Dual-solution-precipitation mechanism of combustion synthesis of TiC-Fe cermet with fine Ti powder

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A Ti-C-Fe powder mixture with a finer Ti powder was used for a combustion front quenching test to investigate the effect of titanium particle size on the mechanism of the combustion reaction, and the microstructural evolution in the quenched specimen was then observed with scanning electron microscopy, and the combustion temperature was also measured. The results showed that the nature of the combustion reaction could be described with a dual-solution-precipitation mechanism and a correspondent model. The melting of the finer Ti particle prior to its reaction was attributed to a combined effect of two factors: a decrease of its size-controlled melting point, and a decrease of its composition-controlled melting point. The use of the finer Ti powder led to a more complete combustion reaction and hence a higher combustion temperature. As a result, the combustion-synthesized TiC-Fe cermet had a greater average size of TiC particles and layer-shaped pores that was confirmed to be a consequence of gathering of the evolved gases into the combustion wavefront.
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1. Introduction

TiC-Fe cermets are very attractive because of its high hardness and toughness attributes. In addition, it can be annealed so as to be worked by normal machining techniques and can also be hardened by subsequent heat treatments. Traditionally, the TiC-Fe cermet is fabricated by liquid-phase sintering of TiC and Fe powders. Recently, the TiC-Fe cermet has been prepared by a combustion synthesis from Ti, C, and Fe powders, and the mechanism of the combustion synthesis of TiC-Fe cermet has been investigated by means of various methods [1–4], including a combustion front quenching method (CFQM). By this CFQM, a combustion front that is self-propagating in a compact of reactant powders is quenched, thus, the mechanism of the combustion reaction can be revealed by a microstructural observation of the sample with the quenched combustion front. The CFQM was used first by Rogachev *et al.* [5] for observation of structure transitions in the gasless combustion of titanium-carbon and titanium-boron systems, henceforth, it was used by Lebrat *et al.* [6] for investigating mechanism of combustion syntheses of Ni_3Al and Ni_3Al-matrix composites. Recently, the CFQM is improved and used for investigating mechanisms of combustion synthesis of TiC [7] and TiC-Fe [4] by Fan *et al.* In the study of combustion synthesis of the TiC-Fe [4], 56 wt% coarse titanium powder (135–154 μm diameter), 14 wt% carbon black (0.033–0.079 μm diameter) and 30 wt% coarse iron powder (135–154 μm diameter) were used, and the com-

bustion reaction of the mixture was found to proceed with a ternary-reaction-diffusion/solution-precipitation mechanism, that is, the reaction in the Ti particle took place in the solid state by a ternary-reaction-diffusion mode, whereas the reaction in the Fe particle occurred in the liquid state by a solution-precipitation mode. However, it has been demonstrated experimentally that a small size of a reactant would lead to the increases in both the combustion temperature and rate and a decrease in the activation energy for combustion reaction [8]. Then, the mechanism of combustion synthesis of the TiC-Fe cermet may be affected by use of a finer Ti powder. In the present work, therefore, a Ti-C-Fe mixture with a finer Ti powder was used for investigating the effect of titanium particle size on the mechanism of combustion synthesis of the TiC-Fe cermet.

