



Pergamon

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Materials Research Bulletin 38 (2003) 1387–1392

Materials
Research
Bulletin

www.elsevier.com/locate/matresbu

In situ synthesis of TiC from nanopowders in a molten magnesium alloy

H.Y. Wang, Q.C. Jiang*, X.L. Li, J.G. Wang, Q.F. Guan, H.Q. Liang

*Department of Materials Science and Engineering, Jilin University at Nanling Campus,
No.142 Renmin Street, Changchun 130025, PR China*

Received 19 November 2002; received in revised form 21 April 2003; accepted 10 May 2003

Abstract

The synthesis of in situ formed TiC/Mg(ZM5) composite utilizing the exothermic reaction of the preforms consisting of Al, C and Ti powders in molten magnesium was investigated. The result showed that the reactant particle size has a great effect on the reaction. For a nano-size Al and C, and micron-size Ti powders system, in situ TiC/Mg(ZM5) composite was fabricated successfully.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: A. Alloys; A. Composites; D. Microstructure

1. Introduction

In recent years, magnesium alloys are raising more and more interest for the industrial applications due to their relatively low density, high-damping capacity, good castability and mechanicability. However, the low strength, elastic modulus and wear resistance at elevated temperature have restricted their applications as engineering materials [1–3]. Although high strength even at elevated temperatures can be achieved by using cost intensive magnesium alloys, other properties like, e.g. a lower coefficient of thermal expansion, a higher elastic modulus and wear resistance can be realized only by the addition of strong and stiff second phases to magnesium [2–5]. Magnesium matrix composites produced using the various conventional routes sometimes suffer from the thermodynamic instability of interfaces between reinforcement and matrix [6]. Furthermore, the reinforcing phases were prepared separately prior to the composite fabrication. In this case, the scale of the reinforcing phase is limited by the starting powder size, which is typically in the 10–20 μm size ranges [3,4,7–9]. To overcome the limitations of conventional processes, new in situ processing techniques have been developed, in which

* Corresponding author. Tel.: +86-431-5705592; fax: +86-431-5705592.
E-mail address: jiangqc@mail.jlu.edu.cn (Q.C. Jiang).

the reinforcements are synthesized in the magnesium matrix by chemical reactions between elements or between an element and a compound during the composite fabrication. Information related to the fabrication of in situ reinforced magnesium matrix composites, however, is limited [6].

In the present study, the feasibility of the synthesis of in situ formed TiC/Mg(ZM5) composite utilizing the exothermic reaction of the preforms consisting of Al, C and Ti powders in molten magnesium was investigated. The material of interest in this study, TiC, is particularly useful in reinforcement because of its hardness, high-temperature stability and low weight. The main objective of the present study was to synthesize fine TiC particulates in a molten magnesium alloy. It is expected that the preliminary result will promote the development of in situ synthesized magnesium matrix composites.

2. Experimental

Two kinds of preforms with different particle size, as shown in Table 1, were made from commercial powders of 10 wt.% aluminum, 18 wt.% carbon and 72 wt.% titanium. Carbon and titanium powders were at a ratio corresponding to that of stoichiometric TiC. Powder blends were thoroughly mixed dry (no milling media or balls) in a glass jar filled with argon gas by mechanical rotation at 50 rpm for 8 h. Then, the blends were pressed into cylindrical preforms, 20 mm in diameter and 15 mm in length, by using a stainless steel die with two plungers. The green preforms were pressed uniaxially at pressures ranging from 70 to 75 MPa to obtain densities of $75 \pm 2\%$ theoretical density. The preforms were dried in a vacuum dry oven at 100 °C for 3 h to remove any trace of moisture. Commercial ZM5 magnesium alloy, of composition listed in Table 2, was selected as the matrix for the composite. About 1 kg of magnesium alloy melts were prepared in a graphite crucible in an electric resistance furnace at 750 °C under a SF₆/CO₂ protective atmosphere. Sixty grams of the two kinds of prepared preforms with different particle sizes were added into the 1 kg of molten magnesium, respectively. After about 10 min, the molten magnesium was stirred at 600 rpm for 20 min using a graphite impeller to facilitate the incorporation and uniform distribution of the generated TiC particulates in the metallic matrix. The composite melts were cast into a copper mould to produce ingots of Φ 55 mm \times 100 mm.

