the in situ formed reinforcing particles are finer in size and their distribution in the matrix is more uniform, yielding better mechanical properties [2,7].

In the past decade, much of the research has been focused on in situ ceramic particulate reinforced aluminum MMCs due to their potentially low fabrication cost [2,6,8–10], while less work has

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been carried out on magnesium MMCs [7,11]. TiC particulate reinforced MMCs are very interesting because TiC is thermodynamically stable and enhances the hardness and wear resistance of the composites. Unfortunately, research efforts on the processing of in situ TiC particulate reinforced magnesium MMCs are rather limited.

In the present study, the feasibility of synthesis of in situ formed TiC/Mg composites utilizing the self-propagating high-temperature synthesis (SHS) reaction of the preforms consisting of Al, Ti and C powders in molten magnesium was investigated. The main objective was to synthesize in situ TiC particulates in a magnesium matrix. It was expected that the preliminary results could be significant in promoting the development of in situ synthesized magnesium matrix composites.

2. Experimental

The preforms in this work were made from commercial powders of 40 wt.% aluminum (98.0% purity), 48 wt.% titanium (99.5% purity), and 12 wt.% graphite (99.9% purity), all with an average particle size less than 44 μm . Titanium and carbon powders were at a ratio corresponding to that of stoichiometric TiC. After being sufficiently mixed, the powders were pressed into cylindrical preforms (20 mm diameter and 15 mm length) by using a stainless steel die with two plungers. The green preforms were pressed uniaxially at pressures ranging from 70–75 MPa to obtain densities of $75\% \pm 2\%$ theoretical density. The preforms were preheated in a vacuum oven at 300, 450 and 600 $^{\circ}\text{C}$ for 3 h, respectively. About 1 kg of commercial AZ91D magnesium alloy melts were prepared in a graphite crucible in an electric resistance furnace at 760 $^{\circ}\text{C}$ under a SF_6/CO_2 protective atmosphere. Hundred grams of green preforms prepared at 300 and 450 $^{\circ}\text{C}$ were placed in the 1 kg sample of molten magnesium. After about 10 min, the molten magnesium was stirred with a graphite stirrer for 20 min to assist the dispersion of the generated TiC particulates into the molten magnesium. The composite melts were cast into a copper mold to produce ingots of $\Phi 55 \times 100$ mm.

The SHS reaction mechanism of the Al–Ti–C system that occurred in molten magnesium was investigated by the use of water-quenched preform experiments. The interaction between each component in the reactant mixtures of the Al–Ti–C, Al–Ti, Al–C and C–Ti systems was studied by differential thermal analysis (DTA) (Model Rigaku-8150, Japan) and X-ray diffraction (XRD) (Model D8 DISCOVER, Germany). Microstructure and phase of the reacted preforms and composites were investigated by using scanning electron microscopy (SEM) (Model JSM-5310, Japan) and XRD (Model D/Max 2500PC Rigaku, Japan).

3. Results and discussion

When the preform preheat temperature was 450 $^{\circ}\text{C}$, an exothermic reaction in the melts was immediately observed after the addition of the preforms to molten magnesium; when the preheat temperature was 300 $^{\circ}\text{C}$, the reaction in the melts could not occur, and there was a substantial amount of unreacted carbon that floated on the surface of the melts during stirring. Furthermore, a large amount of residue was found in the bottom of the melts after stirring. XRD analysis ($\text{CuK}\alpha$) showed the residue consisted of Ti and Mg. When the preheat temperature was 600 $^{\circ}\text{C}$, the reaction to form TiC in the preforms had occurred in the vacuum oven.

The SHS reaction of the Al–Ti–C system can be ignited by heating the top surface of the preform by passing an electric current through a resistance coil [12,13]; however, the SHS reaction can also be ignited throughout the preform when it is heated to the ignition temperature by heating the entire preform at a constant rate [14]. In the present study, the exothermic reaction of the preform with a preheat temperature of 450 $^{\circ}\text{C}$ was initiated throughout the entire preform by the heat of molten magnesium, and the heat liberated by the reaction can further raise the temperature, facilitating a faster and faster reaction. Thus, it can be considered a SHS reaction with a simultaneous combustion mode.