2. Experimental

56 wt% titanium powder (<45 μm diameter), 14 wt% carbon black (0.033–0.079 μm diameter) and 30 wt% iron powder (135–154 μm diameter) were mixed thoroughly. The mixture was used for the following tests: (1) a measurement of the combustion temperature; (2) an X-ray diffraction (XRD) inspection of the combustion-synthesized product; (3) a combustion front quenching test; and (4) scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analyses of microstructural evolution of the quenched sample. These experimental procedures are identical with those in a previous work [4].
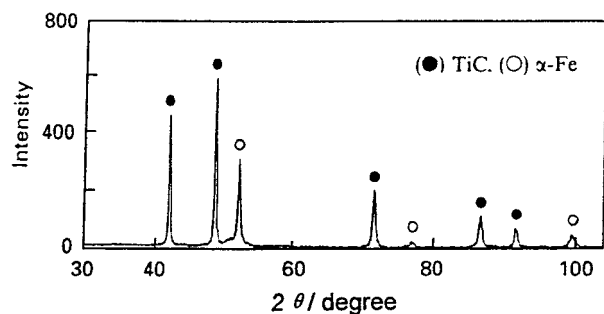
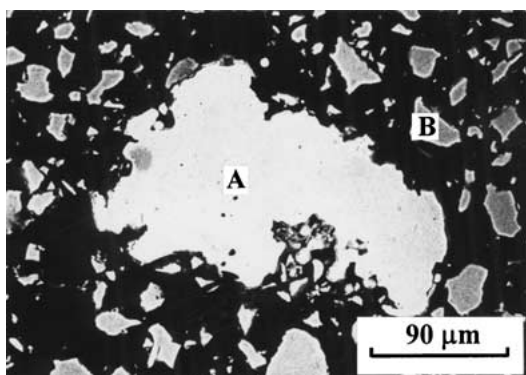*Figure 1* XRD pattern of the combustion-synthesized product.

Figure 2 SEM photograph of the initial reactants.

3. Results
3.1. Combustion temperature and phase constituent of the synthesized product

The measured combustion temperature is 2263 K, which is higher than that (1926 K) for the case of the use of coarser Ti powder [4]. Fig. 1 shows the XRD pattern of the combustion-synthesized product, which consists of TiC and α-Fe. However, a small amount of a residual phase, $TiFe_2$, existed in the final product in the case of the coarser Ti powder used [4].

3.2. Microstructural evolution

Microstructural observation results showed that the quenched sample could be divided into three zones: an unreacted zone, a reacting zone, and a reacted zone. Fig. 2 shows an SEM photograph of the reactants in the unreacted zone. The EDS results indicated that the bright particle "A" was Fe, and the gray ones such as "B" were Ti, but the carbon black particles were too fine to be found.

In the reacting zone, the combustion reaction took place, respectively, in Ti particles and in Fe particles, and the former was earlier that the latter, this was identical with that in a previous work [4].

Fig. 3 shows the sequence of the stages of reaction in a Ti particle. A Ti particle that just started changing is shown in Fig. 3a, and a crack could be seen at the interface between the central region "C" and the surface region "D" of the Ti particle. The appearance of the crack implies a fusion of the surface region "D" because this fusion just resulted in a difference in volume contraction between these two regions so as to form the crack as the Ti particle cooled. The microstructure of the central region "C" is shown in Fig. 3b, and its average composition was determined as 84.86 at%Ti, 6.76 at%C, and 8.38 at%Fe. Fig. 3c shows the microstructure of the surface region "D" with an average composition of 81.20 at%Ti, 17.03 at%C, and 1.77 at%Fe, which is not significantly different from the microstructure in Fig. 3b, but this type of microstructure is not understood yet. The much higher carbon content in the region "D" than region "C" probably resulted from a faster solution of C than Fe into the molten region "D". Fig. 3d shows a formation of TiC particles in the Ti droplets such as "E", its microstructure shows in Fig. 3e. The EDS analysis showed that the gray particles such as "F" were TiC ones that contained a small amount of Fe atoms (Fe/Ti atom ratio of 15.80/84.20) and had an average diameter of about 1.5 μm. Each of the TiC particles was surrounded by a laminated structure that composed of two phases perpendicular to the surface of the TiC particle, a gray phase being the same as the TiC, and a white one having a Fe/Ti atom ratio of 44.30/55.70 and a small amount of C. According to the Ti-Fe phase diagram [9], the white phase was FeTi compound. Apparently, the laminated structure is a eutectic that consists of TiC and FeTi. Thus it could be suggested that the TiC particles formed after melting of the Ti particle and by precipitating out of the saturated Ti-C-Fe liquid solution. Consequently, the process of the reaction between Ti and C in Ti particle should include the melting of Ti particle, the solving of C and Fe into the molten Ti droplet, and the precipitating of the TiC particles out of the saturated Ti-C-Fe liquid solution. This process is significantly different from that [4] for using the coarser Ti powder, where the reaction in Ti particle took place in the solid state by a ternary-reaction-diffusion of C and Fe into the Ti particle to form TiC particles and a Ti-rich binder.

