*Journal of Alloys and Compounds, 203* (1994) 127–132
*JALCOM 854*

# Preparation and microstructure of $Al_2O_3$–TiC composites by self-propagated high temperature synthesis

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(Received April 13, 1993; in final form June 14, 1993)

## Abstract

This investigation was concerned with the production of ceramic composites based on $Al_2O_3$–TiC by means of self-propagated high temperature synthesis. When titanium and carbon black mixed with $Al_2O_3$ powder reacted, the ignition and adiabatic temperature showed a dependence on the reactant mixture composition and the amount of precompaction. The effects of these parameters on the product morphology are presented. Conditions under which the reaction ceased to self-propagate are also identified. The reaction mechanism for the reaction between $TiO_2$, Al and carbon black is also discussed. The microstructures of the products from the two reactions are compared.

## 1. Introduction

The conventional route of production of high temperature refractory materials incurs costly penalties in both time and energy because high temperatures and long processing times may be necessary. Self-propagating high temperature synthesis (SHS) is a potential cost-effective production technique since it uses the sizable amount of heat given off during reaction to reduce production times. The technique involves ignition of an exothermic reaction whereby the evolution of heat is sufficient to ignite subsequent layers of the compacted reactants, thus sustaining the reaction.

The possibility of producing materials by means of SHS was first investigated in the 1950s [1, 2]. During the next 30 years researchers in the Soviet Union including Merzhanov and Borovinskaya [3–5] and Novozhilov [6] led the way in the development of the SHS process. By the mid-1980s materials including refractories, intermetallics, composites, abrasives and electronic materials were commercially produced [7]. It has been claimed that materials produced by SHS have superior properties to those prepared by conventional methods [8] and are more sinterable [9]. Another advantage is that the *in situ* processing may promote a stronger bond between components of composite materials. The main problems of the process are the lack of control after ignition and the porous nature of the products [4].

$Al_2O_3$–TiC ceramic composites typically containing between 50% and 70% $Al_2O_3$ are commonly used as cutting tool bits because of their high strength and hardness. They are conventionally manufactured by mechanically mixing powders of the two components and sintering. Two different SHS routes were studied here since they were thought to be more energy efficient and would result in greater homogeneity and a stronger bond between the two components. The first route can be expressed by

$$Ti+C+Al_2O_3 \longrightarrow TiC+Al_2O_3 \tag{1}$$

where $Al_2O_3$ can be used not only to moderate the reaction but also to vary the composition of the ceramic.

The reaction

$$3TiO_2+4Al+3C \longrightarrow 2Al_2O_3+3TiC \tag{2}$$

was also studied for comparison. Products from this route had a fixed composition of 53.1% $Al_2O_3$ and 46.9% TiC.

$Al_2O_3$ composites using SHS by reaction (2) have previously been prepared by Cutler *et al.* [10]. The same reaction was studied by Abramovici [11], who showed that the composite powder can be sintered to 95% relative density. Adachi *et al.* [12], who performed the same process under the application of pressure, reported compacts of superior fracture toughness $K_{IC}$ to commercial ones.

The objective of this study was to examine and compare the preparation and microstructure of composite powders by the two routes already described. Some results which are in contrast with previous studies are observed.

*SSDI* 0925-8388(93)00854-R

## 2. Experimental procedure

The raw materials used were Ti, Al, $TiO_2$, $Al_2O_3$ (in the form of corundum, varying from 20 to 150 μm in particle diameter) and carbon black. Appropriate amounts of each reactant were weighed out and thoroughly mixed. Each mixture, which weighed a total of 20 g, was placed in a graphite crucible and patted down with a metal rod. The effect of compaction was studied by pressing samples under various pressures in the graphite crucible. All experiments were conducted in an induction furnace under a static argon atmosphere at atmospheric pressure. A constant heating rate of about 400 °C $min^{-1}$ was used throughout. Temperature measurement was carried out by means of a pyrometer connected to a computer for accurate date reading and storage. Reacted samples were allowed to cool in the furnace for 1–2 h. The products were characterized by X-ray diffraction (XRD) and optical microscopy.

