JOURNAL OF MATERIALS SCIENCE **32** (1997) 4319–4323

# Role of iron addition in the combustion synthesis of TiC–Fe cermet

QUNCHENG FAN
*School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

HUIFEN CHAI, ZHIHAO JIN
*State Key Laboratory for Mechanical Behavior of Materials, Xi'an 710049, People's Republic of China*

Coarse iron powders were incorporated into a mixture of titanium and carbon black powders, and the mixture was used for a combustion front quenching test. The quenched sample was analysed by scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis to study the microstructural evolution in the iron powders. Also, the phase constituent of the combustion-synthesized product was analysed by X-ray diffraction (XRD). The results showed that the microstructural evolution in the iron powders could be described by the solution–precipitation model. Diffusion of carbon into the iron powders brought about a decrease in the melting point of the Fe–C alloy and a melt of the Fe powders, thus accelerating the solution of Ti into the molten droplets; then, TiC particles precipitated out of the saturated droplets. Therefore, it was suggested that iron addition mainly played the role of a source of reaction, i.e. it not only made necessary preparations for the combustion reaction of Ti + C, but also it provided another source for the precipitation of TiC particles.

## 1. Introduction

TiC ceramic has a high hardness and a low toughness, but addition of iron or cobalt can improve the toughness of TiC-metal cermet so that the cermet can be used as cutting, machining and wear resistance materials. Traditionally, the TiC–metal cermet is prepared by liquid-phase sintering of TiC and metal powders.

Recently, the combustion synthesis of TiC–Fe cermet from Ti, C and Fe powders has been studied [1–3]. However, the role of their addition on combustion synthesis is not well known.

Choi and Rhee confirmed that the combustion reaction between Ti and C in a Ti–C–Fe system prevailed, and they suggested that Fe addition mainly served as a diluent and contributed to the binding of TiC grains in the matrix [1]. However, how the Fe powders became the matrix was not established.

Saidi *et al.* [2] investigated the ignition temperature of compacted Fe–Ti–C powder using the thermal explosion mode. The results showed that the heating rate and the titanium particle size did not have a significant effect on the ignition temperature, which was about 1100 °C, when the reacting samples contained up to 80 wt% iron. This ignition characteristic was explained by them as follows. During the heating period, Ti and Fe powders reacted in the solid state to produce $FeTi_2$, which was an eutectic compound having a melting point of 1085 °C. At the ignition temperature, which almost matched the melting point of Fe–Ti alloy, carbon dissolved in the molten droplets of $FeTi_2$ and the subsequent production of TiC released enough heat to initiate a self-sustaining reaction. Also, they examined this model by heating a precompacted mixture of Fe–Ti–C to 1100 °C and quenching the sample just before ignition. SEM inspection of this sample showed some liquid droplets around the iron particles. Because the maximum temperature attained by the sample was well below the melting point of both iron and titanium, it was suggested that diffusion of either carbon or titanium in iron had produced the low melting point phase. Point analysis of these particles, using X-ray fluorescence, confirmed the latter. These experimental results by Saidi *et al.* revealed the microstructural evolution in the sample that had been quenched just prior to thermal explosion. However, the microstructural evolution in the sample and the formation of TiC from $FeTi_2$ during the thermal explosion are not known, because observation of microstructural evolution during thermal explosion is impossible. In fact, the XRD pattern for the sample heated the mixture of Ti + Fe powders up to 1200 °C at the rate of $8\,^{\circ}C\,min^{-1}$ was composed of TiFe, $TiFe_2$, Ti and Fe, but not $FeTi_2$ [1]. In addition, in the mixture of Ti, C and Fe powders, it is impossible that the diffusion of titanium in iron in the solid state to form $FeTi_2$ is faster than the diffusion of carbon in iron.

For the investigation of the role of iron addition on the combustion synthesis of TiC–Fe cermet, the best approach is an observation of the microstructural evolution of iron powders on the sample with a quenched combustion front. For example, a combusting compact in a selfpropagating mode is quenched, thus the initial, intermediate and end reaction products are frozen in the quenched sample, then the microstructural evolution on the quenched sample can be analysed by SEM. By using this combustion front quenching method and SEM, Rogachev *et al.* [4] observed the microstructural evolution successfully during combustion synthesis of TiC: afterwards, Fan *et al.* [5] studied the microstructural evolution in combustion synthesis of TiC and proposed a shell–core model. Also, by using these methods, the effects of iron addition on microstructural evolution during combustion synthesis of TiC were studied [3], and it was found that the combustion reaction between C and Ti took place in the Ti powders and could be described by a ternary-reaction-diffusion model. In that test, however, microstructural evolution in the Fe powders could not be found; probably because the combustion reaction did not take place in the Fe powders, or the Fe powders were too fine ( < 45 μm diameter) to be observed.