The interaction between each component in the reactant mixtures of the nanoaluminum–microtitanium, and nanoaluminum–nanocarbon–microtitanium systems was studied by differential thermal analysis (DTA) (Model Rigaku-8150, Japan) and X-Ray diffraction (XRD) (Model D8

Table 1
Particle size of aluminum, carbon and titanium powders

Preform	Aluminum	Carbon	Titanium
I	~50 nm	~50 nm	<15 μ m
II	<29 μ m	<38 μ m	<15 μ m

Table 2
Chemical composition of ZM5 magnesium alloy (wt.%)

Mg	Al	Zn	Mn	Si	Fe	Ni	Cu	Be
Bal.	8.625	0.533	0.265	0.061	0.012	0.002	0.002	<0.001

DISCOVER, Germany). Microstructures and phases of the preform and composite 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 preforms consist of nano-size Al and C, and micron-size Ti powders, an exothermic reaction in the melts was observed immediately after the preforms were added into the molten magnesium; however, when the preforms consist of micron-size Al, C and Ti powders, the reaction in the melts could not occur. The unreacted preform was removed from the molten magnesium and water-quenched immediately.

Fig. 1 shows the SEM microstructure and XRD pattern of the composite fabricated by the exothermic reaction of the preforms consisting of nano-size Al and C, and micron-size Ti powders in molten magnesium. An as-cast microstructure of the in situ processed composite reveals a relatively uniform distribution of spherical TiC particulates with size of $\sim 4 \mu\text{m}$. Because the reinforcement phases were formed in situ in the molten magnesium alloy, the interfaces between TiC particulates and matrix were clean.

Fig. 2a and b show the SEM microstructure and XRD pattern of the water-quenched preform, respectively. The XRD results show that the quenched preform consists of Al, Ti, C and Mg.

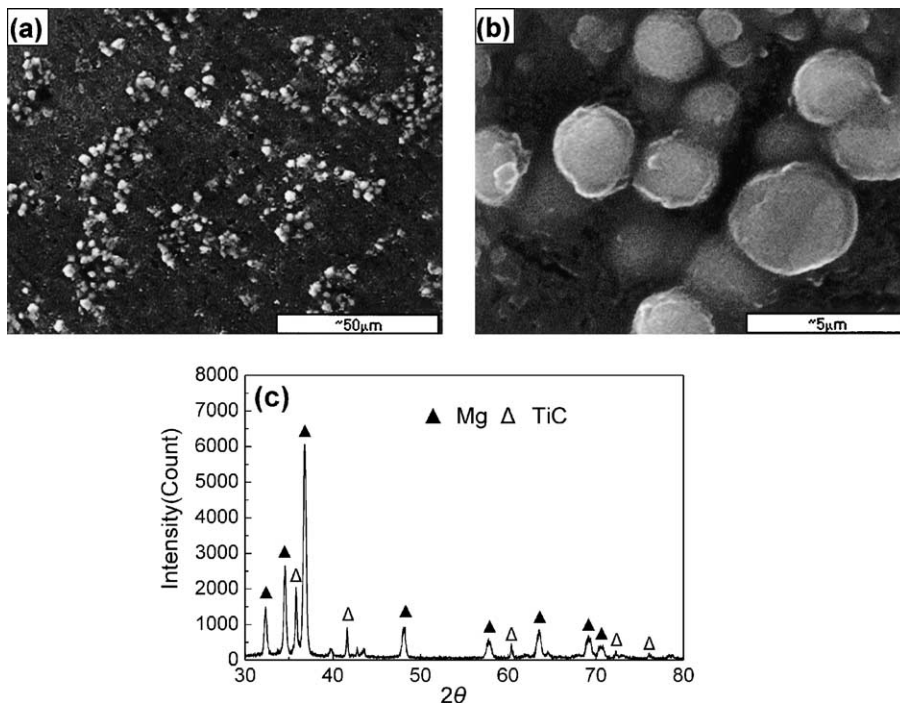


Fig. 1. TiC/Mg(ZM5) composite fabricated by the exothermic reaction of the preforms consisting of nano-size Al and C, and micron-size Ti powders in molten magnesium. (a) SEM microstructure, (b) high magnification of TiC particulates and (c) XRD pattern.