## 3. Results

### 3.1. Reaction (1)

Results in Fig. 1 show that for loose powder mixtures of Ti, $Al_2O_3$ and carbon black the ignition temperature became higher as the $Al_2O_3$ content increased. The samples reacted fairly violently in the form of an explosion. Since a constant heating rate of 400 °C $min^{-1}$ was used, the time to ignition was between 2.5 and 3 min depending on the ignition temperature. Once ignited, the reaction released such a large amount of heat that the temperature rose quite sharply. The maximum temperature obtained was taken as the adiabatic temperature. The time of reaction was equivalent to the time taken to reach the adiabatic temperature after ignition. Most reactions were complete within about 1 s of ignition as shown in Figs. 2–5. For simplicity, in these plots the time at ignition is shown as the time 0 s. As expected, the time of reaction was shorter for lower $Al_2O_3$ contents in the reaction mixtures. The maximum temperature attained decreased with increasing $Al_2O_3$ composition. On completion of the reaction, the sample particles bonded together in the form of a large porous agglomerate.

Figures 6 and 7 show the difference between a sample containing 35% $Al_2O_3$ that has reacted in a self-propagating manner and a sample (50% $Al_2O_3$) which has not. In the former case $Al_2O_3$ was wholly distributed within TiC particles with a significant amount of granular porosity present. The cut-off point where the reaction changes to a non-SHS mode was at an $Al_2O_3$ composition of 41%. However, further investigation showed that the odd occasion occurred where reaction did take place in an explosive fashion even at 53% $Al_2O_3$ composition as has been shown in Fig. 5. It was concluded from a closer examination that SHS was possible with

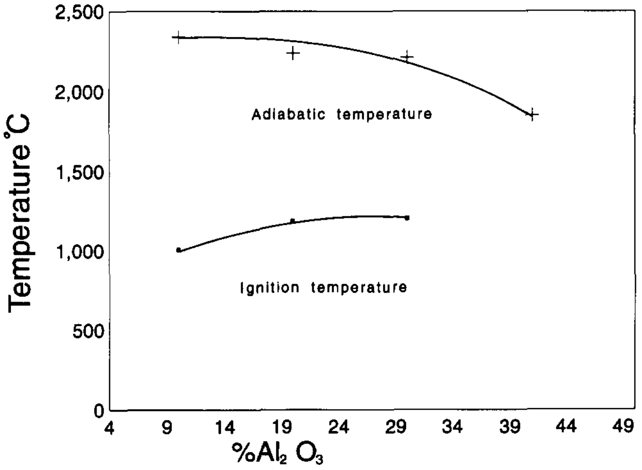

Fig. 1. Plot of adiabatic and ignition temperatures as a function of $Al_2O_3$ content.

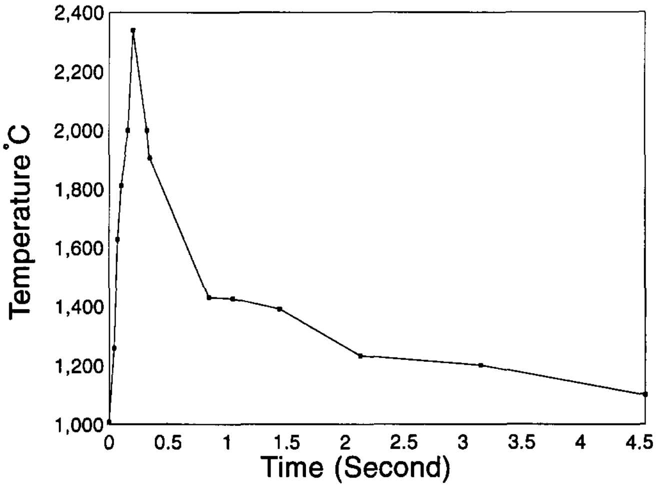

Fig. 2. Variation in temperature with time for reaction between Ti and carbon black in 10% $Al_2O_3$.