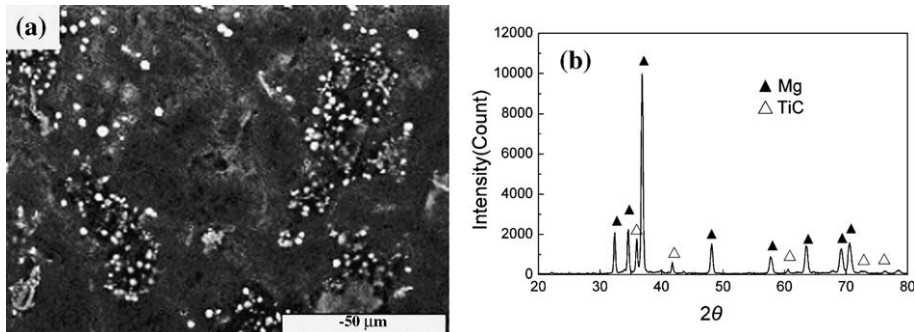


Fig. 1. (a) SEM microstructure of TiC/AZ91D composites fabricated by the SHS reaction of Al–Ti–C system preforms with a preheat temperature of 450 °C and (b) XRD pattern of the composites.

Fig. 1(a) and (b) show the SEM microstructure and XRD pattern of TiC/AZ91D composites fabricated by the SHS reaction of Al–Ti–C system preforms with a preheat temperature of 450 °C. The as-cast microstructure of the in situ processed composites reveals a relatively uniform distribution of TiC particulates with spherical sizes ranging from 0.1 to 1 μm. Because the reinforcement phases were formed in situ in the molten magnesium, the interfaces between TiC particulates and matrix are clean, and the interfacial contact strength may be high. However, several questions still remain about the preheat temperature: (a) why does not the SHS reaction occur in molten magnesium when the preform is preheated to 300 °C? (b) What is the optimum preheat temperature for the SHS reaction? These questions are the subject for further studies in our group.

Fig. 2(a) and (b) show the SEM microstructure and XRD pattern of the Al–Ti–C preform after

preheating at 600 °C for 3 h. The preheat temperature is below the aluminum melting point, therefore, solid–solid interfacial reactions are the important mechanisms for the TiC particulate formation. Solid Al and solid Ti react to form solid TiAl₃, which reacts with carbon to form the more thermodynamically stable TiC [2].

To develop an understanding of the SHS reaction in the Al–Ti–C system in molten magnesium, a water-quench experiment was carried out. When the SHS reaction began, the reacting preform was removed from the molten magnesium and quenched immediately. Figs. 3 and 4 show the SEM microstructures and XRD patterns of the interior and the exterior of the quenched preform, respectively. The XRD analysis indicated that the interior of the preform consisted of TiAl₃, TiAl, TiC, Mg, and residual C, while the exterior of the preform only consisted of TiC, Mg and Al phases, and the TiAl₃, TiAl, and C had disappeared. Based

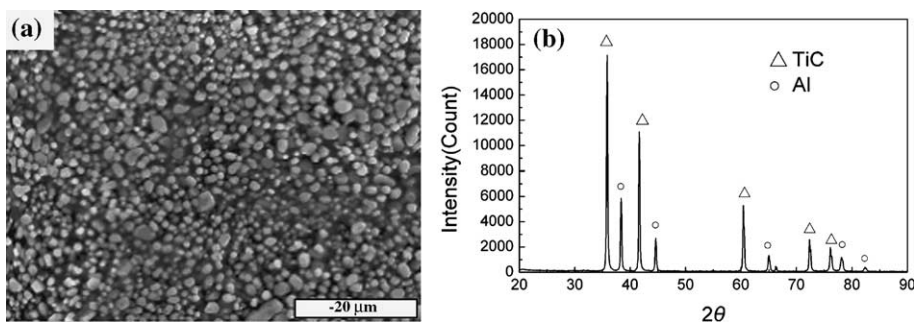


Fig. 2. (a) SEM microstructure of the Al–Ti–C preform with a preheat temperature of 600 °C for 3 h and (b) XRD pattern of the reacted preform.

