

Effects of particle size of reactant on characteristics of combustion synthesis of TiC-Fe cermet

QUNCHENG FAN, HUIFEN CHAI, ZHIHAO JIN

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
E-mail: qcfan@263.net

Four Ti-C-Fe powder mixtures, with a same molar ratio but a different particle size, were used for a combustion synthesis of TiC-Fe cermet to investigate effects of the particle size on the characteristics of the combustion synthesis. The results showed that the mixture with the finer Ti powder gave out a higher combustion temperature, a higher reaction velocity, a higher product density, a layer-shaped pore, and a greater size of TiC particles whether the Fe powder was finer or coarser. While in the case of the coarser Ti powder used, a small amount of residual phase remained in the product, and what is more interesting that the mixture with the finer Fe powder gave out a lower reaction velocity than that by the mixture with the coarser Fe powder. These effects were successfully explained with the previously proposed mechanisms of the combustion synthesis of TiC-Fe, and the mechanisms were proved to be valid thereby. © 2002 Kluwer Academic Publishers

1. Introduction

The TiC-Fe cermet has extremely high hardness and toughness. It can be worked by normal machining techniques after annealing and again hardened by subsequent heat treatment before using. The TiC-Fe cermet could be prepared by a liquid-phase sintering of TiC and Fe powders or by a combustion synthesizing from a Ti-C-Fe powder mixture [1–12].

Choi and Rhee [1] investigated the effect of the iron addition on the TiC combustion synthesis, and it was found that the incorporation of Fe (0 to 40 wt%) into the mixture of Ti/C = 1.0 changed the shape of the TiC grains from angular to spherical. Also, the grains were formed not as agglomerated particles, but as isolated particles surrounded by the metal phase. The size of the grain decreased with an increasing amount of the iron addition. Based on the activation energy from the Arrhenius plot, it was postulated that the TiC formation rate was controlled by carbon diffusion into the liquid mixture of Ti-Fe. The authors suggested that the combustion reaction between Ti and C was prevailing in the Ti-C-Fe system. The iron additive mainly served as a diluent and contributed to the binding of TiC grains in a matrix.

For a combustion synthesis of TiC, it has been proved that both the maximum temperature and the propagating velocity of combustion wave decreased as the particle size of Ti powder increased [13]. Maybe the particle size of Ti and Fe powders would affect the characteristics of the combustion synthesis of TiC-Fe cermet, such as the combustion temperature, the reaction velocity, the completeness of the reaction, the density and the phase constituent of the product, the shape and con-

tribution of the pores as well as the particle size of TiC in the product. However, this has not been investigated. In addition, for the combustion synthesis of the TiC-Fe cermet, it has been found that the combustion reaction took place by a dual-dissolution-precipitation mechanism when a finer Ti and a coarser Fe powders were used [12], while when a coarser Ti powder was used the reaction did by a ternary-reaction-diffusion/dissolution-precipitation mechanism whether the Fe powder was coarser or finer [6, 8]. From these mechanisms, it can be deduced that the particle size of Ti and Fe powders would influence the characteristics of the combustion synthesis of TiC-Fe cermet, however this needs to be proved by testing.

In view of the stated above, it is necessary to study the effects of the particle size of reactant on the characteristics of combustion synthesis of TiC-Fe cermet. In the present work, four Ti-C-Fe powder mixtures, with a same molar ratio but a different particle size of the reactant, were used for the following tests: a measurement for the temperature-time profiles of combustion reactions; a measurement for the reaction velocity; an X-ray diffraction (XRD) inspection of the combustion-synthesized products; a measurement for the density of the products; and a scanning electron microscope (SEM) observation of the products. The experimental results were analyzed with the previously proposed mechanisms of the combustion synthesis of TiC-Fe cermet so as to prove the availability of the mechanisms.