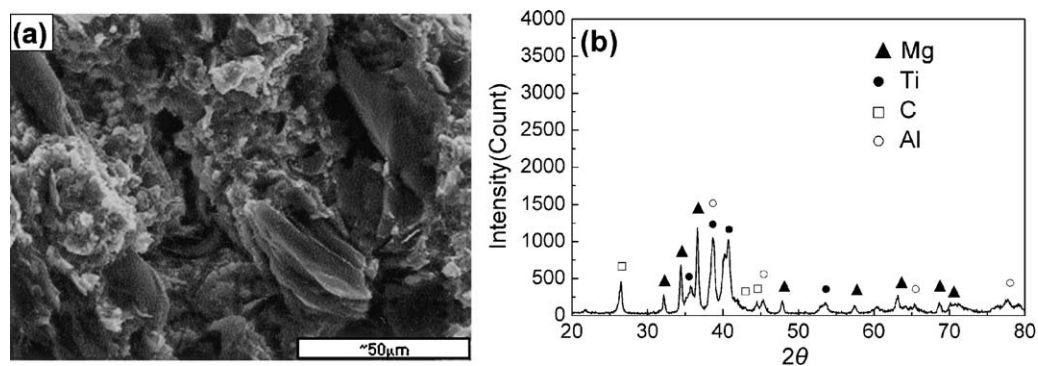


Fig. 2. (a) SEM microstructure and (b) XRD pattern of the water-quenched preform consisting of the micron-size Al, C and Ti powders.

The presence of Mg phase was attributed to the infiltration and diffusion of the molten magnesium into the preform. These indicate that the TiC formation reaction in the preform did not occur. The dot mapping results indicate that the Ti surface is coated with Al and Mg layer. In this case, a slight exothermic reaction between Al and Ti to form titanium aluminides (the $TiAl_x$ could not be detected because of its low density in the XRD analysis) is believed to occur, however, the slight heat liberated by the reaction cannot further initiate the TiC formation reaction.

The surface energy of the nanopowders is higher than that of the micropowders [10], which can be considered as a decrease in activation energy. Furthermore, the contact surface areas of the nanopowders are larger than that of micropowders; consequently, the reaction in the contact areas of the nanopowders is more favourable than that in the contact areas of the micropowders. It may be the main reason that the TiC formation reaction in the preforms consisting of nano-size Al and C, and micron-size Ti powders occur easily, but it can not occur in the preforms consisting of micron-size Al, C and Ti powders.

To study the exothermic reaction of the Al–Ti–C system in molten magnesium, 45 mg of reactant mixtures of the nanoaluminum–microtitanium (with a molar ratio of Al/Ti = 3.0), and nanoaluminum–nanocarbon–microtitanium (with a molar ratio of C/Ti = 1.0 mixed with 10 wt.% Al) were heated at 20 °C/min to about 1000 °C under argon atmosphere in the DTA apparatus, respectively. The DTA curves and the XRD patterns of the DTA products are shown in Figs. 3 and 4, respectively. Fig. 3a shows only one endothermic peak with the minimum at 656 °C, which corresponds to the melting of aluminium. There are three exothermic peaks with maximums at 632, 668 and 716 °C, respectively. According to the XRD pattern, the product was $TiAl_3$, as shown in Fig 4a. It is reasonable to accept that the formation of $TiAl_3$ was favourable though the powder mixtures were rich in Ti since the formation energy of $TiAl_3$ ($-146.935 \text{ kJ mol}^{-1}$) is more negative than that of $TiAl$ ($-74.967 \text{ kJ mol}^{-1}$) [11,12]. Therefore, the three peaks correspond to the reactions between Al and Ti to form titanium aluminides. It is interesting to note that the exotherm of 632 °C was a reaction between solid Al and solid Ti to form solid titanium aluminides. However, the exotherm of 632 and 668 °C corresponding to the reaction to form $TiAl_3$ and $TiAl$, or the reversible, are as yet not clear. It is the subject for further studies in our group. Fig. 3b shows only one exothermic peak with the maximum at 632 °C. According to the XRD pattern, the DTA products consist of Ti, TiC , Al and residual C, as shown in Fig. 4b.

The only one peak corresponds to the TiC formation reactions. However, with mixtures of nanoaluminum–nanocarbon, and nanocarbon–microtitanium systems, no exotherm was observed in the

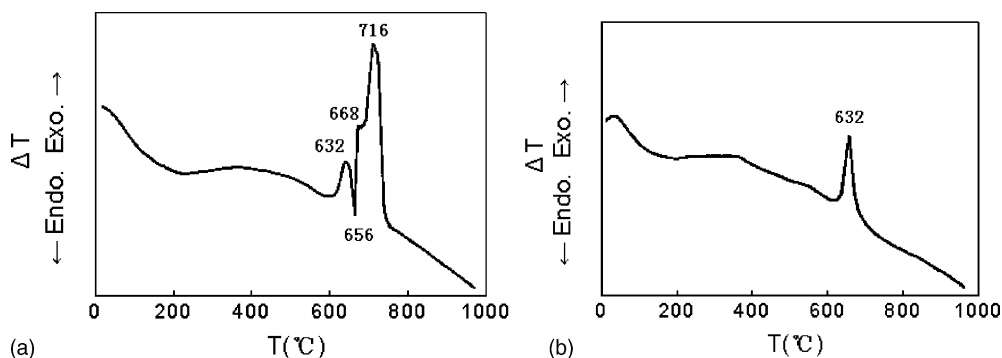


Fig. 3. DTA curves of the mixtures of (a) the nanoaluminum–microtitanium (with a molar ratio of Al/Ti = 3.0) and (b) nanoaluminum–nanocarbon–microtitanium (with a molar ratio of C/Ti = 1.0 mixed with 10 wt.% Al) heated at 20 °C/min under an argon atmosphere.

