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Microstructural evolution in the combustion synthesis of titanium carbide

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Microstructural evolution in the combustion synthesis of titanium carbide was investigated using the combustion front quenching method and scanning electron microscopy. The results showed that the combustion reaction between titanium and carbon began with reaction diffusion of carbon into the surface layer of titanium powder, leading to the formation of a TiC shell around the titanium powder. The titanium powder coated with the TiC shell melted and became a molten core, as the carbon atoms diffused into the core through the TiC shell, TiC grains gradually crystallized. In the final products, the morphology and size of the initial titanium powder were maintained in the form of the TiC granule which was composed of isometrical TiC grains. In addition, a lamellar eutectic was present at the centre of some TiC granules. The microstructural evolution in the combustion synthesis of TiC has been described with a shell–core model.

1. Introduction

From the outset of work on combustion synthesis, the Ti–C system has been extensively studied by a number of researchers, and it has been commonly considered to be a typical system for combustion synthesis. Research on the mechanism of Ti–C combustion synthesis has particularly attracted the interest of the investigators.

Using carbon-coated titanium wires, Vadchenko *et al.* [1] have investigated the ignition and combustion processes between titanium and carbon. They concluded that the combustion process was preceded by melting of titanium and that the formation of the carbide took place in a subsequent crystallization from a molten phase. Rogachev *et al.* [2] placed mixtures of titanium powders and carbon black into a wedge-shaped notch in a massive copper block, and the combustion reaction was initiated at the base of the wedge by means of an incandescent tungsten spiral. Because of the intense transfer of heat to the cooling copper block, the combustion was quenched; at the same time, the intermediate products were frozen. The electron microscope observations showed that the onset of the reaction coincided with the melting of titanium, and the metallic melt spread over the surface of the particles of carbon in the form of a thin film. Simultaneously, a reaction took place on the boundary between the carbon and the melt leading to the formation of rounded titanium carbide particles within the liquid film. Aleksandrov *et al.* [3] have demonstrated, with a transmission-type electron microscopy *in situ*, that the reaction between titanium and carbon began only after a liquid phase had appeared. Millins and Riley [4] and Choi *et al.* [5] investigated the effect of carbon morphology on the combustion synthesis of titanium carbide. It was found that the morphology of the original carbon fibre was maintained in the final products, therefore they suggested that one possible mechanism is the shrinking core model, in which molten titanium surrounds the carbon fibre and reacts with the outer surface of the carbon fibre; then the molten titanium diffuses through the TiC layer to react with the unreacted portion of the carbon fibre. Another possible mechanism is based upon a solution/precipitation model. The titanium is heated above its melting point and spreads around the carbon fibre; the carbon dissolves into the molten titanium and then TiC crystals precipitate as the solution cools. It can be seen that the preceding researchers have suggested that the combustion reaction between titanium and carbon took place only after the titanium had melted. The morphology of the final products differed from that of the initial titanium powders.

Although many research results on the microstructural evolution and mechanism in the combustion synthesis of TiC, as mentioned above, have been reported, more detailed experimental observation and a description of the microstructural evolution are still lacking. In addition, it is possible that the size of the reactants used in a test greatly affects the combustion process and mechanism. Therefore, it is necessary to observe more carefully the microstructural evolution and to study further the mechanism of Ti + C combustion synthesis. The objective of the present work was to investigate more carefully the microstructural evolution in the combustion synthesis of coarser titanium powders and a finer carbon black than that used in preceding tests.

2. Experimental procedure

Coarse titanium powders (135–154 μm) and fine carbon black (0.033–0.079 μm) were used in the present study. The reactants were mixed stoichiometrically and were uniaxially pressed in a steel die forming a green compact (14 mm diameter and 15 mm length) with a relative density of about 55%. Then, part of the compact was pushed out of the die, with the remaining part being left in the die. In a reaction chamber with 0.1 MPa argon, the compact was ignited with an incandescent graphite flat which was 2 mm above the compact. Because of the cooling effect of the steel die, the combustion front was quenched at approximately 12 mm from the top of the compact. The quenched specimen was cut longitudinally and prepared as a metallographic sample. After the sample was etched, its microstructure was analysed with a scanning electron microscope.