2. Experimental

56 wt% titanium powder with two size ranges (135–154 μm and $<45 \mu\text{m}$), 14 wt% carbon black

TABLE I The four Ti-C-Fe powder mixtures and their characteristics of combustion synthesis

| Mixture | Particle size of reactant (μm) | | | T_c (K) | Average velocity of rise in temperature ($\text{K} \cdot \text{S}^{-1}$) | Wave velocity ($\text{mm} \cdot \text{S}^{-1}$) | Phase constituent of product | Density of product (%) | Size of TiC (μm) |
|---------|---|-------------|-----------------|--------------|--|---|------------------------------------|------------------------------|-------------------------------------|
| | Ti | Fe | C | | | | | | |
| 1 | <45 | <45 | 0.033 ~0.079 | 2396 | 1905 | 9.1 | TiC + Fe | 66.8 | 3.6 |
| 2 | <45 | 135 ~154 | 0.033 ~0.079 | 2263 | 1510 | 8.0 | TiC + Fe | 46.5 | 3.5 |
| 3 | 135 ~154 | 135 ~154 | 0.033 ~0.079 | 1926 | 602 | 3.1 | TiC + Fe + Fe_2Ti | 38.2 | 3.2 |
| 4 | 135 ~154 | <45 | 0.033 ~0.079 | 1938 | 315 | 2.0 | TiC + Fe + FeTi | 37.3 | 3.2 |

(0.033–0.079 μm) and 30 wt% iron powder with two size ranges (135–154 μm and <45 μm) were mixed thoroughly to form four Ti-C-Fe powder mixtures with a same molar ratio but a different particle size of the reactants, as listed in Table I.

2.1. Measurement for temperature-time profiles of combustion reactions

The four mixtures were compressed respectively to form a compact (14 mm in diameter and 18 mm in length) with a relative density of about 60%. A small hole (2 mm in diameter and 9 mm in depth) was drilled in the bottom of the compact, and a thermocouple pair of W-3%Re vs. W-25%Re (0.1 mm in diameter) was inserted into the hole and linked with an X-Y recorder, as shown in Fig. 1. The compact was ignited in a reaction chamber by an incandescent flat of graphite placed 2 mm above the top surface of the compact at a pressure of 0.1 MPa of argon at an initial temperature of 298 K. This arrangement allowed recording of a temperature-time profile during the combustion synthesis process.

2.2. Measurement for wave rates of combustion reactions

The four mixtures were compressed respectively to form a bigger compact (18 mm in diameter and 36 mm in length) with a relative density of about 60%. Two pairs of the thermocouples were set against the outside of the compact with the junctions of the thermocouples 20 mm apart from each other in the axial direction of the compact, as shown in Fig. 2. The compact was ignited in the reaction chamber, and two signals of the temperature-time profile were recorded with one X-Y recorder. Thus a propagating rate of the combustion

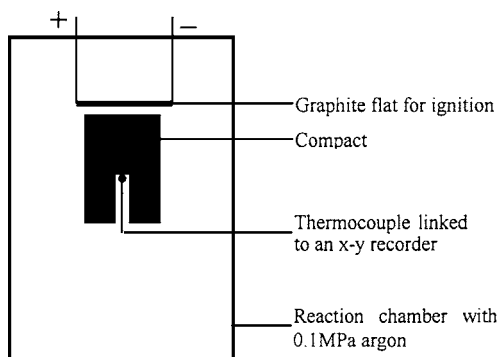


Figure 1 Schematic of the measurement for the temperature-time profile during the combustion synthesis.

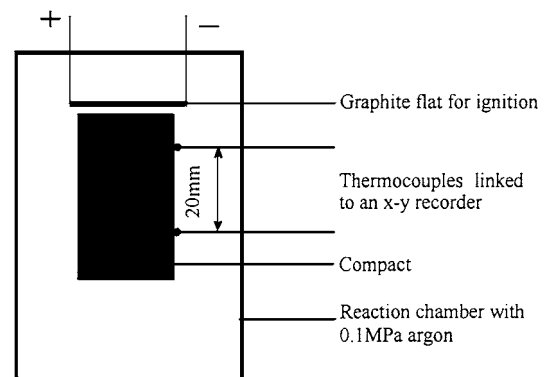


Figure 2 Schematic of the measurement for the wave velocity during the combustion synthesis.

wave could be given out by $\Delta t/20 \text{ mm}$, where the Δt is the time interval between the two profiles.

2.3. Measurement for density of combustion-synthesized products

After the measurement of the wave rates, the density of the combustion-synthesized compacts was measured by using Archimedes' method.