At the same time, a diffusion of C into Fe particle caused a decrease in melting point and melting of the Fe, accelerating solving of Ti into the molten Fe droplet, and the TiC particles precipitated out when the Ti-C-Fe solution was saturated. Reacting Fe droplets fused with the reacted Ti droplets, this accelerated the interdiffusion between Fe and Ti atoms and promoted the accomplishment of the combustion synthesis. These processes are identical with those [4] for using the coarser Ti powder. However, the combustion-synthesized product was markedly different from that [4] for using the coarser Ti powder. The former is composed of TiC-Fe cermet and layer-shaped pores, the TiC particles having an average diameter of about 3.6 μm, and these layered pores being perpendicular to the axis of the cylindrical compact, as shown in Fig. 4. Whereas in the latter, a small amount of a residual phase, $TiFe_2$, was inspected, those TiC particles had a smaller average diameter of about 2.5 μm, and those pores randomly distributed in various shapes.

4. Discussion
4.1. Melting of Ti particle

In the case of using the finer Ti powder, the melting of the Ti particle prior to its reaction is mainly because the finer Ti particle has a lower melting point than that of the coarser one. On the one hand, the finer particle has a
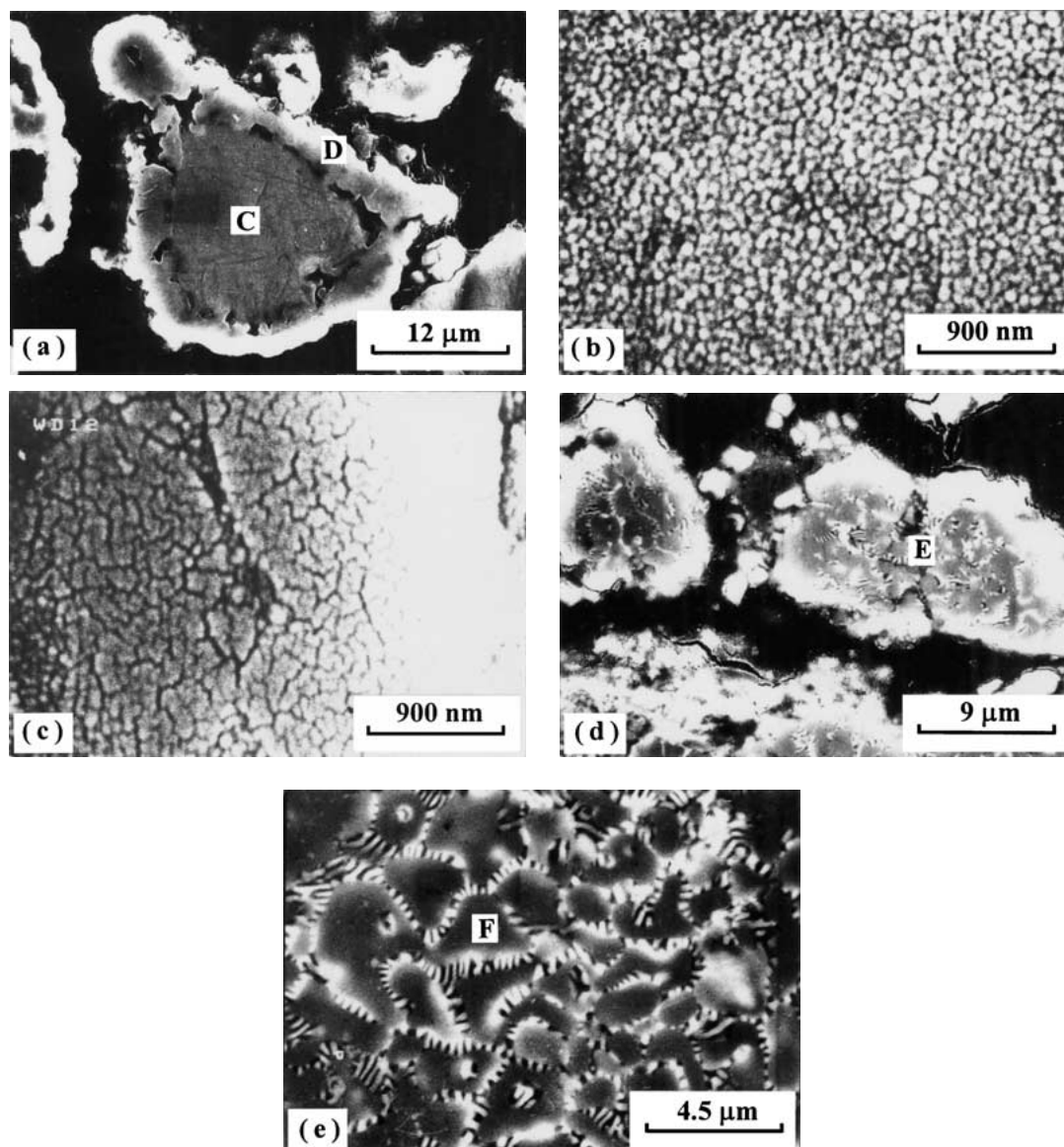
Figure 3 SEM photographs of the reaction in Ti particle: (a) melting of the surface region "D" of the Ti particle; (b) the microstructure of the central region "C" of the Ti particle in (a); (c) the microstructure of the surface region "D" of the Ti particle in (a); (d) a formation of the TiC particles in the Ti droplet "E"; and (e) the microstructure of the Ti droplet "E" in (d).