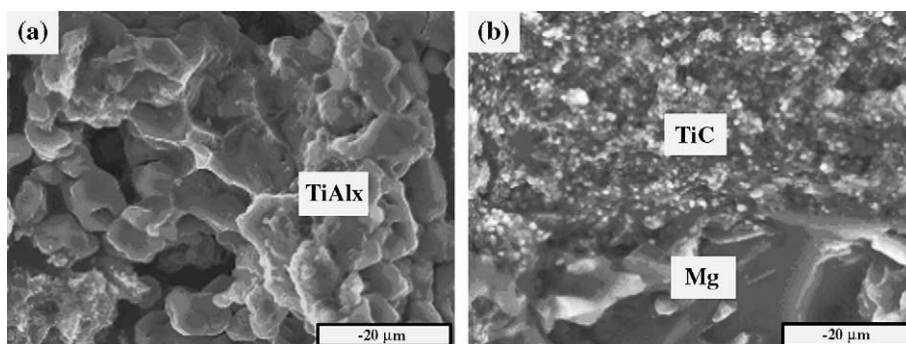


Fig. 3. SEM microstructures of (a) reacting region and (b) reacted region of the water-quenched preform.

on the SEM and XRD results, the interior and the exterior of the preform were named reacting region and reacted region, respectively. The products in the reacting region showed that the reactions between Al and Ti to form titanium aluminides (TiAl_3 , TiAl) in the preform had occurred. In the reacted region, the titanium aluminides had reacted with C to form TiC entirely. The presence of Mg phase in the reacted region in the quenched Al–Ti–C preform (Fig. 4(b)) was attributed to the infiltration and diffusion of the molten magnesium during the SHS reaction process.

To study the interaction between each component in the Al–Ti–C system, 45 mg reactant mixtures with a molar ratio of $\text{Ti}/\text{C} = 1.0$ mixed with 40 wt.% Al, $\text{Al}/\text{Ti} = 3.0$, $\text{Al}/\text{C} = 4/3$, and $\text{C}/\text{Ti} = 1.0$ were heated at $20\text{ }^\circ\text{C}/\text{min}$ to $1000\text{ }^\circ\text{C}$ under argon atmosphere in the DTA apparatus. The

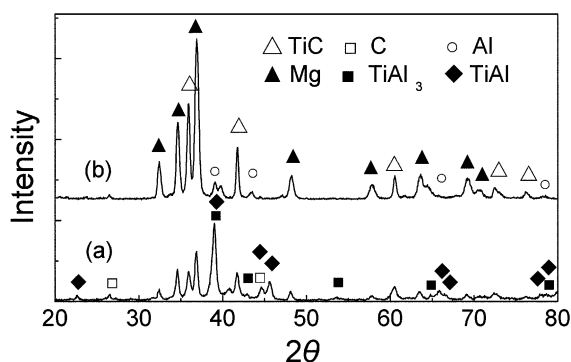


Fig. 4. XRD patterns of (a) reacting region and (b) reacted region of the water-quenched preform.

DTA curves and the XRD patterns of the DTA products are shown in Figs. 5 and 6, respectively. Fig. 5(a) shows only one endothermic peak with the onset at $648\text{ }^\circ\text{C}$ and the minimum at $660\text{ }^\circ\text{C}$, which corresponds to the melting of aluminium. There are two exothermic peaks with maximums at 738 and $756\text{ }^\circ\text{C}$. According to the XRD pattern, the DTA products consist of TiAl_3 , TiAl , TiC , and residual Ti and C, as shown in Fig. 6(a). The peaks correspond to the exothermic reaction between Al and Ti to form titanium aluminide compounds (TiAl , TiAl_3). The reactions between titanium aluminides and C to form TiC were initiated by the heat liberated by the Al–Ti reactions [12,13]. Fig. 5(b) shows only one exothermic peak with its maximum at $756\text{ }^\circ\text{C}$. According to the XRD pattern, the product was TiAl_3 , as shown in Fig. 6(b). Therefore, the peak corresponds to the reaction between Al and Ti to form TiAl_3 . An exotherm corresponding to the solid-state reaction between solid aluminium and solid titanium that formed TiAl_x in the preform was not found in the DTA curve. This is due to a very low rate of heat release to the surroundings. Fig. 5(c) shows only one endothermic peak corresponding to the melting of aluminium, while Fig. 5(d) shows no exothermic or endothermic peak on the curve. The XRD patterns of Fig. 6(c) and (d) show that the products consist of Al and C, and Ti and C, respectively. These indicate that the exothermic reaction between Al and C to form Al_4C_3 , and Ti and C to form TiC had not occurred. The results suggest that the Al–Ti reactions to form ti-