2.4. XRD inspection of combustion-synthesized products

After the measurement of temperature-time profiles, the combustion-reacted compacts were cut longitudinally and inspected by XRD (Co K_α) to study the phase constituent.

2.5. SEM observation of combustion-synthesized products

After the XRD inspection, the combustion-synthesized compacts were prepared as the metallographic specimens and then observed with SEM.

3. Results

3.1. Phase constituent of combustion-synthesized products

The XRD patterns of the combustion-synthesized products are shown in Fig. 3, and it can be seen that in the case of using the finer Ti powder, the product is composed of TiC and α -Fe, as shown in Fig. 3a for mixture 1 and Fig. 3b for mixture 2, whether the Fe powder was finer or coarser. In the case of using the coarser Ti powder, however, a small amount of a residual phase, Fe_2Ti , remained in the product of mixture 3 with the coarser Fe powder, as shown in Fig. 3c, and a small amount of

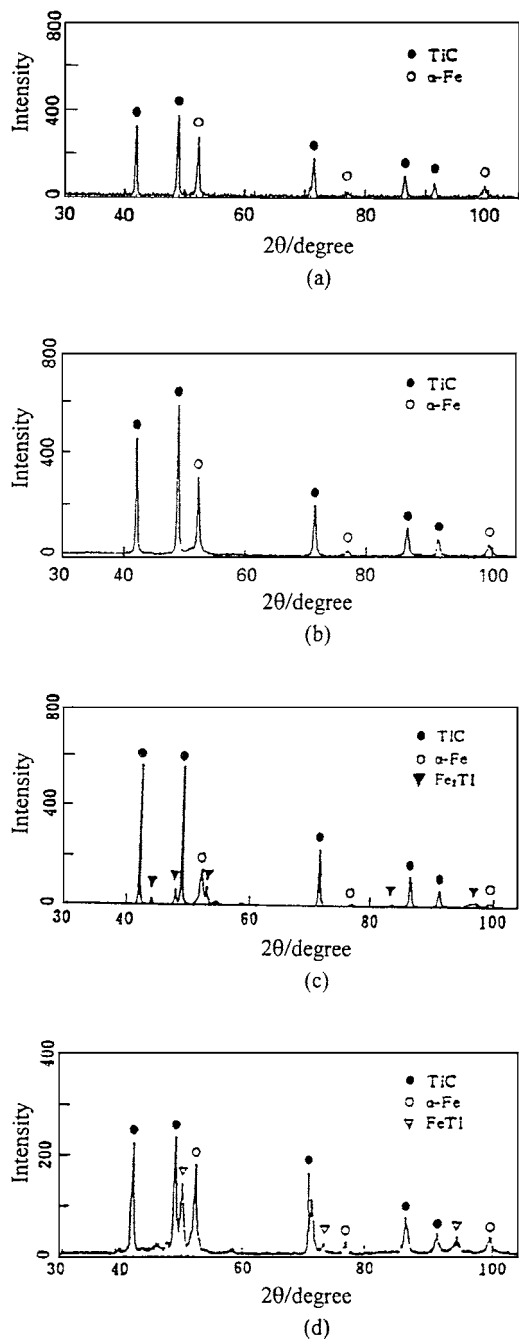


Figure 3 XRD patterns of the combustion-synthesized products of (a) mixture 1, (b) mixture 2, (c) mixture 3, and (d) mixture 4.

a residual phase, FeTi, remained in the product of mixture 4 with the finer Fe powder, as shown in Fig. 3d. The phase constituents of the combustion-synthesized products for the four mixtures are listed in Table I.