greater specific surface area, this accelerating the diffusion of C and Fe into the Ti particle so as to result in a fast decrease in the composition-controlled melting point of the Ti particle. According to the phase diagrams of Ti-C and Ti-Fe [9], the diffusion of C into Ti leads the melting point of Ti to a minimum of $1645°C$ at 4.4 at%C, and the diffusion of Fe into Ti decreases the melting point of Ti to a minimum of $1085°C$ at 29.00 at%Fe. On the other hand, it is more important that the melting point of the finer particle has a small-size effect [10], that is, the finer particle has more specific surface atoms and hence a higher surface energy and activation, resulting in a decrease in the size-controlled melting point of the particle with decreasing particle size.

4.2. Mechanism and model
Based on the observations of the microstructural evolution, the combustion synthesis of the TiC-Fe cermet from the mixture with the finer Ti powder could be described by a dual-solution-precipitation mechanism. The reaction between Ti and C took place, respectively, in Ti and Fe particles, and the reaction in the Ti particle occurred prior to that in the Fe particle and by a solution-precipitation mode, and the reaction in the Fe particle took place by a solution-precipitation mode too. A schematic drawing of a model corresponding to the dual-solution-precipitation mechanism is shown in Fig. 5.

4.3. Combustion-synthesized product
The decrease in size and the melting of the Ti particle were beneficial to the diffusion and solution of Ti into the Fe particle (and subsequent Fe droplet). Thus even the central region of the Fe droplet became saturated so that the TiC particles also precipitated out of the central region. Consequently, no residual phase was remained in the final product. This complete reaction made the higher combustion temperature and hence the greater size of the TiC particles.

