

Study on In situ Synthesis of TiC Particle Reinforced Iron Matrix Composite

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A casting penetration technology combined with in situ synthesis is applied to produce a TiC particle reinforced iron matrix composite. The interface between reaction zone and matrix is in good quality and no defects are found. The TiC particles in the reaction zone are fine with the average size of 2-5 μm , which may be beneficial for the interface quality and reinforcing effect. Analysis shows the growth of TiC particles is mainly controlled by the diffusion of carbon atoms.

Keywords composite, diffusion, in situ synthesis, TiC particle

1. Introduction

Composites are a leading candidate for applications where a good combination of strength and plasticity is required. Among all kinds of composites, ceramic particle reinforced metal matrix composites have excellent wearability, corrosion resistance, and high temperature creep resistance. Up to now, the methods of producing ceramic particle reinforced metal matrix composites include common powder metallurgy, conventional melting, and casting as well as some subsequently developed technologies [e.g., mechanical alloying associated with heat treatment (Ref 1-6) or laser melting (Ref 7, 8)]. However, in order to obtain desirable microstructure, a series of complicated technological parameters must be considered during optimization of the composites. For example, it is necessary to study the technological parameters for improving the linking performance between ceramic reinforcing phase and metal matrix. Previous study showed that in situ synthesis could be used for the preparation of composites (Ref 6, 7, 9). However, the effect of in situ synthesis on the interface of reinforcing phase and matrix was seldom addressed. In the present work, this effect is focused on. Besides, a casting penetration technology combined with in situ synthesis is put forward. This new technology can not only ensure excellent linking performance between reinforcing phase and matrix, but also provide a simple practical method to produce the composites with excellent properties.

In recent years, particle reinforced iron matrix composites have been a focus within the scope of new materials. Due to fine wettability with liquid iron, TiC particles with high hardness are widely used as the reinforcing phase for iron matrix composites (Ref 10, 11). Nowadays, the preparation

technologies of TiC particle reinforced iron matrix composites mainly include casting method and self-propagating high-temperature synthesis (SHS) (Ref 12-14). However, there exists some limitation for both technologies: the flowability of casting liquid is greatly affected by the volume fraction of TiC and the segregation of TiC is prone to occur during casting; composites produced by SHS cannot be directly used as structural material because of porous microstructure. Therefore, it is very meaningful to seek a proper method of producing TiC particle reinforced iron matrix composites with excellent properties. Fortunately, the simple casting penetration technology combined with in situ synthesis in this study can be used to avoid the above difficulty.

2. Experimental

The raw materials used in this experiment are cast iron and titanium wire, whose compositions are listed in Table 1. Titanium wires with the diameter of 0.7 mm were uniformly fixed at the bottom of the graphite crucible. The initial distance between the wires was set as ~ 2 mm. Then liquid cast iron was poured to the graphite crucible at about 1400 °C and cooled to room temperature, leading to the formation of Ti/Fe composite (hereafter, specimen A). Specimen A in size of $8 \times 8 \times 15$ mm obtained through wire cutting was wrapped with graphite paper and held at 1138 ± 5 °C for an hour in a tube furnace. After cooling to room temperature, specimen B was formed. Argon was used as protection against oxidation during the whole heat treatment. Microscopic observation and composition analysis were made by SEM (JEOL JSM-6301F) after mechanical polishing and etching in 4% nitric acid/alcohol. Phase identification was carried out by x-ray diffractometer (XRD TTR-3). Phase transformations in the tube furnace were characterized by differential thermal analysis (DTA DZ3320A).

3. Results and Discussion

3.1 Microstructure and Morphology Analysis

Figure 1(a) shows the cross section of reaction zone for a single titanium wire. The cross section of reaction zone is in

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Table 1 Composition of raw materials (wt.%)

Raw materials	C	Si	Mn	P	S	N	H	O	Fe	Ti
Cast iron	4.22	0.58	0.268	0.224	0.024	Balance	...
Titanium	0.05	0.10	0.03	0.015	0.10	0.15	Balance