3.2. Temperature-time profiles during combustion reactions

Fig. 4 shows the temperature-time profiles during the combustion reactions for the four mixtures. Four exothermic peaks are presented on the four profiles respectively with a maximum temperature (i.e. the combustion temperature T_c) of 2396 K (profile 1 for mixture 1), 2263 K (profile 2 for mixture 2), 1926 K (profile 3 for mixture 3), and 1938 K (profile 4 for mixture 4). Obviously, the mixture with the finer Ti powder gave out a much higher combustion temperature than

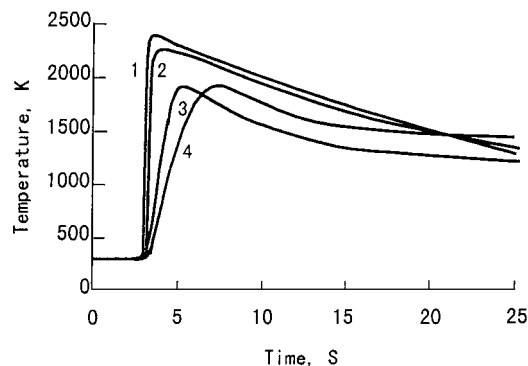


Figure 4 Temperature-time profiles during combustion reaction: profile 1 for mixture 1; profile 2 for mixture 2; profile 3 for mixture 3; and profile 4 for mixture 4.

that by the mixture with the coarser Ti powder, and in the case of the same particle size of Ti powder, the mixture with the finer Fe powder gave out a slightly higher combustion temperature than that by the mixture with the coarser Fe powder. The combustion temperatures for the four mixtures are listed in Table I.

An average rate of rise in the reaction temperature can be calculated from $(T_c - T_0)/\Delta t$, where the T_c is the combustion temperature, the T_0 is the initial temperature of the combustion reaction, and the Δt is the time interval in which the reaction temperature rises to T_c from T_0 . The calculated results are listed in Table I, and it can be seen that the average rate is remarkably higher in the case of using the finer Ti powder than that in the case of using the coarser Ti powder. What is more interesting that, however, the mixture with the finer Fe powder gave out a higher rate than that by the mixture with the coarser Fe powder when the finer Ti powder was used, while the mixture with the finer Fe powder gave out a lower average rate than that by the mixture with the coarser Fe powder when the coarser Ti powder was used.

3.3. Rate of wave propagation

For the effect of the particle size of reactant on the propagating rate of the combustion wave, a similar result to that for the effect on the average rate of rise in the reaction temperature was obtained, as listed in Table I. The rate of wave propagation is much higher in the case of using the finer Ti powder than that in the case of using the coarser Ti powder, and the mixture with the finer Fe powder gave out a higher rate than that by the mixture with the coarser Fe powder when the finer Ti powder was used, while the mixture with the finer Fe powder gave out a lower rate than that by the mixture with the coarser Fe powder when the coarser Ti powder was used.

3.4. Densities of combustion-synthesized products

As shown in Table I, the dependence of the relative density of the combustion-synthesized product on the particle size of the reactant is basically consistent with that of the combustion temperature on the particle size, that is, the mixture giving out a higher combustion temperature gave out a higher relative density.

3.5. Structures of combustion-synthesized products

The macrostructures of the combustion-synthesized products are respectively shown in Fig. 5a for mixture 1, Fig. 6a for mixture 2, Fig. 7a for mixture 3, and Fig. 8a for mixture 4. Although these products consist of the cermet and pores, the shape and distribution of

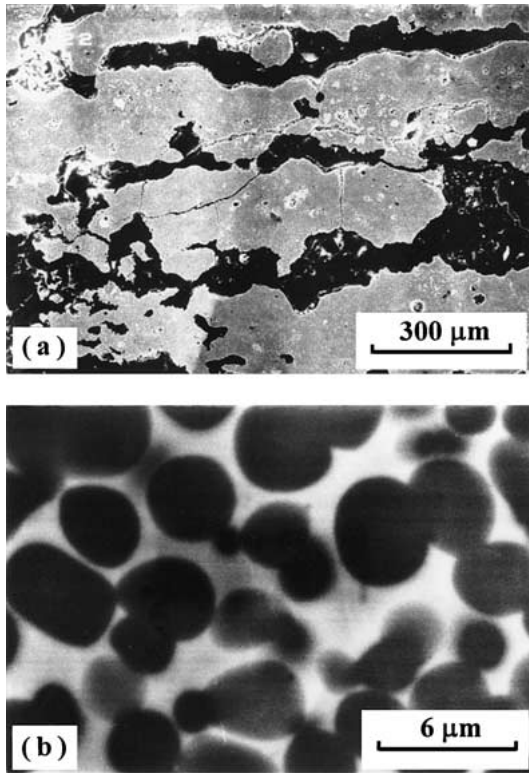


Figure 5 SEM photographs showing the combustion-synthesized product of mixture 1: (a) macrostructure; and (b) microstructure.