In the present work, coarse Fe powders were incorporated into a mixture of titanium and carbon black powders, then the mixture was used for the combustion front quenching test, and the quenched sample was analysed by SEM and EDX. Also, the phase constituent of the combustion-synthesized product was analysed by XRD. Based on these results, a model of the microstructural evolution in the Fe powders was proposed, and the role of iron addition in the combustion synthesis was discussed.

## 2. Experimental procedure

Some 30 wt % iron powders (135–154 μm) were incorporated into a mixture of titanium powders ( < 45 μm) and carbon black (0.033–0.079 μm) with a Ti/C molar ratio of 1.0. Then, the reactants were mixed thoroughly and used for the following tests: (i) the combustion front quenching test, (ii) XRD analysis of the combustion-synthesized product, and (iii) SEM and EDX analyses of the quenched sample. These experimental procedures were identical with those in the literature [5].

## 3. Results

### 3.1. Solution of the carbon and titanium into the iron powders

Fig. 1 shows the morphology of the initial reactants in an unreacted region of the quenched specimen. EDX analyses indicated that the bigger, white particles marked “A” were Fe, and the smaller, grey particles marked “B” around the Fe powder, were Ti, but the carbon black particles could not be found because they were too fine.

Fig. 2 shows the gradual solution of C and Ti into Fe powders. In Fig. 2a, an obvious change is seen in the surface layer “C” of the Fe powder. EDX analyses showed that some carbon and titanium had dissolved in the Fe powder, but the C and Ti contents in the

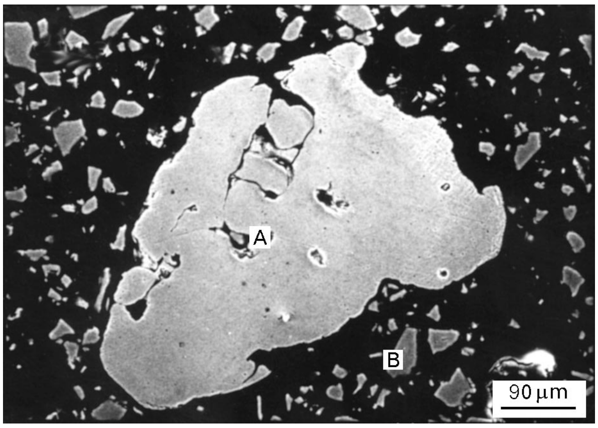

*Figure 1* Scanning electron micrograph of initial reactants in an unreacted zone of the quenched sample.