3. Results and discussion

3.1. Formation of the TiC shell

Fig. 1 shows the morphology of an initial titanium powder in an unreacted region of the quenched specimen. However, the carbon powders could not be found, because they were very fine and were peeled off the surface of specimen during preparation.

Fig. 2 shows the microstructures in the initial reaction zone of the quenched specimen. In Fig. 2a, a TiC shell, about 5 μm thick, is seen to have formed on surface of the titanium powder. Fig. 2b shows the primary TiC particles within the shell to be about 2 μm diameter. Saidi *et al.* [6] heated a mixture of titanium powders (> 100 μm) and carbon black up to 1450 °C, at a rate of 350 °C min^{-1}, the reaction did not self-propagate. However, X-ray diffraction analysis showed evidence of the formation of TiC by solid-state diffusion of carbon at the TiC/Ti interface, and an optical micrograph showed the development of a thin TiC layer around a titanium particle. Clearly, both titanium (melting point 1941 K) and TiC (melting point 3210 K) were presented in the solid state at 1450 °C. Therefore, it is reasonable to suggest that the structure in Fig. 2a is a solid titanium powder coated with a TiC shell. Obviously, the formation of the TiC shell resulted from reaction diffusion of carbon to the surface of the titanium powder.

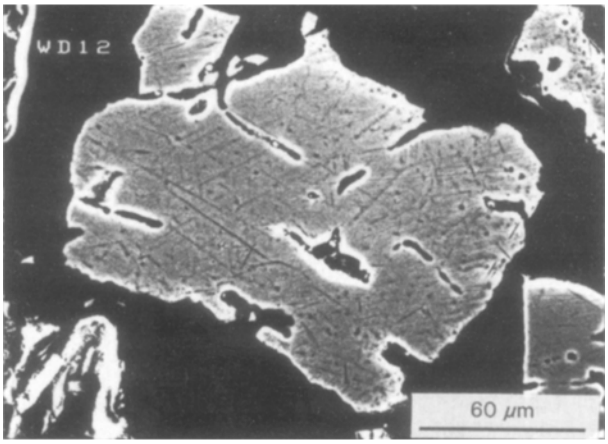

Figure 1 Scanning electron micrograph of an initial titanium powder in an unreacted zone of the quenched specimen.

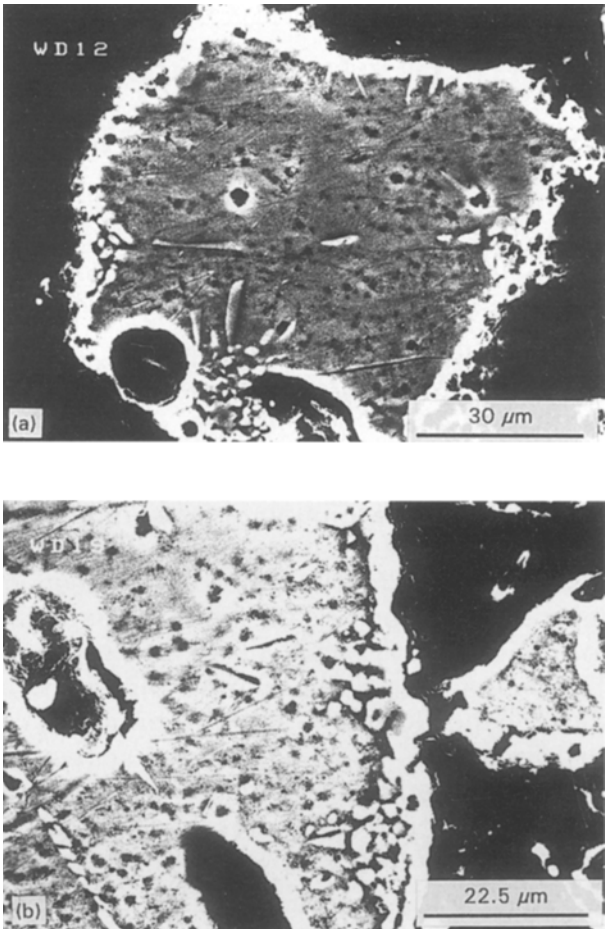

Figure 2 Scanning electron micrographs in the primary reaction zone of the quenched specimen: (a) titanium powder coated with a TiC shell; (b) the TiC shell.