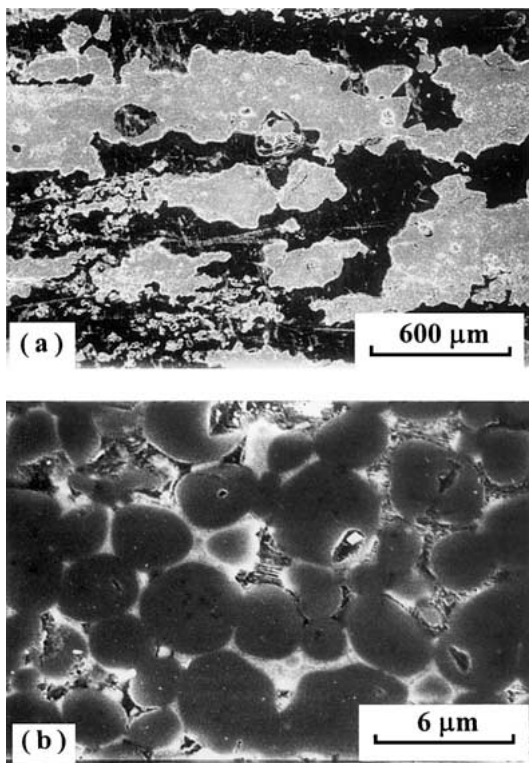


Figure 6 SEM photographs showing the combustion-synthesized product of mixture 2: (a) macrostructure; and (b) microstructure.

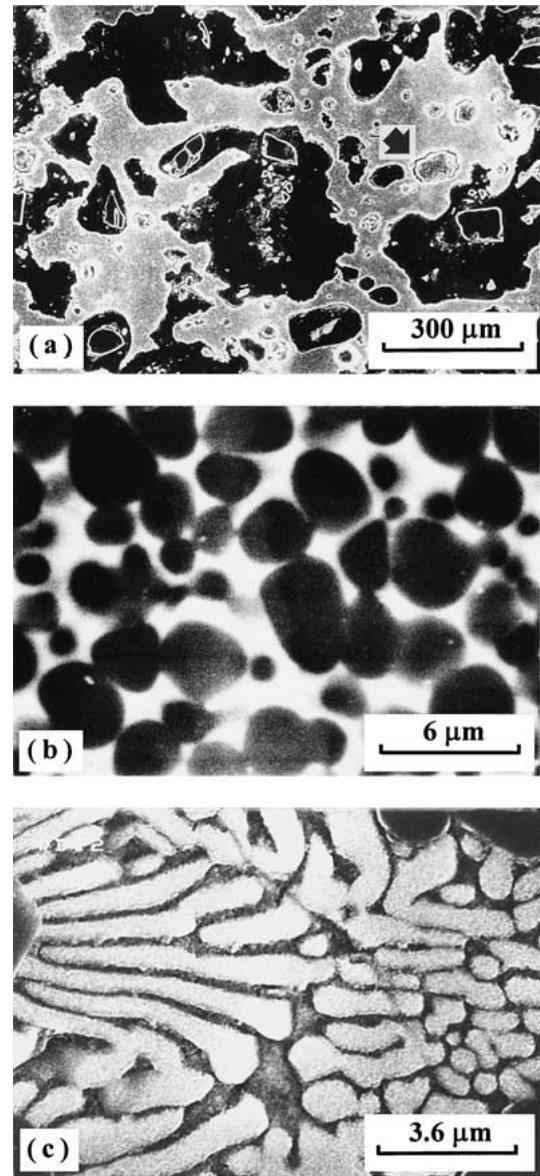


Figure 7 SEM photographs showing the combustion-synthesized product of mixture 3: (a) macrostructure; (b) microstructure; and (c) microstructure of the incomplete reaction zone indicated by an arrow in (a).

the pores are influenced by the particle size of the reactant. Whether the Fe powder was finer or coarser, the pore is layer-shaped in the case of using the finer Ti powder, but the pore distributes randomly in various shapes in the case of using the coarser Ti powder.