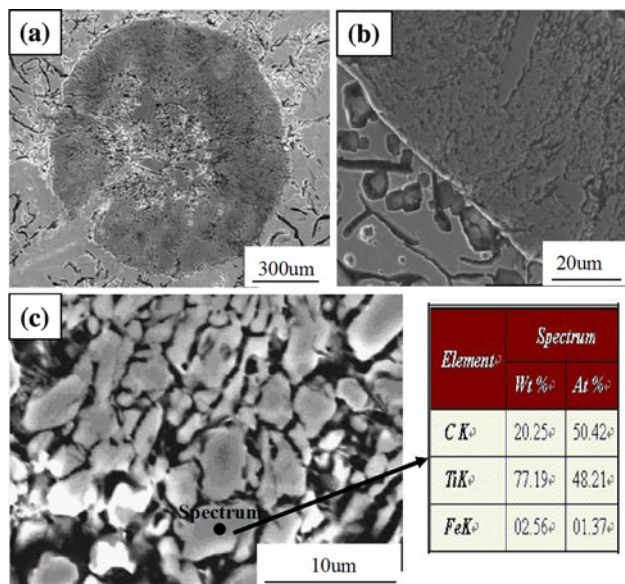


Fig. 1 SEM morphology of (a) the cross section for the reaction zone between a single titanium wire and iron matrix, (b) the interface between the reaction zone and matrix, and (c) particles in the reaction zone

diameter of about 1.3 mm. Figure 1(b) shows the interface between reaction zone and matrix. The interface is in good quality and no defects are found. Particles in nearly equiaxial shape with the size of 2-5 µm distribute in the reaction zone, as shown in Fig. 1(c). From the composition analysis on the point in Fig. 1(c), it is known that the atom rate of Ti:C is about 1:1. Therefore, it is supposed that the particles in the reaction zone are TiC.

Figure 2 exhibits the line scanning composition analysis, from which it can be known that (1) the carbon content within the reaction zone is lower than that in the matrix; (2) Fe diffuses into the reaction zone from the matrix; and (3) a small quantity of Ti can diffuse into the matrix. Notably, mutual penetration between Ti and Fe occurs at the interface between reaction zone and matrix. This may be attributed to the high concentration gradient of Ti and Fe between reaction zone and matrix during isothermal process at 1138 ± 5 °C.

3.2 Thermodynamic Analysis on the In situ Synthesis

During the whole heat treatment process in this study, several main reactions may occur:



The changes of Gibbs free energy ΔG° of the above reactions calculated at 800-1600 °C using thermodynamic data (Ref 15) are shown in Fig. 3(a). It is commonly known that $|\Delta G^\circ|$ affects the driving force of the reactions. A larger $|\Delta G^\circ|$ indicates a stronger driving force and a more stable reaction resultant. From Fig. 3(a), it can be seen that $|\Delta G^\circ|_{\text{TiC}}$ is the largest within the temperature range of 800-1600 °C for the Fe-C-Ti system. Therefore, TiC is the most thermodynamically stable among the above four reaction resultants. Thermodynamic stability of the four resultants, in a descending order, is TiC, Fe₂Ti, FeTi, and Fe₃C.

XRD pattern of specimen B is shown in Fig. 3(b). Only TiC and α-Fe exist in the specimen, which indicates that Ti transforms completely during heat treatment and TiC is finally formed. This is consistent with the above thermodynamic analysis.

3.3 Differential Thermal Analysis

The results of the differential thermal analysis on specimen A are shown in Fig. 3(c). Actually, the analysis process is similar to a simulation for the whole heat treatment process in this article from which we can identify phase transformations in the tube furnace. From Fig. 3(c), it is easily seen that two strong endothermic peaks exist at 755 and 1060 °C; two weak endothermic peaks exist at 1121 and 1131 °C; a strong exothermic peak exists at 1137 °C.

The transformation temperature from α-Fe to γ-Fe for the Fe-C-Ti system could fall within 730-800 °C (Ref 16). Therefore, the endothermic peak at 755 °C may be caused by the allotropic transformation. From Ti-Fe phase diagram, it is known that the eutectic point is about 1085 °C. Therefore, it is supposed that the formation of Fe₂Ti leads to the occurrence of the endothermic peak at 1060 °C. Since XRD pattern of specimen B in Fig. 3(b) identifies the existence of TiC, the formation of TiC from C and Fe₂Ti may be considered as the reason for the occurrence of the strong exothermic peak at 1137 °C. Besides, no Fe₂Ti exists in specimen B, which indicates that Fe₂Ti transforms fully. The endothermic peaks at 1121 and 1131 °C suggest endothermic intermediate reactions caused by some intermediate products such as Fe₂Ti. During the isothermal process at 1138 ± 5 °C, intermediate products may transform to the end product TiC fully. This can be identified by the XRD pattern of specimen B in Fig. 3(b), which shows only the end product TiC and Fe exists in specimen B.