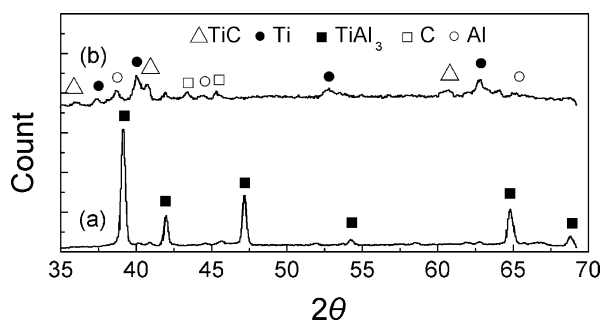


Fig. 4. XRD patterns of the mixtures of (a) the nanoaluminum–microtitanium (with a molar ratio of Al/Ti = 3.0) and (b) nanoaluminum–nanocarbon–microtitanium (with a molar ratio of C/Ti = 1.0 mixed with 10 wt.% Al) heated at 20 °C/min under an argon atmosphere.

DTA curves. These indicate that any exothermic reaction between Al and C, or between C and Ti, did not occur. The results also suggest that the Al–Ti reactions to form titanium aluminides are more favourable than Al–C and C–Ti reactions in Al–Ti–C system.

Based on the experimental results, the TiC formation mechanisms in the nano-size Al and C, and micron-size Ti powders system were as follows: The reactions between solid Al and solid Ti to form solid titanium aluminides occurred initially; as the temperature increases, Al melts and reacts with Ti to form titanium aluminides; the reactions between titanium aluminides and C to form a more thermodynamically stable TiC are subsequently initiated by the heat liberated by the Al–Ti reactions.

Undoubtedly, more research work is underway to better understand the mechanisms of TiC formation in molten magnesium and to synthesize high quality in situ TiC/Mg(ZM5) composites.

4. Conclusions

An in situ TiC particulate reinforced magnesium matrix composite is successfully synthesized utilizing the exothermic reaction of the preforms consisting of nano-size Al and C, and micron-size Ti

powders in molten magnesium. The TiC particulate in the cast composite was fine and spherical, with a size of $\sim 4 \mu\text{m}$.

Acknowledgements

This work is supported by the Natural Science Foundation of China (No. 50171029) and Nanoscience Foundation of Jilin University (No. 2001NM004). The authors wish to thank National Lab of Superhard Materials, Jilin University, for providing us with nanopowders.

References

- [1] S.F. Hassan, M. Gupta, *Mater. Res. Bull.* 37 (2002) 377–389.
- [2] M. Zheng, K. Wu, C. Yao, *Mater. Lett.* 47 (2001) 118–124.
- [3] S.C.V. Lim, M. Gupta, *Mater. Res. Bull.* 36 (2001) 2627–2636.
- [4] A. Luo, *Metall. Mater. Trans. A* 26A (1995) 2445–2455.
- [5] M. Zheng, K. Wu, C. Yao, *Mater. Sci. Eng. A* 318 (2001) 50–56.
- [6] M.A. Matin, L. Lu, M. Gupta, *Scripta Mater.* 45 (2001) 479–486.
- [7] Y. Cai, M.J. Tan, G.J. Shen, H.Q. Su, *Mater. Sci. Eng. A* 282 (2000) 232–239.
- [8] Y. Cai, D. Taplin, M.J. Tan, W. Zhou, *Scripta Mater.* 41 (9) (1999) 967–971.
- [9] S.F. Hassan, M. Gupta, *J. Alloy. Compd.* 345 (2002) 246–251.
- [10] A. Sanfeld, A. Steinchen, *Surf. Sci.* 463 (2000) 157–173.
- [11] F. Zhang, L. Lu, M.O. Lai, *J. Alloy. Compd.* 297 (2000) 211–218.
- [12] K.P. Rao, J.B. Zhou, *Mater. Sci. Eng. A* 338 (2002) 282–298.