The microstructures of the combustion-synthesized products are respectively shown in Fig. 5b for mixture 1, Fig. 6b for mixture 2, Fig. 7b for mixture 3, and Fig. 8b for mixture 4, and the average diameters of the TiC particles are listed in Table I. Although the TiC particles are basically spherical, the average diameter is slightly greater in the case of using the finer Ti powder than that in the case of using the coarser Ti powder, and the dependence of the average diameter on the particle size of the reactant is consistent with that of the combustion temperature on the particle size.

In addition, whether the Fe powder was finer or coarser, some incompletely reacted regions were observed in the combustion-synthesized products with SEM as the coarser Ti powder was used. The energy dispersive spectrometry (EDS) analyses showed that

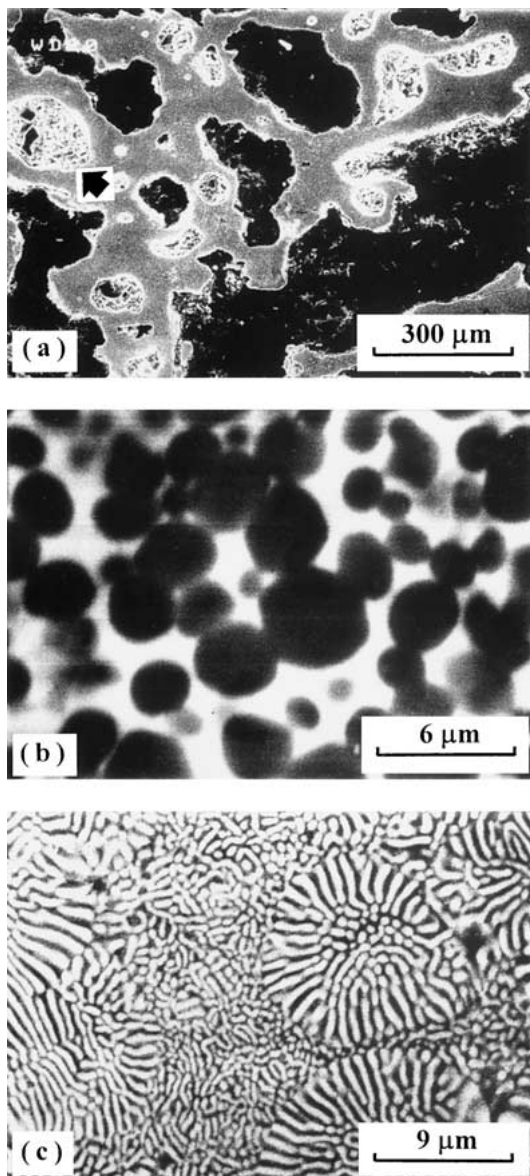


Figure 8 SEM photographs showing the combustion-synthesized product of mixture 4: (a) macrostructure; (b) microstructure; and (c) microstructure of the incomplete reaction zone indicated by an arrow in (a).

the average composition of the region indicated by an arrow in Fig. 7a for mixture 3 is 9.345 at.% C, 17.941 at.% Ti, and 72.714 at.% Fe, which corresponding to a Ti/Fe atom ratio of 19.791/80.209, and the microstructure is shown in Fig. 7c. Clearly, this is a rich-Fe region, and according to the Fe-Ti phase diagram [14], the bright phase (8.712 at.% C, 19.538 at.% Ti, and 71.750 at.% Fe, corresponding to a Ti/Fe atom ratio of 21.403/78.597) is just the TiFe_2 phase in the XRD pattern in Fig. 3c for mixture 3, and the gray structure (12.967 at.% C, 13.780 at.% Ti, and 73.253 at.% Fe, corresponding to a Ti/Fe atom ratio of 15.833/84.167) may be an eutectic structure of TiFe_2 and α -Fe solid solution that is easy to be etched. Of course, both the TiFe_2 and α -Fe phases contain solid-dissolved carbon atoms. Similarly, the region indicated by an arrow in Fig. 8a for mixture 4 is a rich-Ti region (12.378 at.% C, 53.221 at.% Ti, and 34.401 at.% Fe, corresponding to a Ti/Fe atom ratio of 60.739/39.261), and the microstructure is shown in Fig. 8c, in which the bright phase (8.872 at.% C, 49.912 at.% Ti, and 41.216 at.% Fe,