3.4 Analysis on the In situ Synthesis Process

During the whole heat treatment process in the tube furnace, melting does not occur. Therefore, only solid phase reactions take place in the alloy system. The simulated in situ synthesis process is shown in Fig. 4 (denoted by the cross section of a single titanium wire), which can be divided into the following steps:

- (1) During the temperature rising process after specimen A is put into the furnace, carbon atoms in the iron matrix diffuse toward the titanium wire and titanium atoms also

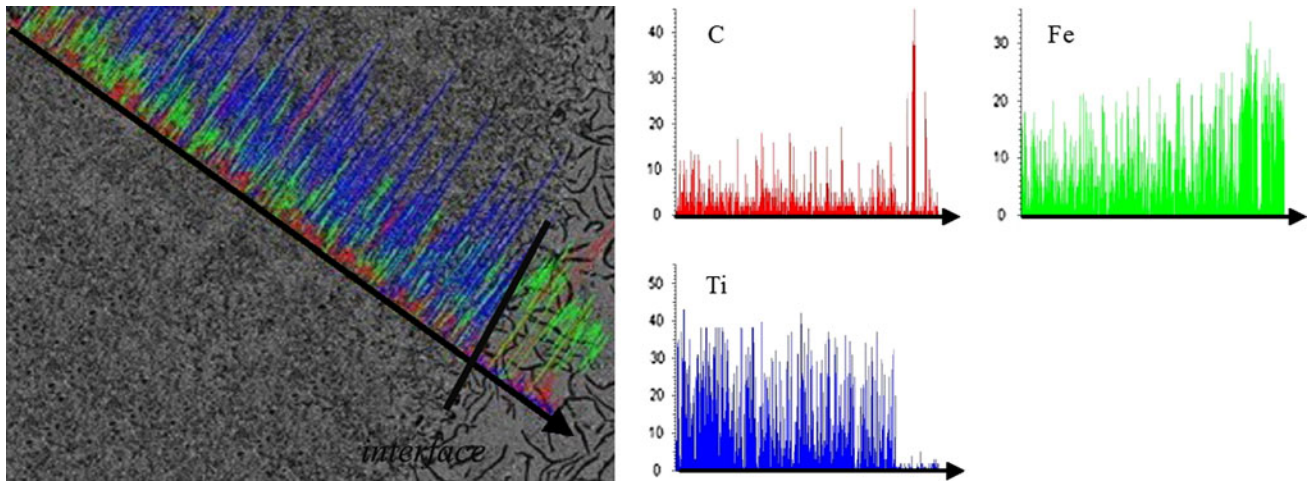


Fig. 2 The line scanning composition analysis from reaction zone to matrix

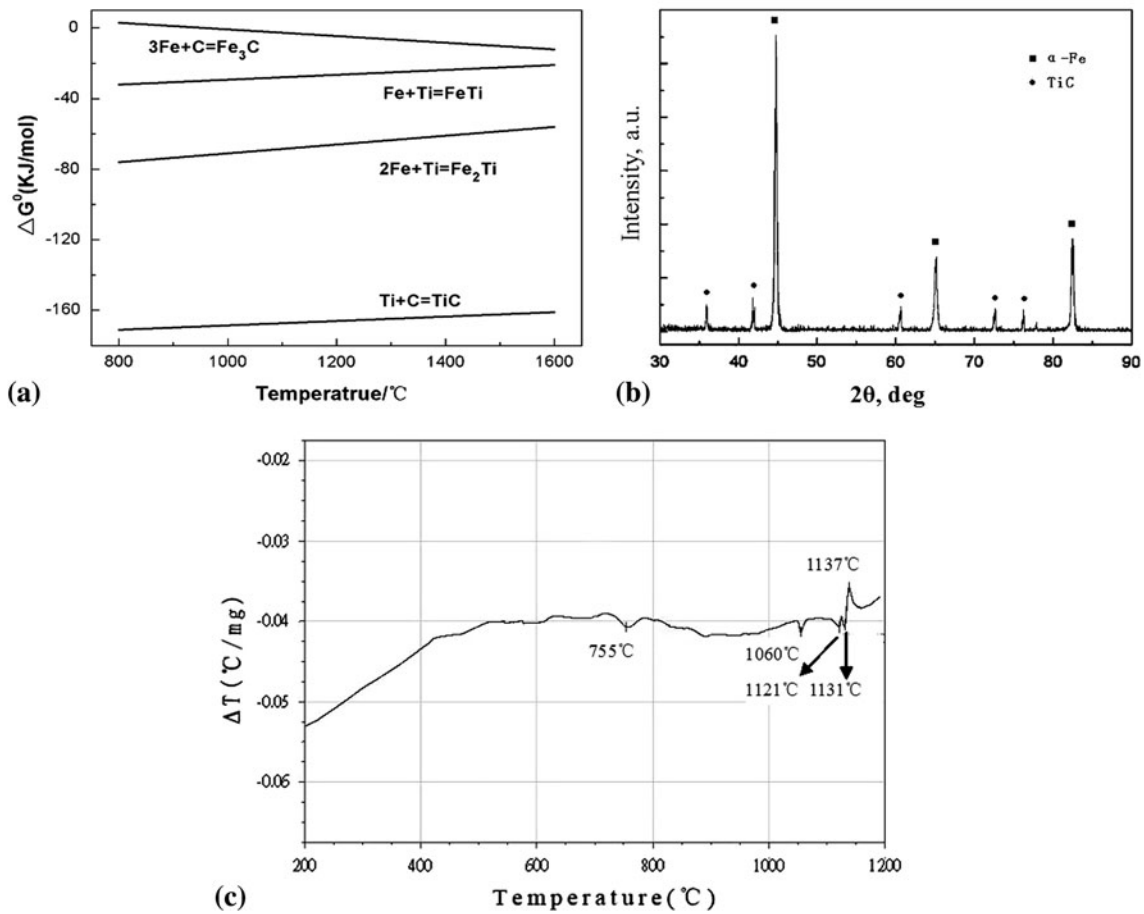


Fig. 3 (a) The ΔG° - T curve of the main reactions during the whole heat treatment process, (b) XRD pattern of specimen B, and (c) the differential thermal analysis result of specimen A

diffuse slowly to the matrix. Due to the relatively low temperature and insufficient diffusion at the beginning, the substance existing state is titanium wire surrounded by iron matrix (as shown in Fig. 4a).

(2) Differential thermal analysis shows that Ti and Fe may form Fe_2Ti when the temperature is enough high (as

shown in Fig. 4b). The formation of Fe_2Ti may accelerate diffusion.

(3) With the continuing rise of temperature, carbon atoms in iron matrix diffuse toward reaction zone very fast and may even react with Fe_2Ti to form TiC_x (as shown in Fig. 4c).