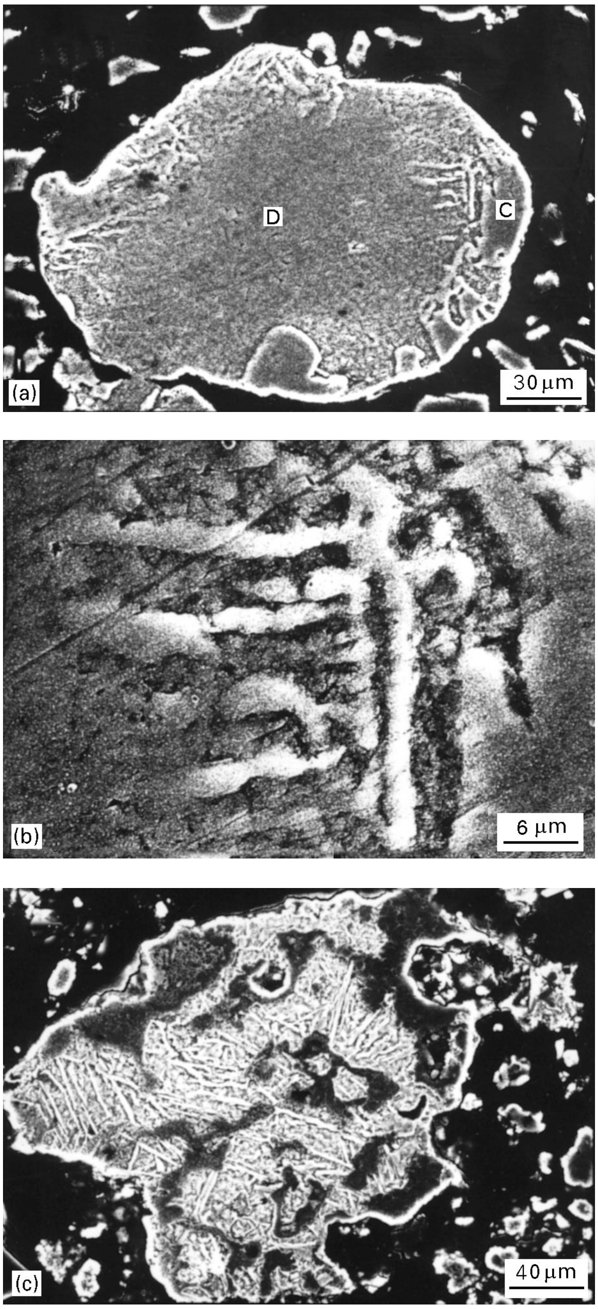

*Figure 2* Scanning electron micrographs of the solution of carbon and titanium into an iron powder: (a) a change in the surface layer “C” of the iron powder caused by the diffusion of carbon, (b) the microstructure of the layer “C” and (c) the solution of titanium in the molten droplet.