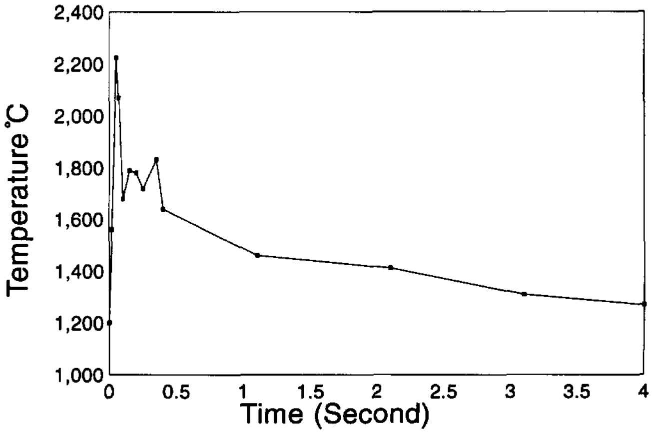

Fig. 3. Variation in temperature with time for reaction between Ti and carbon black in 20% $Al_2O_3$.

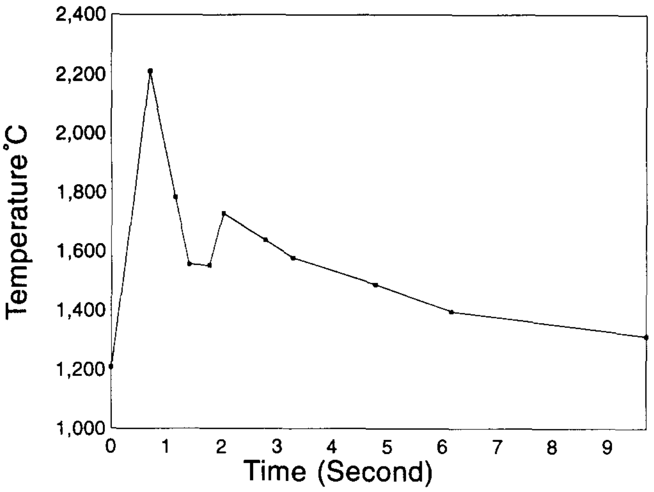

Fig. 4. Variation in temperature with time for reaction between Ti and carbon black in 30% $Al_2O_3$.

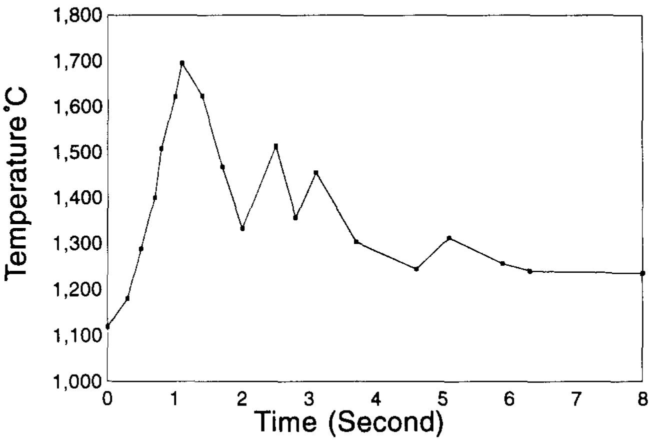

Fig. 5. Variation in temperature with time for reaction between Ti and carbon black in 53% $Al_2O_3$.

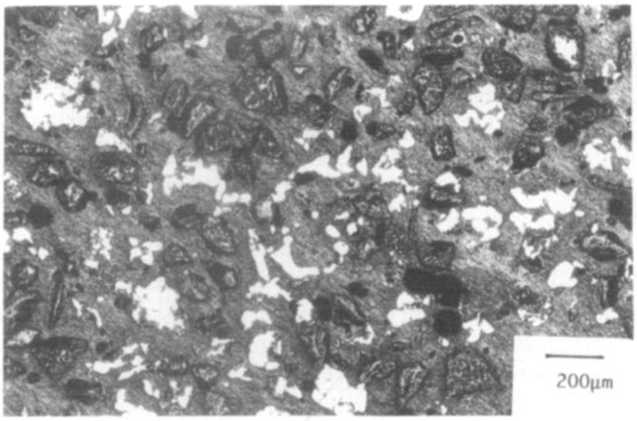

Fig. 6. Micrograph from reaction between Ti and carbon black in 50% $Al_2O_3$. TiC, white; $Al_2O_3$, black.