The small contact areas of titanium powders with carbon powders did not benefit the diffusion. Because the reactants contained oxygen, the following reaction may occur at high temperature

$$2C + O_2 \rightarrow 2CO \qquad (1)$$

The surface of the titanium powder was in full contact with the CO. Then, again, as the CO was unstable, it would resolve and produce an active carbon atom, i.e.

$$2CO \rightarrow CO_2 + [C] \qquad (2)$$

The active carbon atom would be absorbed by the surface of the titanium powder and diffuse into it, but the CO_2 again reacted with carbon black and produced CO, i.e.

$$CO_2 + C \rightarrow 2CO \qquad (3)$$

These reactions would occur repeatedly, as is the case in the process of solid-state carburizing of steel. High-speed motion picture records of the combustion of Ti + C by Holt and Munir [7] have shown evidence of substantial gas evolution. They analysed the nature and content of the evolved gases and concluded that the major gas produced during combustion was hydrogen (86.96 vol %), and carbon monoxide, the next most abundant gas, accounted for 12.13 vol % of the total. At lower temperature, it was difficult for carbon atoms to diffuse into the titanium. With increase in temperature and transition of the crystal structure of titanium from hcp to bcc, the diffusion coefficient of carbon in titanium increased greatly. When the carbon content in the surface layer of the titanium powder was saturated, reaction diffusion would occur and the TiC shell would form on the surface of the titanium powder.

3.2. Crystallization of TiC in the molten titanium core

Fig. 3 shows the nucleation and growth of TiC in the molten titanium core. The heat released by the combustion reaction during the formation of the TiC shell and the heat transferred from the reacted zone caused the titanium coated with the TiC shell to melt, thus forming a shell–core structure composed of a hard TiC shell and a molten titanium core. Because the liquid titanium core could not penetrate the TiC shell, the shell–core structure basically maintains the morphology and size of the initial titanium powder. While carbon atoms diffused into the core, a TiC nucleus formed at the shell/core interface and removed to the centre of the core by surface tension and convection, as shown in Fig. 3a. As the carbon concentration in the core gradually increased, these TiC nuclei grew, as shown in Fig. 3b.