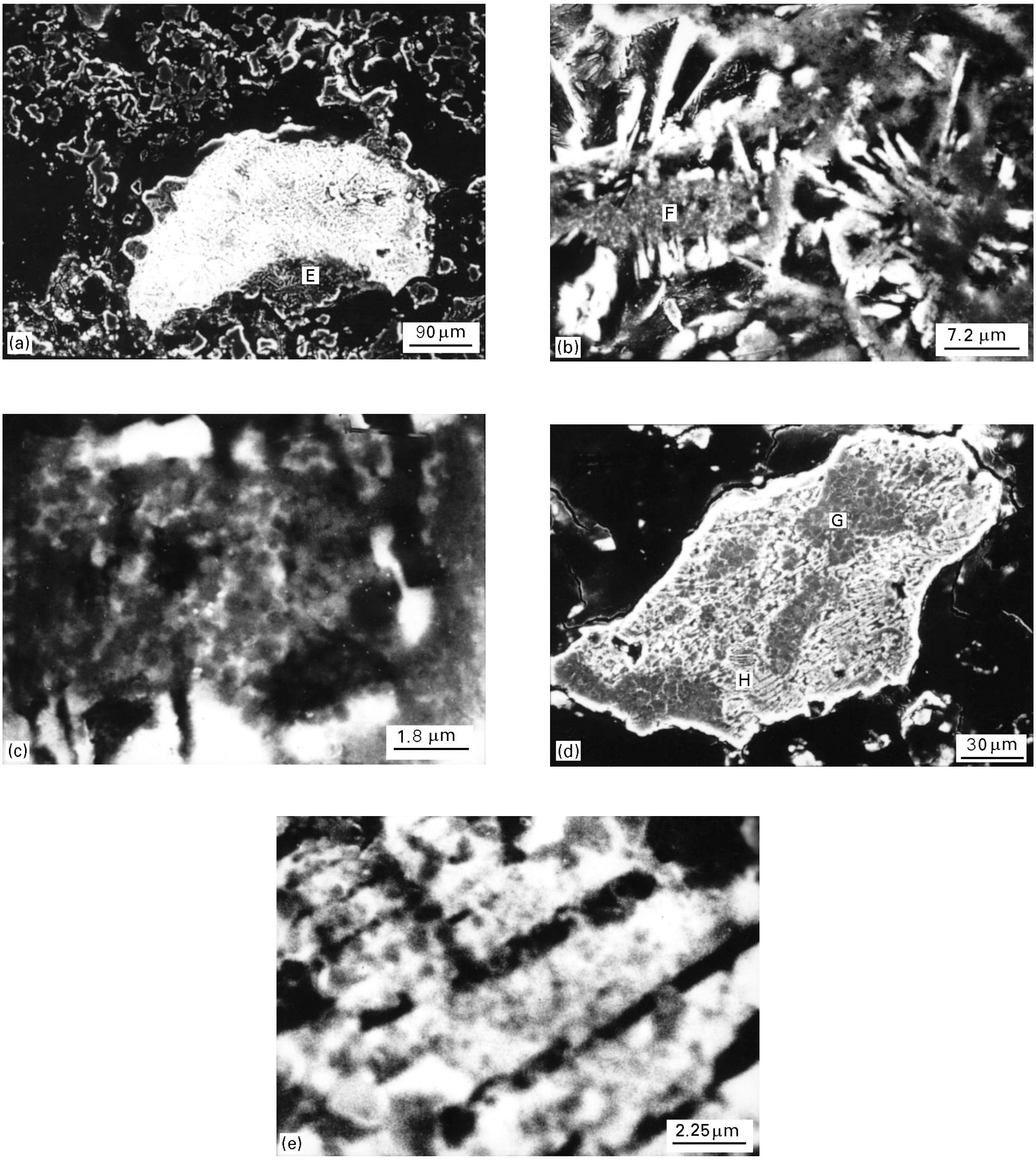

*Figure 3* Scanning electron micrographs of the precipitation of TiC particles in the molten droplet: (a) the precipitation starting from its surface region, “E”; (b) the microstructure of region “E”; (c) the microstructure of region “F” in Fig. 3b; (d) precipitation within the molten droplet; and (e) the microstructure of the region “H” in Fig. 3d.

region “C” (9.58 at % C, 1.01 at % Ti and 89.41 at % Fe) were higher than those in the centre “D” (7.28 at % C, 0.82 at % Ti and 91.90 at % Fe). The microstructure of region “C” is shown in Fig. 2b, which consists of a matrix (7.91 at % C, 0.94 at % Ti and 91.15 at % Fe) and some white twigs (42.63 at % C, 1.12 at % Ti and 56.25 at % Fe) that may be an (Fe, Ti)C compound. Clearly, the above-mentioned change mainly resulted from the diffusion of C into the Fe powder. With increasing temperature and decreasing melting point of Fe powder due to the continuous diffusion of C, the Fe powder gradually melted, as shown in Fig. 2c. In Fig. 2c, some Ti-rich regions (that are grey) are present in the molten Fe droplet, which indicates that the melt of Fe accelerated the solution of Ti into the molten Fe droplet.

## 3.2. Precipitation of TiC particles in the molten Fe droplets

Fig. 3 shows the precipitation of TiC particles in a molten Fe droplet. The precipitation started from the surface region, such as region “E” of the molten Fe droplet in Fig. 3a, and Fig. 3b shows the microstructure of region “E” at a higher magnification. In Fig. 3b, it can be seen that the TiC particles were precipitated in region “F”. The microstructure of region “F” is shown in Fig. 3c, which is composed of an Fe-rich matrix and initial TiC particles with an average diameter of about 0.2 μm. Fig. 3d shows the continuous precipitation and growth of the TiC particles within a molten Fe droplet. In some regions, such as region "G", the TiC particles had grown up to an average diameter of about 2.0 μm, but in other regions, such as region "H", the TiC particles were precipitated. The microstructure of region "H" is shown in Fig. 3e, and it is seen that the initial TiC particles have an average diameter of about 0.2 μm.

### 3.3. Fusing of molten Fe droplets with molten Ti droplets

Fig. 4 shows the fusing of molten Fe droplets with molten Ti droplets. In Fig. 4, the white regions, such as region "I", were Fe-rich where the combustion reaction had not taken place, and the grey regions, such as region "J", were Ti-rich where the combustion reaction had taken place. This fusing benefitted the combustion reaction in the molten Fe droplets because it accelerated interdiffusion between Ti and Fe. Also, it can be seen that a layered structure was formed.

### 3.4. The combustion-synthesized product

The X-ray diffraction pattern indicated, as shown in Fig. 5, that the combustion-synthesized product was composed of TiC and $\alpha$-Fe, thus implying completion of combustion synthesis. However, in a previous study [3], the synthesis was incomplete because a small amount of FeTi phase was retained in the final product.

The macrostructure of the product is shown in Fig. 6a, which is a layered structure composed of the TiC–Fe cermet and pores. The laminae are perpendicular to the propagating direction of the combustion front and have the same shape as the wavefront. The macrostructure is very different from that in the literature [3], where the shape of the pores are arbitrary and their distribution is random. The microstructure of the cermet in the product is shown in Fig. 6b, and it is seen that the TiC particles have an average diameter of about 4.0 μm and they are much bigger than the initial TiC particles.