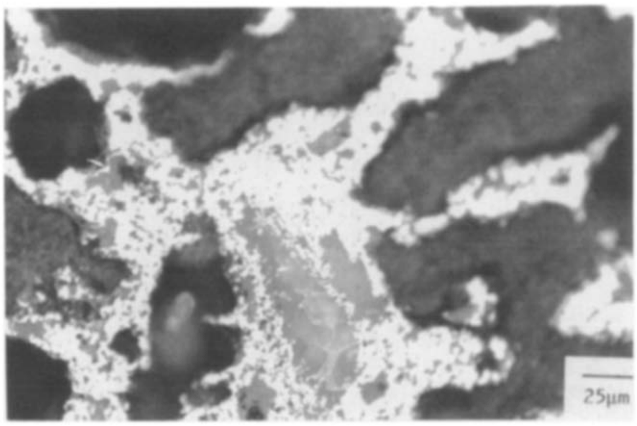

Fig. 7. Micrograph from reaction between Ti and carbon black in 35% $Al_2O_3$. TiC, white; $Al_2O_3$, black.

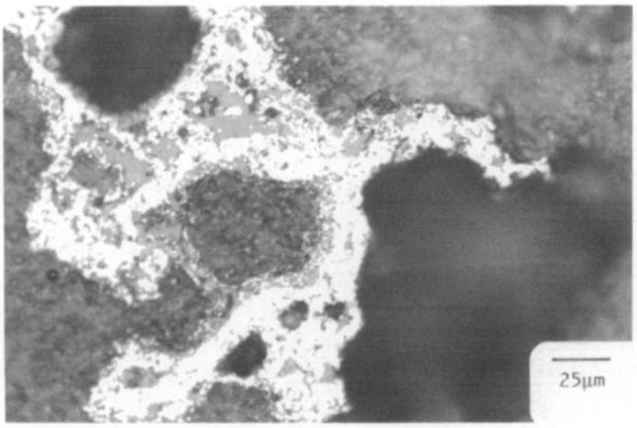

Fig. 8. Micrograph from reaction between Ti and carbon black in 20% $Al_2O_3$. TiC, white; $Al_2O_3$, black.

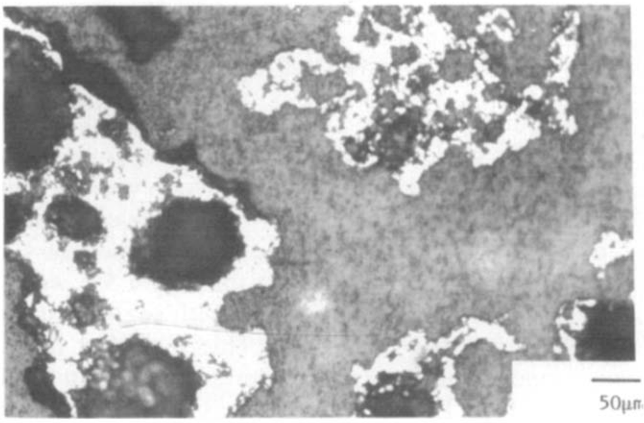

Fig. 9. Micrograph from reaction between Ti and carbon black in 10% $Al_2O_3$. TiC, white; $Al_2O_3$, black.

higher $Al_2O_3$ contents if the reactant powders were not homogeneously mixed. On the other hand, where the reaction did not self-propagate, the TiC and $Al_2O_3$ grains remained separated and no granular porosity was present. Figures 7–9 show the effect of $Al_2O_3$ content on the microstructure. As the amount of $Al_2O_3$ in the starting mixture increases, the $Al_2O_3$ particles distributed in TiC become larger. Porosity appears to