corresponding to a Ti/Fe atom ratio of 54.771/45.229) is just the FeTi phase in the XRD pattern in Fig. 3d for mixture 4, and the gray structure (16.174 at.% C, 58.705 at.% Ti, and 25.121 at.% Fe, corresponding to a Ti/Fe atom ratio of 70.032/29.968) may be an eutectoid structure of TiFe and α -Ti solid solution, but the amount of the α -Ti solid solution was too small to be inspected with XRD.

4. Discussion

4.1. Effects on completeness and temperature of combustion reactions

The XRD inspection and the structural observation of the combustion-synthesized products showed that the phase constituent of the product and the combustion temperature of the reaction were influenced by the particle size of the reactant. In the case of using the finer Ti powder, the combustion reaction was basically complete and gave out a higher combustion temperature thereby whether the Fe powder was finer or coarser. While in the case of using the coarser Ti powder, a small amount of a residual phase, Fe_2Ti , remained in the product as the coarser Fe powder was used, and a small amount of a residual phase, FeTi, remained in the product even if the finer Fe powder was used, and a lower combustion temperature was given out thereby.

The effect stated above can be explained with the mechanism of the combustion reaction. It has been found that in the combustion synthesis of TiC-Fe from Ti-C-Fe mixture, the combustion reaction took place respectively in Ti and Fe particles, and the reaction in Ti occurred earlier than that in Fe [6–8, 12]. In the case of the coarser Ti powder used, the combustion reaction took place by a ternary-reaction-diffusion/dissolution-precipitation mechanism whether the Fe powder was coarser [6] or finer [8], that is, the reaction in the Ti particle occurred in the solid state and by a ternary-reaction-diffusion mechanism, and the reaction in the Fe particle did in the liquid state and by a dissolution-precipitation mechanism. While in the case of the finer Ti powder used, the combustion reaction took place by a dual-dissolution-precipitation mechanism when the coarser Fe powder was used, namely, both the reactions in the Ti and in the Fe particles took place in the liquid state and by a dissolution-precipitation mechanism [12], and it can be deduced that the combustion reaction would occur by the dual-dissolution-precipitation mechanism too when the finer Fe powder was used.

Since the reaction in Ti particle occurred earlier than that in Fe particle, the key to the combustion synthesis lay in the difficult degree of the reaction in the Ti particle. Obviously, the reaction in the finer Ti powder was kinetically more favorable than that in the coarser Ti powder because the former took place in the liquid state and by a solution-precipitation mechanism, but latter did in the solid state and by a ternary-reaction-diffusion mechanism. Therefore, in the case of the finer Ti used, the combustion reactions were basically complete, while in the case of the coarser Ti used, the reactions were incomplete. As for the difference in the residual phases between the mixture 3 and the mixture 4, it is caused by the difference in the particle size

between the Fe powders used. The usage of the finer Fe powder decreased the contact area of the coarser Ti powder with the carbon black, this being not beneficial to the reaction in the Ti particle, thus a residual phase, TiFe, remained in the Ti particle. While the usage of the coarser Fe powder was not helpful to the reaction in the Fe particle so that a rich-Fe residual phase, Fe₂Ti, was remained in the Fe particle.

It is natural that the complete combustion reactions gave out the higher combustion temperatures and the incomplete combustion reactions did out the lower combustion temperatures.