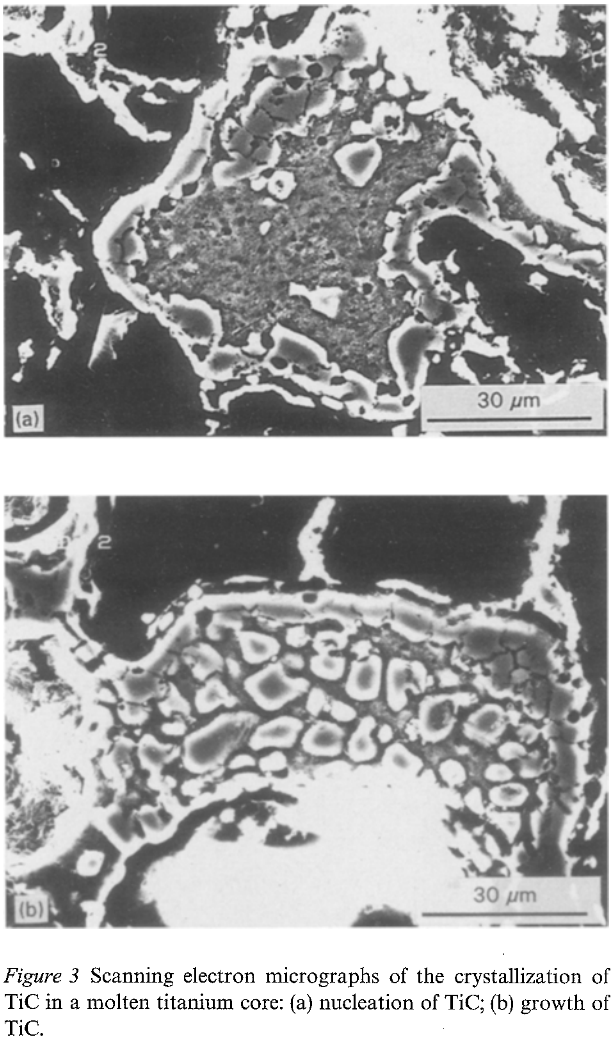

Figure 3 Scanning electron micrographs of the crystallization of TiC in a molten titanium core: (a) nucleation of TiC; (b) growth of TiC.

3.3. Microstructure of the final products

The microstructures of the final products are shown in Fig. 4. Fig. 4a shows that the morphology and size of the initial titanium powder are basically maintained in the final products mainly attributed to the hard TiC shell. The adiabatic temperature of the combustion reaction of the Ti–C system calculated by Holt and Munir [7] is 3210 K, which is the melting point of TiC, and the fraction of the liquid TiC in final products is 0.33. In practice, however, the highest combustion temperature is much lower than the adiabatic temperature because of heat loss. Hence, the TiC shell cannot be melted even at the highest combustion temperature, thus restricting the melted titanium within the hard TiC shell. The structure in Fig. 4a may be called a TiC granule. The connection between these TiC granules caused by slight sintering is so weak that the final products become porous. An individual TiC granule is a polycrystal composed of many isometric TiC grains with an average grain size of approximately 20 μm, as shown in Fig. 4b. These isometric grains resulted from the TiC nuclei which grew until they came into contact with others in the molten titanium core. In addition, as shown in Fig. 4a, a lamellar structure is present at the centre of some TiC granules, and from Fig. 4c, the lamellar structure is seen to possess a typical eutectic morphology.

It is well known that, the greater the size of the reactants, the lower is the combustion temperature, therefore, the coarse titanium powders used in the present test do not benefit the diffusion of carbon into the core of the shell–core structure through the TiC shell, thus causing the average carbon content in the core to be lower than the stoichiometric ratio of TiC. While TiC crystallized gradually, the carbon content in the residual liquid became lower, and the liquid transformed into α-Ti–TiC eutectic during subsequent rapid cooling. A similar structure to that in Fig. 4c was also present in the final products of the thermal explosion synthesis of TiC tested by Saidi *et al.* [6], but was not discussed by them.

3.4. Shell–core model of the combustion synthesis

As mentioned above, the microstructural evolution in the combustion synthesis of TiC could be described as shell–core model. The shell–core model is different from previous research results [1–5], in which the