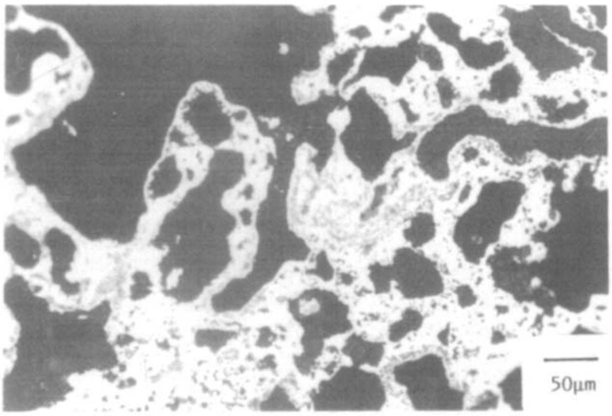

Fig. 10. Effect of precompaction on the microstructure from the reaction between Ti and carbon black in 20% $Al_2O_3$: TiC, white; $Al_2O_3$, black.

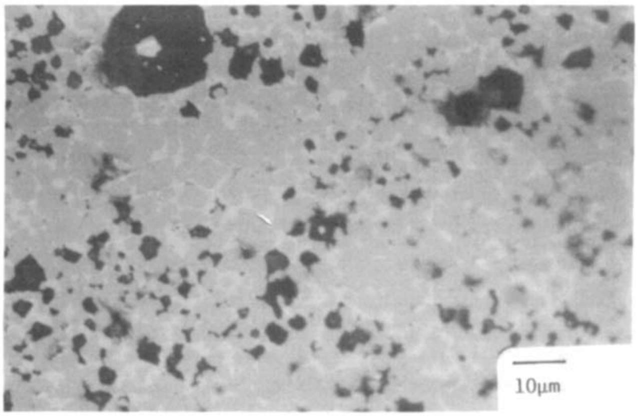

Fig. 11. Micrograph from the reaction $3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3$ showing unreacted Al and Ti wetting the ceramic particles: Al and Ti, white; TiC, light grey; $Al_2O_3$, black.

be unaffected by the changing $Al_2O_3$ composition in the starting material and remains at around 40% throughout. XRD showed that TiC and $Al_2O_3$ were present in all samples. Most of the $Al_2O_3$ was in the form of corundum, but some $\chi$-$Al_2O_3$ was also observed. The amount of $\chi$-$Al_2O_3$ in the reaction product increased as the $Al_2O_3$ sample content became higher.

Precompaction seemed to decrease the ignition temperature. For precompaction pressures exceeding 2.8 MPa the reaction was no longer self-propagating. Precompaction had a significant effect on the microstructure by the creation of a continuous grain structure as shown in Fig. 10. There appeared to be no overall effect on the porosity.

### 3.2. Reaction (2)

The ignition temperature for the reaction

$$3TiO_2+3C+4Al \longrightarrow 3TiC+2Al_2O_3$$

was measured at 1310 °C. The reaction did not take place in the explosive mode but as a wave front propagating through the sample. The reaction was initiated at the sample edge and the wave front moved through the sample in about 4 s. Some gas evolution of CO was observed which was accompanied by a 5% weight loss. Gas evolution was associated with swelling of the compact just prior to ignition. This suggested that a small amount of $TiO_2$ was reacting with carbon black to form TiC. This observation was substantiated by XRD analysis of samples which were quenched just prior to ignition. During reaction the temperature increased in two distinct bursts. The first step was a temperature rise to 1700 °C after about 1 s followed by a second burst to about 2100 °C.

XRD analysis confirmed the production of TiC and $Al_2O_3$ but also indicated the presence of minor amounts of unreacted Al and some metallic $\alpha$-Ti. There was no evidence of any unreacted $TiO_2$. This was further substantiated by close examination of the product microstructure (Fig. 11) at high magnifications, when tiny specks of Al and Ti are visible. No titanium aluminides were detected. TiC and $Al_2O_3$ were fairly intimately mixed with each other, indicating that melting of $Al_2O_3$ had taken place, supported by the fact that it had a re-formed appearance and size from its starting morphology.