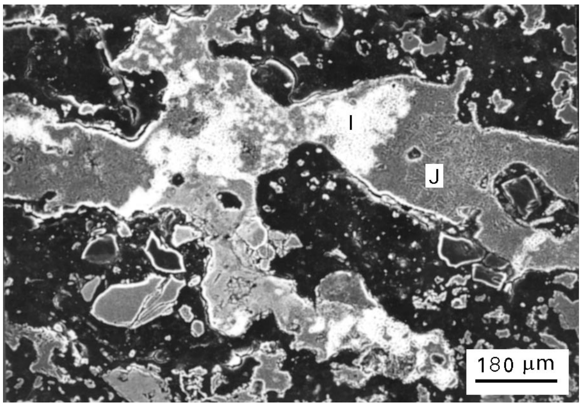

*Figure 4* Scanning electron micrograph of the fusing of molten iron droplets with molten titanium droplets.

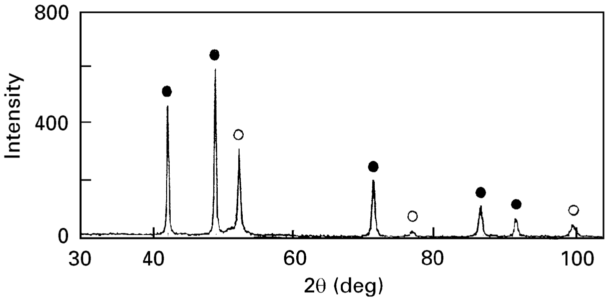

*Figure 5* X-ray diffraction pattern of the combustion-synthesized product: (●) TiC, (○) $\alpha$-Fe.

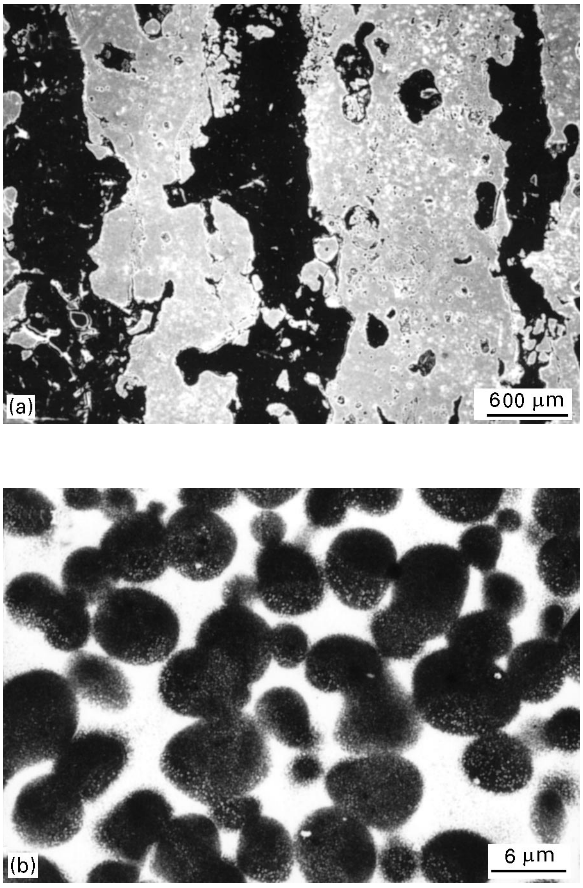

*Figure 6* Scanning electron micrographs of the combustion-synthesized product: (a) the layered structure, and (b) the microstructure.

## 4. Discussion

### 4.1. Model of the combustion reaction in the Fe powders

The above-mentioned microstructural evolution indicates that combustion reaction between Ti and C took place in the Fe particles and could be described by a solution–precipitation model. The diffusion of C into the Fe powders caused the melting point of the Fe–C alloy to decrease, thus leading to a melt of the Fe powders with increasing temperature. Then, the melt accelerated the solution of Ti into the molten Fe droplets, and when the concentrations of C and Ti were saturated, the TiC particles precipitated out of the saturated Fe droplets. However, in a previous work by Saidi *et al.* [2], the melt of Fe droplets resulted from diffusion of Ti in Fe. Perhaps, this difference in the observations of the present work and that of the previous work could be due to the difference in the particle size of the reactants.