4.2. Effect on velocity of combustion reaction

Both the average rate of the rise in reaction temperature and the rate of the combustion wave propagation indicate the reaction velocity of the combustion synthesis, and the experimental results showed that the dependence of them on the particle size of Ti and Fe is consistent with each other. Because of the liquid-state reaction in the finer Ti particle and the solid-state reaction in the coarser, the mixture with the finer Ti powder gave out a much higher reaction velocity than that by the mixture with the coarser Ti powder. As for the effect of the particle size of Fe powder, it would be related to the participation of the Fe powder in the reaction forming the TiC. In the case of the finer Ti used, since both the reactions in Ti and Fe particles occurred in the liquid state, and the reaction in the finer Fe powder was kinetically more favorable than that in the coarser Fe powder, the mixture with the finer Fe powder gave out a higher reaction velocity than that by the mixture with the coarser Fe powder. While in the case of the coarser Ti powder used, the reaction in the Ti particle took place in the solid state, and the reaction in the Fe particle did in the liquid state, and what is more important that, the finer Fe powder caused the reaction in the Ti particle more difficult due to a decrease in contact area of the Ti powder with the carbon black, so the mixture with the finer Fe powder gave out a lower reaction velocity than that by the mixture with the coarser Fe powder.

4.3. Effect on combustion-synthesized products

The experimental results showed that the particle size of the reactant obviously affected the density of the combustion-synthesized product, the shape and distribution of the pore, and the size of the TiC particle in the product. The size of the TiC particles is mainly controlled by the combustion temperature, therefore the effect of the particle size of the reactant on the size of the TiC particles is consistent with that on the combustion temperature, the mixture giving out a higher combustion temperature would give out a greater size of the TiC particles. In addition, Holt and Munir [15] have proved evolution of a substantial amount of gas during the combustion reaction of TiC. A portion of the evolved gas would escape out of the sample, but the other remains in the sample due to a high combustion rate and tends to gather together to reduce the free en-

ergy of the system. The amount of the gas remaining in the sample is related to the fluidity and the combustion temperature of the product in the wavefront. A recent research [11] on a formation of pore in TiC-Fe cermet prepared by the combustion synthesis showed that the remained gas tended to gather into the wavefront and formed the layer-shaped pore with a same shape as the wavefront. An alternately laminar structure of TiC-Al₂O₃ ceramic and pores was also observed by Bowen and Derby [16]. In the present work, the finer Ti powder gave out a higher combustion temperature and a higher fluidity of the product in the wavefront, on one hand, this being beneficial to the escaping of the evolved gas so as to give out a higher density of the product, on the other hand, this being helpful to the gathering of the remained gas into the wavefront so as to form the layer-shaped pore with the same shape as the wavefront. While the coarser Ti powder gave out a lower combustion temperature and hence the pore with the arbitrary shape and random distribution.

5. Conclusions

1. The characteristics of the combustion synthesis of TiC-Fe cermet are obviously influenced by the particle size of the reactant, and the effects can be explained with the previously proposed mechanisms of the combustion synthesis, and the mechanisms are proved to be valid thereby.

2. In the case of the finer Ti powder used, the combustion reaction occurs by a dual-dissolution-precipitation mechanism so as to be complete and give out a higher combustion temperature, while in the case of the coarser Ti powder used, the combustion reaction does by a ternary-reaction-diffusion/dissolution-precipitation mechanism so that it is incomplete and gives out a lower combustion temperature.

3. Because of the liquid-state reaction in the finer Ti powder and the solid-state reaction in the coarser Ti powder, the mixture with the finer Ti powder gives out a higher reaction velocity than that by the mixture with the coarser Ti powder. In the case of the finer Ti powder used, the liquid-state reaction in the finer Fe powder is kinetically more favorable than that in the coarser Fe powder, so the mixture with the finer Fe powder gives out a higher reaction velocity than that by the mixture with the coarser Fe powder. While in the case of the coarser Ti powder used, the finer Fe powder caused the solid-state reaction in the Ti particle more difficult due to a decrease in contact area of the Ti powder with the carbon black, so the mixture with the finer Fe powder gives out a lower reaction velocity than that by the mixture with the coarser Fe powder.

4. Giving out a higher combustion temperature and a higher fluidity of the product in the wavefront, the mixture with the finer Ti powder gives out a combustion-synthesized product with a higher density, a greater size of the TiC particles, and a layer-shaped pore with the same shape as the wavefront.

Acknowledgements

We gratefully acknowledge the support of this work by the Doctorate Foundation of Xi'an Jiaotong University.

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*Received 18 September 2001
and accepted 30 January 2002*