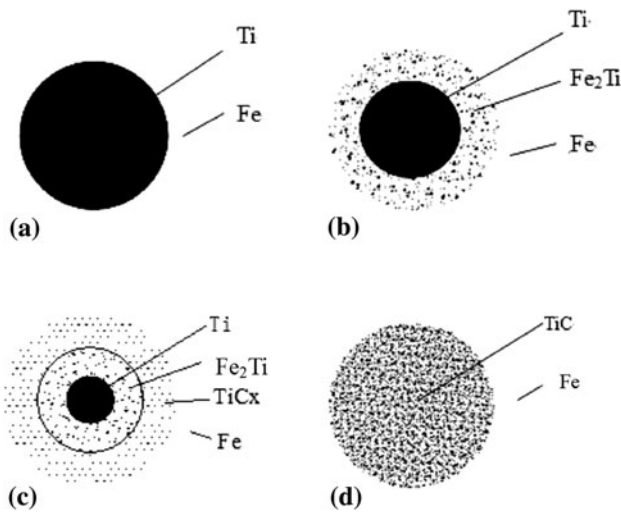


Fig. 4 The simulating scheme of in situ synthesis process

- (4) With all reactions going on, carbon atoms in iron matrix may continue to diffuse toward the reaction zone, leading to the formation of TiC by reacting with TiC_x. Finally, Fe₂Ti disappears (as shown in Fig. 4d).

According to the above analysis, the whole in situ synthesis process is mainly controlled by diffusion. The growth of TiC particles occurs along with the diffusion process. Therefore, the growing rate is slow. As a result, the TiC particles obtained in this technology are relatively fine with the average size of 2-5 μm, in accordance with SEM results in Fig. 1(c).

4. Conclusion

- (1) A TiC particle reinforced iron matrix composite is synthesized by a casting penetration technology combined with in situ synthesis. After the in situ synthesis is completed, the cross section diameter of the reaction zone for a single titanium wire is about twice as large as that of the original titanium wire. The interface between reaction zone and matrix is in good quality and no defects are found.
- (2) The formation of Fe₂Ti occurs during the in situ synthesis process. With carbon atoms continuing to diffuse at high temperature, Fe₂Ti may react with C so that Fe₂Ti disappears and TiC is finally obtained. Thermodynamic

analysis shows that TiC is the most stable reaction resultant.