As for the layer-shaped pores, the possible two causes should be considered. The one is the residual tension stress in the reactant compact due to it was compressed
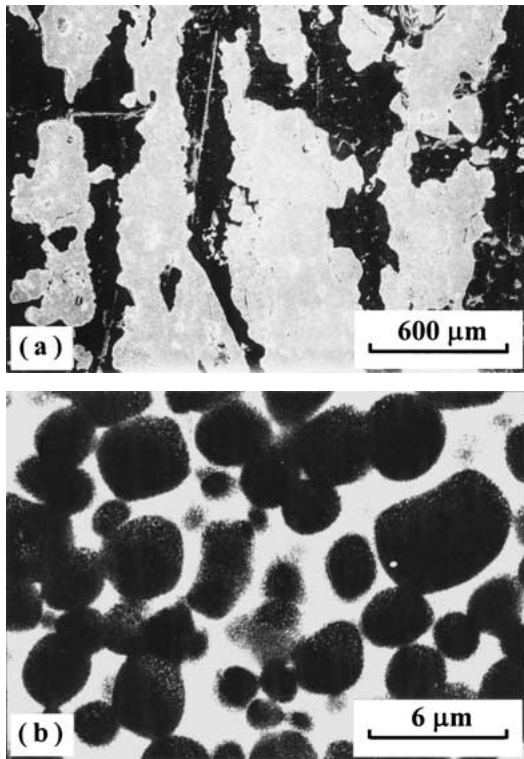
Figure 4 SEM photographs of the combustion-synthesized product: (a) a macrostructure; and (b) a microstructure of the TiC-Fe cermet.

Figure 6 A supplementary test for distinguishing the cause of forming the layer-shaped pores: (a) a schematic diagram of the test; (b) a schematic diagram of the layer-shaped pores in the cut sample in (a); and (c) an optical micrograph of the sample in (b).

in the direction parallel to the axis of the cylindrical compact. The other one is the combustion wavefront propagating in a plane-shaped form. However, the mode of the ignition at the top surface of the compact made
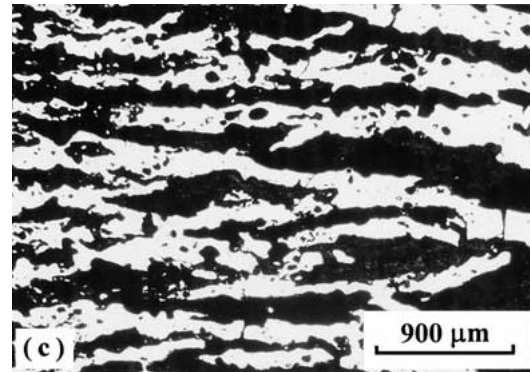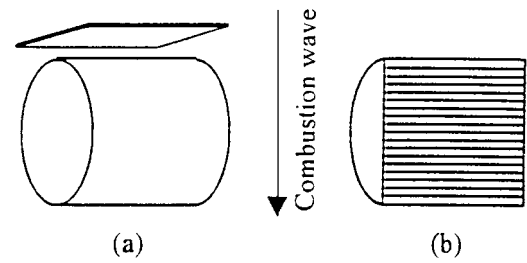
these two possible factors mixed up together with each other. A supplementary test was carried out so as to distinguish the true cause. As shown in Fig. 6a, a cylindrical compact that was same as that being used in the combustion front quenching test was placed horizontally and ignited by the incandescent graphite flat that
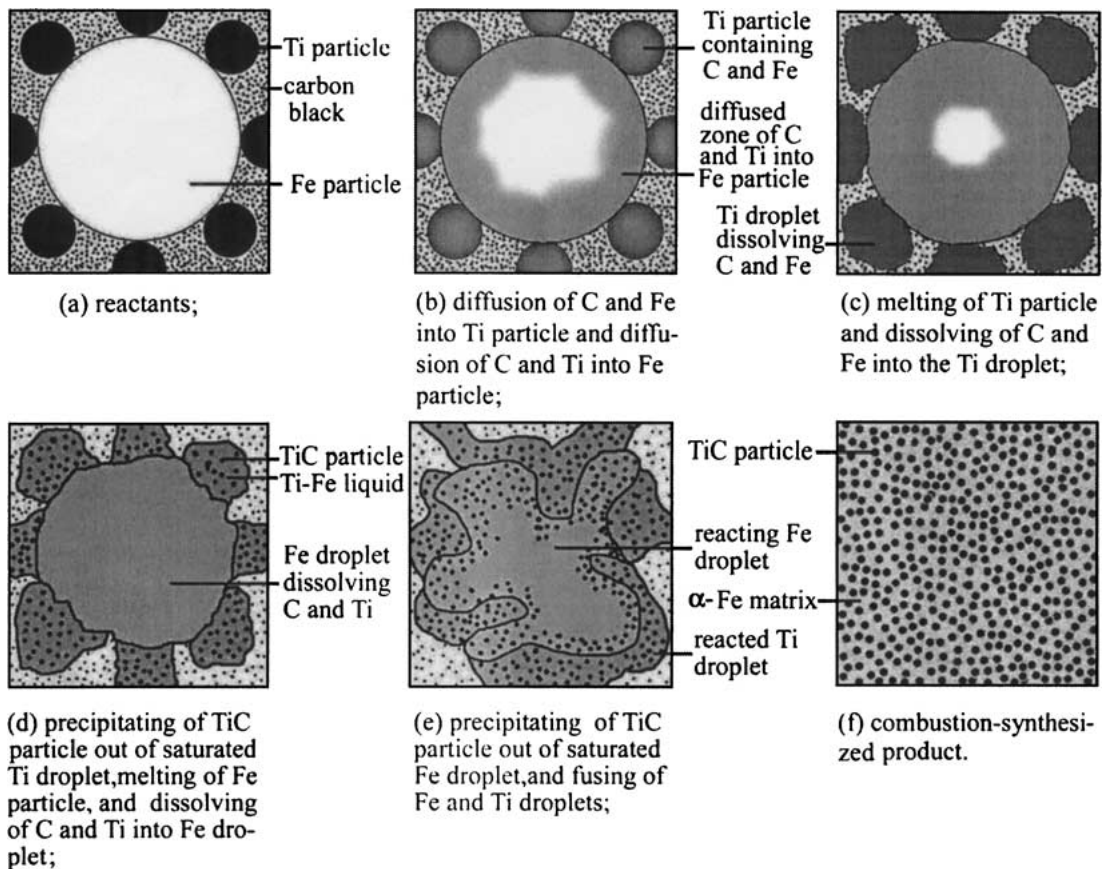