It is reasonable to believe that the reaction between Ti and C had taken place in the Ti powders before it did in the Fe powders. First, the diffusion rate of atoms into the body centred cubic (b.c.c.) crystal is higher than that into face centred cubic (f.c.c.) crystal [6]. Ti is a b.c.c. crystal at 882–1667 °C, but Fe is an f.c.c. crystal at 912–1394 °C; and second, the rate of interstitial diffusion is higher than that of substitutional diffusion [7]. Diffusion of C into Ti and into Fe is by the interstitial mechanism, but the diffusion of Ti into Fe occurs by substitutional diffusion. However, in the present work, it was difficult to observe microstructural evolution in the Ti powders because the Ti powders were too fine and the evolution was too fast. Perhaps, the evolution took place by a ternary-reaction-diffusion model, as reported in the literature [3].

In the present work, compared with the previous work [3] where the coarser Ti powders (135–154 μm) and the finer Fe powders ( $< 45$ μm) were used, both completion of the combustion synthesis and the layered structure of the product resulted from an increase in the combustion temperature, which was due to the use of finer Ti powders. It was reported that the combustion temperature and the rate of Ti + C increased significantly with a decrease in size of the Ti powders [8]. Also, it was confirmed by the authors that the combustion temperature of the Fe–Ti–C system increased with decreasing Ti particle size (to be reported). Therefore, although coarse Fe powders were used in the present work, the combustion reaction was still complete because the increase in the combustion temperature accelerated the solution of C and Ti into the Fe powders. Also, the fluidity of the molten Fe and Ti droplets was increased, thus promoting the formation of the layered pores by the removal and collection together of the produced gases into an isothermal layer of the combustion wavefront.

### 4.2. Role of iron addition

Microstructural evolution in the iron powders indicated that the iron addition played not only the role of diluent and binder, but was also the source of the reaction. Iron addition not only made the necessary preparations for the combustion reaction of Ti + C by solution of C and Ti into the Fe powders, but also provided another source for the precipitation of TiC particles.

Choi and Rhee suggested that the major role of Fe was that of diluent and binder in the combustion reaction of the Ti–C–Fe system [1]. Of course, from the point of view of thermodynamics, Ti–C reaction in the Ti–C–Fe system was more favourable than any other reaction. But from the point of view of microstructural evolution, iron addition participated in the combustion reaction because the combustion reaction between Ti and C took place not only in the Ti powders but also in the Fe powders.

Saidi *et al.* postulated that titanium and iron powders reacted in the solid state to produce molten $FeTi_2$ and, then, carbon dissolved in the molten droplets of $FeTi_2$ and TiC formed [2]. As stated in the present study, the melt of Fe powders mainly resulted from the diffusion of C into Fe but not from the formation of $FeTi_2$. This is because diffusion of C was faster than that of Ti into the Fe powder, and diffusion of C allowed the melting point of the Fe–C alloy to be lowered down to a minimum value of 1148 °C.

## 5. Conclusions

1. During the combustion synthesis of TiC–Fe cermet, the microstructural evolution in the Fe powders can be described by a solution–precipitation model. The diffusion of C into the Fe powders leads to a decrease in the melting point of the Fe–C alloy, and the melt of the Fe powders accelerates the solution of Ti into the molten droplets; then, the TiC particles precipitate out of the saturated droplets.

2. In the combustion synthesis, Fe addition not only serves as diluent and binder, what is more, it plays the role of source of the reaction. It not only makes the necessary preparations for the combustion reaction of Ti + C by the solution of C and Ti into the Fe powders, but also it provides another source for the precipitation of the TiC particles.

## References

1. Y. CHOI and S. W. RHEE, *J. Mater. Res.* **8** (1993) 3202.
2. A. SAIDI, A. CHRYSANTHOU, J. V. WOOD and J. L. F. KELLIE, *J. Mater. Sci.* **29** (1994) 4993.
3. Q. C. FAN, H. F. CHAI and Z. H. JIN, *Mater. Sci. Technol.* submitted.
4. A. S. ROGACHEV, A. S. MUKUS'YAN and A. G. MERZHANOV, *Dokl. Phys. Chem.* **297** (1987) 1240 (trans.).
5. Q. C. FAN, H. F. CHAI and Z. H. JIN, *J. Mater. Sci.* **31** (1996) 2573.
6. A. G. GUY and J. J. HREN, "Elements of physical metallurgy" (Addison-Wesley, Reading, MA, 1974).
7. J. D. VERHOEVEN, "Fundamentals of physical metallurgy" (Wiley, NY, 1975).
8. T. S. AZATYAN, V. M. MAL'TSEV, A. G. MERZHANOV and V. A SELEZNEV, *Combust. Explos. Shock Waves* **13** (1977) 156 (trans.).

*Received* 19 *April* 1996
*and accepted* 26 *February* 1997