## 4. Discussion

### 4.1. Reaction (1)

That the ignition temperature should increase with $Al_2O_3$ content was to be expected, because when more $Al_2O_3$ particles are present, the contact between Ti and carbon black becomes smaller. As a consequence there are fewer points where the reaction may ignite. In addition to this, the geometry and the homogeneity of the reactant mixture as well as the thermal conductivity of the sample play a major role in determining the ignition temperature and indeed in whether SHS takes place. As the $Al_2O_3$ concentration becomes higher, gradually more $Al_2O_3$ is present to absorb heat than Ti and carbon black and this will impair the SHS process. The availability of exothermic heat to both Ti and carbon is a necessary factor if self-propagation is to happen at all. If a greater percentage of exothermic heat is absorbed by $Al_2O_3$, a greater amount of heat must be generated to make the reaction explosive and this is reflected in the increase in the temperature of ignition. Results have shown that the reaction will cease to be self-propagating at $Al_2O_3$ compositions exceeding a critical value of about 41% assuming that all factors affecting self-propagation remain constant. In practice it is very difficult or practically impossible to keep such factors constant. For example, the particle size of Ti and $Al_2O_3$ was not constant but varied for both from approximately 20 to 150 μm. In any mixing procedure which may be followed there can be no guarantee that the particle size and range as well as the homogeneity of the mixture will be identical This helps to explain why some odd cases occurred where SHS did take place at $Al_2O_3$ fractions exceeding this critical value. A sampling containing 53% $Al_2O_3$ which was intentionally prepared without homogeneous mixing of the powders was indeed observed to ignite. Non-homogeneity ensured that there was more Ti–carbon black contact than otherwise and this led to an SHS type of reaction taking place.

It must be stressed that reaction does take place even if it does not self propagate. $Al_2O_3$ tends to absorb an increasing amount of exothermic heat from the reaction between Ti and carbon black such that an additional amount of energy is required to make the reaction explosive. However, by the time this does happen, the TiC product layer which forms on Ti may become so thick that the reaction rate will be determined by the rate of solid diffusion of carbon through the product, which is slow. The kinetics therefore become so slow that not enough heat per unit time can be generated for the reaction to ignite. The amount of $Al_2O_3$ present tends also to affect the time for complete reaction, which is considered to be the time taken to reach the adiabatic (or maximum) temperature from the ignition temperature. By examination of Figs. 3–5 it is apparent that a number of extra temperature rises (or bursts) occur after the maximum temperature has been reached and while the sample is cooling down. This provides further support to the theory that the reactants may be less homogeneously mixed as the fraction of $Al_2O_3$ increases, giving spots where self-propagation is delayed owing to a variation in the composition on the reacting bed. This is also substantiated by the fact that XRD analysis showed that some unreacted Ti remains as the percentage of $Al_2O_3$ is increased (carbon black is not crystalline and gives no peaks). It is also apparent that the reaction time increases with $Al_2O_3$ content and that the reaction becomes less explosive and starts to occur as a wave front through the sample. This suggests that the temperature of the powder bed is unlikely to be homogeneous and the reaction may ignite in various places at different times.

The effect of precompaction produced a continuous microstructure of TiC. This was to be expected, because the constraints which are applied bring the components of the mixture closer together. This is apparent from the fact that the ignition temperature also decreases as some pressure is applied. For instance, for TiC–20%$Al_2O_3$ the ignition temperature dropped from 1192 to 1170 °C at 1.36 MPa. At precompaction pressures exceeding 2.8 MPa no ignition was observed. This observation necessitates further investigation. It is possible that since the reactant sample is more dense, it is likely to be more conductive and conduct heat away from local hot spots to effectively prevent ignition.

### 4.2. Reaction (2)

Reaction (2) took place in two distinctive steps. The first is the aluminothermic reduction of TiO via

$$3TiO_2 + 4Al \longrightarrow 3Ti + 2Al_2O_3 \tag{3}$$

which initiates at 1310 °C. The amount of exothermic heat released by this reaction increases the compact temperature to 1700 °C, whereupon the reaction between Ti and carbon black takes place. At first, Al powder started to melt during the heating of the sample. Al surrounds the $TiO_2$ and then starts to react with it. At the adiabatic temperature for reaction (3), Ti is in the molten state and can freely move within the compact to react with carbon black. Solid TiC forms, and because Ti is in the molten state, it is able to come into further contact with the carbon black for the reaction to continue without the need for carbon to diffuse through the product. At the highest temperature which was measured both Ti and $Al_2O_3$ are in the liquid state. Since the reaction is so fast, it is reasonable to assume that there is very little time available for them to separate. The resulting microstructure is therefore an intimate and homogeneous mixture of $Al_2O_3$ and TiC with a good bond between the two components. As solid TiC starts to form, $Al_2O_3$ flows alongside it and into the porous areas within the TiC grains where it solidifies. Evidence of this is provided by the micrograph shown in Fig. 12, where $Al_2O_3$ surrounds the pores in the structure. This is in sharp contrast with the microstructure obtained from reaction