Figure 5 A model corresponding to the dual-solution-precipitation mechanism.

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was parallel but not perpendicular to the axis of the compact. The combusted sample was then cut longitudinally, as shown in Fig. 6b, and its microstructure shown in Fig. 6c indicated that the pores are still layer-shaped and parallel to the combustion wavefront but not perpendicular to the axis, this meaning that the shape of the pores is related to the combustion wavefront but not the residual tension stress.

Rapid-speed motion picture records of the combustion of Ti + C were carried out by Holt and Munir [11] and revealed evidence of the evolution of a substantial amount of gas. A portion of the produced gas escaped from the sample, but the other was retained in the sample due to a high combustion rate and an attempt to form larger bubble to reduce the free energy of the system. The finer Ti particle had a lower melting point and a higher combustion temperature, this increasing the fluidity of the liquid solution. The higher fluidity benefited moving and gathering of the retained gas into the isothermal layer of the combustion wavefront so that the pores formed in the same shape as the wavefront. An alternately laminar structure of TiC-Al$_2$O$_3$ ceramic and pores was also observed by Bowen and Derby [12] and the heat flow was considered to be in the direction perpendicular to the laminar structure.

5. Conclusions

1. When 56 wt% finer Ti powder ($<45\,\mu$m diameter) is added to a mixture of 14 wt%C powder (0.033–0.079 μm diameter) and 30 wt%Fe powder (135–154 μm diameter), the nature of the combustion reaction can be described by a dual-solution-precipitation mechanism which is significantly different from that previous ternary-reaction-diffusion/solution-precipitation mechanism for using a coarser Ti powder.

2. The melting of the finer Ti particle prior to its reaction mainly results from a combined effect of two factors: a decrease in its size-controlled melting point due to a small-size effect of a particle; and a decrease in its composition-controlled melting point with faster diffusion of C and Fe into the finer Ti particle.

3. The use of the finer Ti powder leads to a more complete combustion reaction, and hence a higher combustion temperature. As a result, the combustion-synthesized TiC-Fe cermet has a greater average size of TiC particles and layer-shaped pores that is confirmed to be a consequence of gathering of the evolved gases into the combustion wavefront.

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