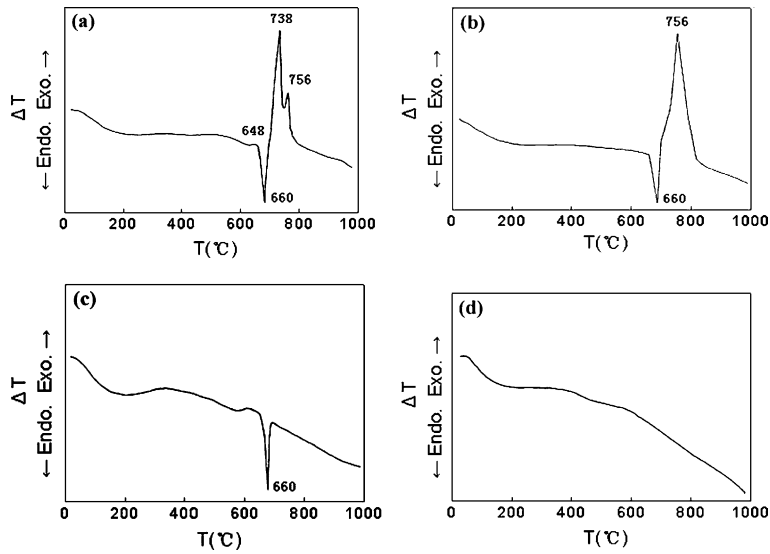


Fig. 5. DTA curves of the mixtures with a molar ratio of (a) Ti/C = 1.0 mixed with 40 wt.% Al, (b) Al/Ti = 3.0, (c) Al/C = 4/3 and (d) C/Ti = 1.0 heated at 20 °C/min under an argon atmosphere.

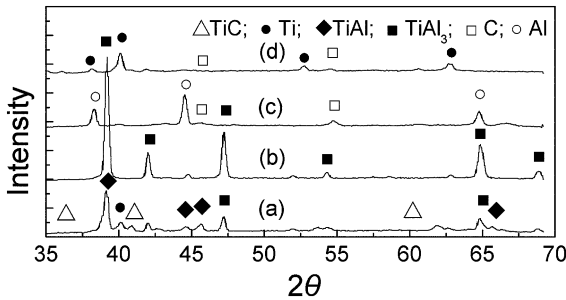
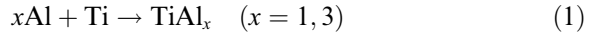


Fig. 6. XRD patterns of mixtures with a molar ratio of (a) Ti/C = 1.0 mixed with 40 wt.% Al, (b) Al/Ti = 3.0, (c) Al/C = 4/3 and (d) C/Ti = 1.0 heated at 20 °C/min under an argon atmosphere.

tanium aluminide compounds are more favourable than Al–C and Ti–C reactions in Al–Ti–C system.

Based on the results, it is believed that aluminum serves not only as a diluent but also as a reactant and participates in the SHS reaction. The addition of aluminum provided an easier route for the TiC formation in the Al–Ti–C system. The SHS reaction mechanism in molten magnesium may be summarized as follows:



More research work is underway to better understand the mechanisms of TiC formation in molten magnesium and to synthesize in situ TiC/Mg composites.

4. Conclusions

In situ formed TiC/Mg composites utilizing the SHS reaction of liquid Mg and preforms consisting of Al, Ti and C powders were synthesized successfully. The result showed that the preform preheat temperature has a great effect on the SHS reaction in molten magnesium.

Acknowledgements

This work is supported by The Natural Science Foundation (no. 50171029) and The Nanoscience Foundation (no. 2001NM004).

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