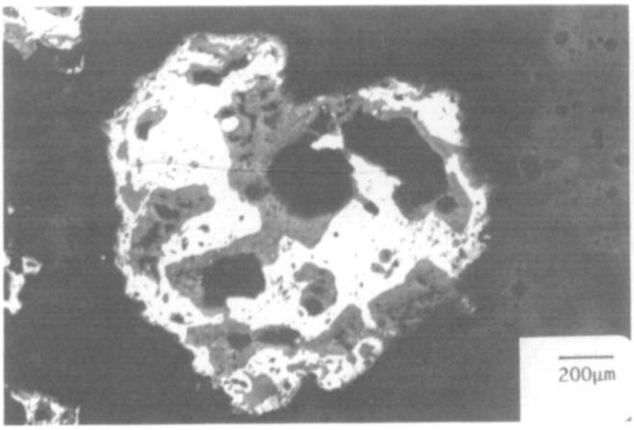

Fig. 12. Micrograph showing $Al_2O_3$ near pores in the structure of $Al_2O_3$–TiC by the reaction $3TiO_2 + 4Al + 3C \rightarrow 3TiC + 2Al_2O_3$: TiC, white; $Al_2O_3$, black.

(1) which is explosive and occurs much faster, giving little time for liquid $Al_2O_3$ to diffuse. As a result $Al_2O_3$ particles from reaction (1) are finer and more uniformly mixed with TiC.

The presence of Ti and unreacted Al in the final product accompanied by the absence of $TiO_2$ suggests that some other means of $TiO_2$ reduction has also taken place. It is likely that some limited carbothermic reduction of $TiO_2$ occurs as expressed by the reaction

$$TiO_2 + C \longrightarrow TiC + 2CO \qquad (4)$$

According to thermodynamic data compiled by Turkdogan [13], this reaction is possible at about 1290 °C. Of course, if a more reactive form of carbon is used such as carbon black, this temperature will be lower. The fact that reaction (4) takes place was confirmed by XRD analysis and by the observation that the reacting powder bed swells owing to the evolution of CO just prior to ignition. Al and Ti appear to wet the $Al_2O_3$–TiC particles completely. This effect was not apparent in previous studies of the reaction [10–12].

## 5. Conclusions

The investigation has shown that it is possible to produce $Al_2O_3$–TiC composite powders by the two reaction routes which were studied. The rate of reaction of Ti and carbon black as well as the ignition and maximum temperatures attained were all dependent on the amount of $Al_2O_3$ present, which moderates the reaction. This reaction was fairly explosive. Fine precipitates of $Al_2O_3$ in TiC were obtained. The reaction did not follow a self-propagating mode if more than 41% $Al_2O_3$ was present unless the reactants were inhomogeneously mixed. This has led to the conclusion that it is possible to generate enough heat for self-propagation of samples containing 50%–70% $Al_2O_3$ by the introduction of regions of high Ti and carbon concentration in the reacting powders. The effect of precompaction was to create a continuous grain structure, though at pressures exceeding 2.8 MPa the reaction was not self-propagating but occurred via solid diffusion of carbon through solid Ti.

The aluminothermic reduction of $TiO_2$ in the presence of carbon black took place through the sample in the form of a wave front. Reaction started at 1310 °C by the reaction of $TiO_2$ and Al releasing exothermic heat. A second reaction between Ti and carbon black then followed, reaching a maximum temperature of 2100 °C. The product microstructure was very different from the one obtained by the previous route. TiC and $Al_2O_3$ were again intimately mixed but the $Al_2O_3$ particles were much larger than in the previous reaction.

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