- (3) TiC particles formed by the casting penetration technology combined with in situ synthesis are relatively fine with the average size of 2-5 μm.

References

1. C. Biseli, D.G. Morris, and N. Randall, Mechanical Alloying of High-Strength Copper Alloy Containing TiB₂ and Al₂O₃ Dispersoid Particles, *Scr. Metall. Mater.*, 1994, **30**, p 1327-1332
2. S.J. Dong, Y. Zhou, Y.W. Shi, and B.H. Chang, Formation of a TiB₂-Reinforced Copper-Based Composite by Mechanical Alloying and Hot Pressing, *Metall. Mater. Trans. A*, 2002, **33A**, p 1275-1280
3. R.H. Palma, A.O. Sepulveda, R.G. Espinoza, A.P. Zuniga, M.J. Dianez, J.M. Criado, and M.J. Sayagues, High-Temperature Mechanical Behaviour of Cu-Ti-C, Cu-Al and Cu-Ti-Al-C Alloys Obtained by Reaction Milling, *Mater. Sci. Eng. A*, 2004, **384**, p 262-269
4. M.T. Marques, V. Livramento, J.B. Correia, A. Almeida, and R. Vilar, Study of Early Stages of Cu-NbC Nanocomposite Synthesis, *Mater. Sci. Eng. A*, 2005, **399**, p 282-386
5. L. Liu, F. Padella, W. Guo, and M. Magini, Solid State Reactions Induced by Mechanical Alloying in Metal-Silicon (Metal=Mo, Nb) Systems, *Acta Metall. Mater.*, 1995, **43**, p 3755-3761
6. G.J. Fan, M.X. Quan, Z.Q. Hu, J. Eckert, and L. Schultz, In situ Explosive Formation of NbSi₂-Based Nanocomposites by Mechanical Alloying, *Scr. Mater.*, 1999, **41**, p 1147-1151
7. D.D. Gu, Z.Y. Wang, Y.F. Shen, Q. Li, and Y.F. Li, In situ TiC Particle Reinforced Ti-Al Matrix Composites: Powder Preparation by Mechanical Alloying and Selective Laser Melting Behavior, *Appl. Surf. Sci.*, 2009, **255**, p 9230-9240
8. S.W. Huang, M. Samandi, and M. Brandt, Abrasive Wear Performance and Microstructure of Laser Clad WC/Ni Layers, *Wear*, 2004, **256**, p 1095-1105
9. X.H. Wang, M. Zhang, Z.D. Zou, S.L. Song, F. Han, and S.Y. Qu, In situ Production of Fe-TiC Surface Composite Coatings by Tungsten-Inert Gas Heat Source, *Surf. Coat. Technol.*, 2006, **200**, p 6117-6122
10. J. Lee, K. Euh, J.C. Oh, and S. Lee, Microstructure and Hardness Improvement of TiC/Stainless Steel Surface Composites Fabricated by High-Energy Electron Beam Irradiation, *Mater. Sci. Eng. A*, 2002, **233**, p 201-259
11. P. Persson, A.E.W. Jarfors, and S. Savage, Self-Propagating High-Temperature Synthesis and Liquid-Phase Sintering of TiC/Fe Composites, *J. Mater. Process. Technol.*, 2002, **127**, p 131-139
12. C. Raghunath, M.S. Bhat, and P.K. Rohagi, In situ Technique for Synthesizing Fe-TiC Composites, *Scr. Metall. Mater.*, 1995, **32**, p 577-582
13. Q.F. Guan, Q.C. Jiang, Y.Q. Zhao, and C.H. Liu, In situ Production of Fe-TiC Composites by Self-Propagative High-Temperature Synthesis Reaction in Liquid Iron Alloy, *ISIJ Int.*, 2002, **42**, p 673-675
14. H. Berns and B. Wewers, Development of an Abrasion Resistant Steel Composite with in situ TiC Particles, *Wear*, 2001, **251**, p 1386-1395
15. D.L. Ye and J.H. Hu, *Thermodynamic Databook of Practical Inorganics*, Metallurgical Industry Press, Beijing, 2002
16. K. Aigner, W. Lengauer, and P. Ettmayer, Interactions in Iron-Based Cermet Systems, *J. Alloys Compd.*, 1997, **262-263**, p 486-491