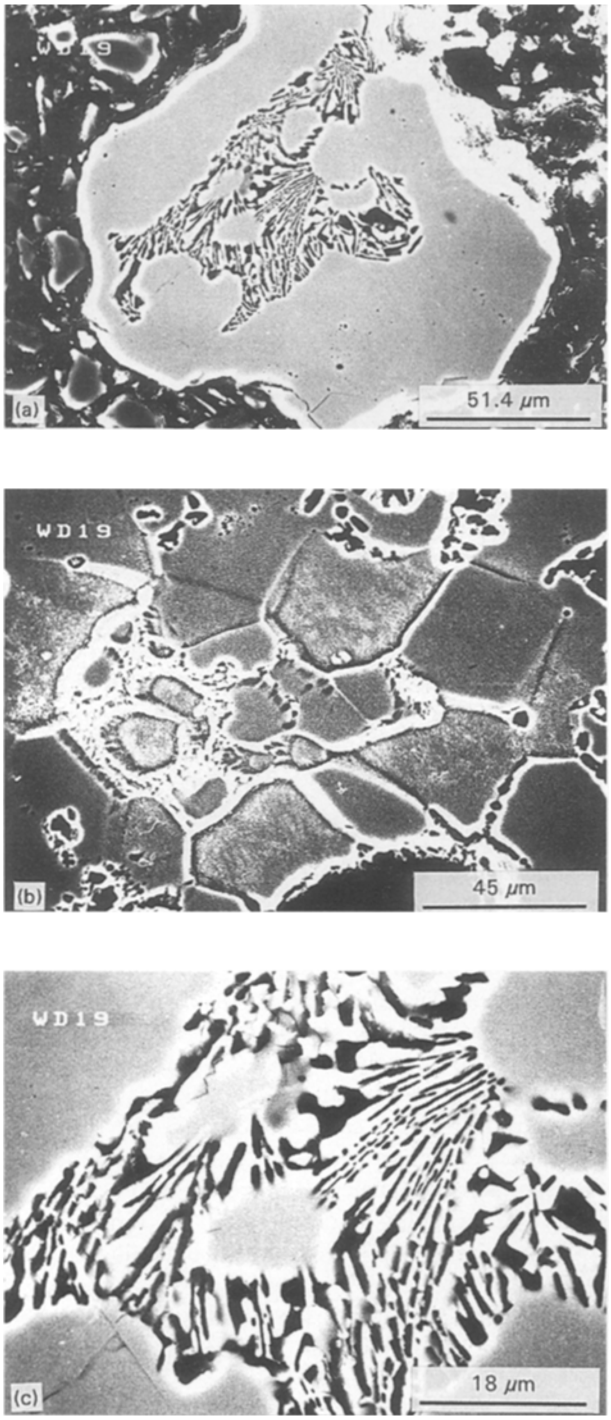

Figure 4 Scanning electron micrographs of the final products: (a) a TiC granule; (b) the isometric TiC grains making up the TiC granule; (c) the lamellar eutectic present at the centre of the TiC granule.

combustion process was preceded by the melting of titanium and took place with diffusion of titanium into carbon, and the final products of TiC appeared to be either rounded, which was independent of the morphology of the initial reactants [2], or fibriform which retained the morphology of the initial carbon fibre [4, 5].

The difference between the shell–core model and the others can be explained as follows. During the initial stage of the combustion synthesis, the reactants underwent two processes at the same time. One of them was the diffusion of carbon into the titanium powder, which would result in the formation of the TiC shell when carbon was saturated in titanium. The other one was the melting of the titanium powder due to the increase in temperature. The two processes competed with each other and resulted in two different results. If the former was dominant, i.e. the TiC shell had formed before the titanium powder melted, combustion synthesis would take place by the shell–core model. If the latter was dominant, i.e. the titanium had melted before the TiC shell formed, the combustion process would be preceded by the melting of titanium. The coarser the titanium powder, the lower was the combustion rate; thus it was not easy to melt the titanium. Therefore, for the coarse titanium powder used in the present test, the combustion synthesis should take place by the shell–core model.

Compared to the present test, finer titanium powder and coarser carbon material have been used in the above-mentioned tests [1–5], so the combustion process was preceded by the melting of titanium. On the contrary, when coarser titanium powder was used, Saidi *et al.* [6] also found a thin TiC layer around the titanium particle, and a similar lamellar structure to that in Fig. 4c also appeared in the final products. Consequently, the shell–core model of the combustion synthesis of TiC may be related to the coarser titanium powder and the finer carbon black. When the melting process occurred behind the diffusion process, the TiC shell formed before the titanium powder melted. Thus, the model of combustion synthesis of TiC depends on the size of the initial reactants.

4. Conclusions

1. The combustion synthesis of TiC starts from a reaction diffusion of carbon atoms into the surface layer of titanium powder, and results in the formation of a hard TiC shell.
2. After the titanium powder coated with the TiC shell melts, the titanium powder becomes a shell–core structure and TiC grains crystallize in the core.
3. The final products are composed of many TiC granules which retain the morphology and size of initial titanium powder. An individual granule is a polycrystal composed of many isometric TiC grains and the lamellar eutectic appears at the centre of some TiC granules.
4. The microstructural evolution in the combustion synthesis of titanium carbide may be described as a shell–core model that is different from preceding research results, and it may be related to the coarser titanium powder and the finer carbon black used in the present test.

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