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Direct combustion synthesis of SiC powders

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In this study, we examine the possibility to direct combustion synthesize SiC powders from elements using four reactant combinations (Si and graphite; Si and carbon black; ground Si and carbon black; both Si and carbon black ground) under two reacting environments (heated by an oxy-acetylene torch in air, and heated by tungsten coils in vacuum). The experimental results showed that high-purity SiC product with no oxide present was obtained if pellet, made of Si and carbon black, was burned by an oxy-acetylene torch in air. Also, ground reactant particles yielding deteriorated effect on product conversion is also discussed. © *1999 Kluwer Academic Publishers*

1. Introduction

Self-propagating high-temperature synthesis (SHS), or combustion synthesis, is emerging as an attractive way to produce advanced materials, because the SHS method has proven advantages [1]: lower energy requirement, higher product purity, simpler and cheaper equipment, higher sinterability and possible nonequilibrium phases in the final products. In SHS, reactant pellet is subjected to an external heat source (e.g., a heated coil, a laser beam, etc.) on one end and is then ignited at this end. Due to the highly exothermic reaction, a self-sustained combustion wave propagates from this heated end to the other and converts the reactant pellet into the final product. A lot of advanced materials [1–5] such as refractories, intermetallic materials, super alloys, cermets, and superconductors, etc. can be synthesized by this method.

For advanced materials to be synthesized by the SHS method, two empirical criteria [2] must be met such that combustion wave can be sustained: $\Delta H/C_p$ at 298 K must be greater than 2000 K, and T_{ad}, the adiabatic temperature, must exceed 1800 K. In the case of SiC (with a relatively low heat of formation −69 kJ/mol and T_{ad} 1800 K), either $\Delta H/C_p$ or T_{ad} is below or near the threshold value so that the combustion synthesis of SiC is not feasible under normal reaction conditions (1 atm and 298 K). Therefore, in order to combustion synthesize SiC from elements, several techniques can be found in the literature: preheat the reactant pellet to raise the adiabatic temperature [6–8]; use high-pressure nitrogen atmosphere to have silicon-nitrogen gas phase reaction first and then Si-C reaction can be induced [9]; use chemical or oxidative additives to change reaction mechanisms [10, 11]; increase the heating surface under high pressure (HPCS) [12]. Note that typical particle sizes of Si and C used in the literature were near or much smaller than 1 μm.

Although SiC could be successfully synthesized by the aforementioned techniques, we are still wondering a fundamental question: is it possible to produce SiC by combustion synthesis *directly*? In other words, if no external auxiliaries are utilized, can the Si-C reaction still take place? In this study, we found that if the green pellet was burned by an oxyacetylene torch in air, self-propagating combustion wave can be sustained in a short range (about 5 mm) and high-purity SiC powders can be obtained.

2. Experimental

In the present study, powers of Si (99.5% pure, −325 mesh, Cerac), Graphite (99.9% pure, −325 mesh, Cerac) and Carbon black (99% pure, under 2 μm, China Synthetic Rubber) were used. In some cases, in order to produce smaller particle sizes, powders were subjected to a fine grinder (DAP-7, Struler) for 50 min. The desired molar ratios of powders were first dispersed and well mixed in *n*-hexane for 30 min by a mechanical stirrer. The resulting slurry was air dried and the dried mixture was cold pressed into a cylindrical pellet by an uniaxial single acting press at 5–30 MPa. The apparent density of the pellet was in the range between 30 to 45% of the theoretical density and the dimension was 9 and 12 mm in length and diameter, respectively. Two external heat sources in different reacting environments were used to investigate the combustibility of the green pellets. One was to burn the green pellets by an oxy-acetylene torch in air, in which flow rates of acetylene and oxygen were controlled in the range of 510–600 and 530–700 ml/min, respectively. The other was to heat the reactive mixtures by tungsten coils in vacuum with 40 A current and 26 V voltage. A high-speed charge coupled device (CCD) (Toshiba, jk-c40) focused on the pellet was used to monitor the progress of the combustion, and to record the reaction sequences into a video tape for later analysis. Four types of powder combinations, which included (1) Si and graphite, (2) Si and carbon black, (3) ground Si and carbon black, and (4) ground Si and ground carbon black, were all

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subjected to two different reaction schemes. The experimental observations are as follows.

3. Results and discussions

3.1. Si and graphite

First, for Si and graphite both the oxy-acetylene torch and the tungsten coil could not initiate any reaction at all for any stochiometric combinations. This may due to the fact that the particle sizes of Si and graphite were too large, compared to those used in the literature. There was a thin layer of whitish material, probably SiO_2, formed at the heated surface of pellets when the heat source was a torch. For this reason, the carbon source was switched from graphite to the fine-size

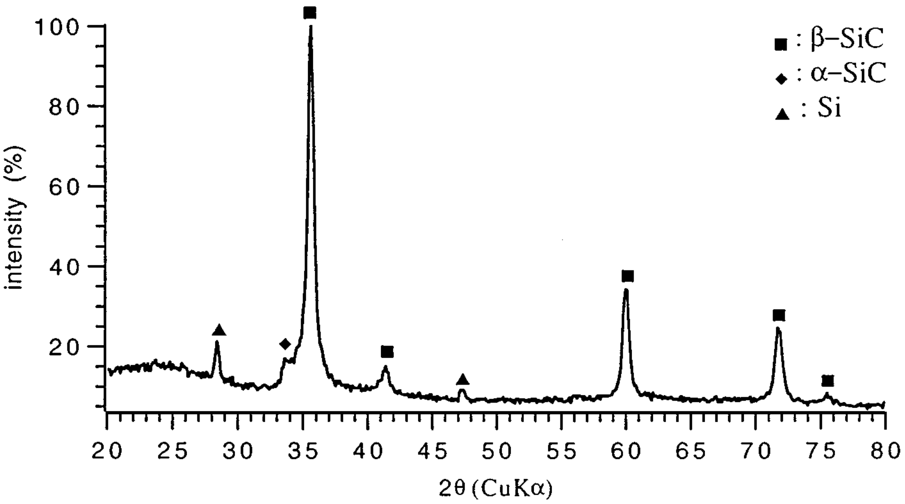

Figure 1 The XRD patterns of powders produced in the tungsten-coil reactor.

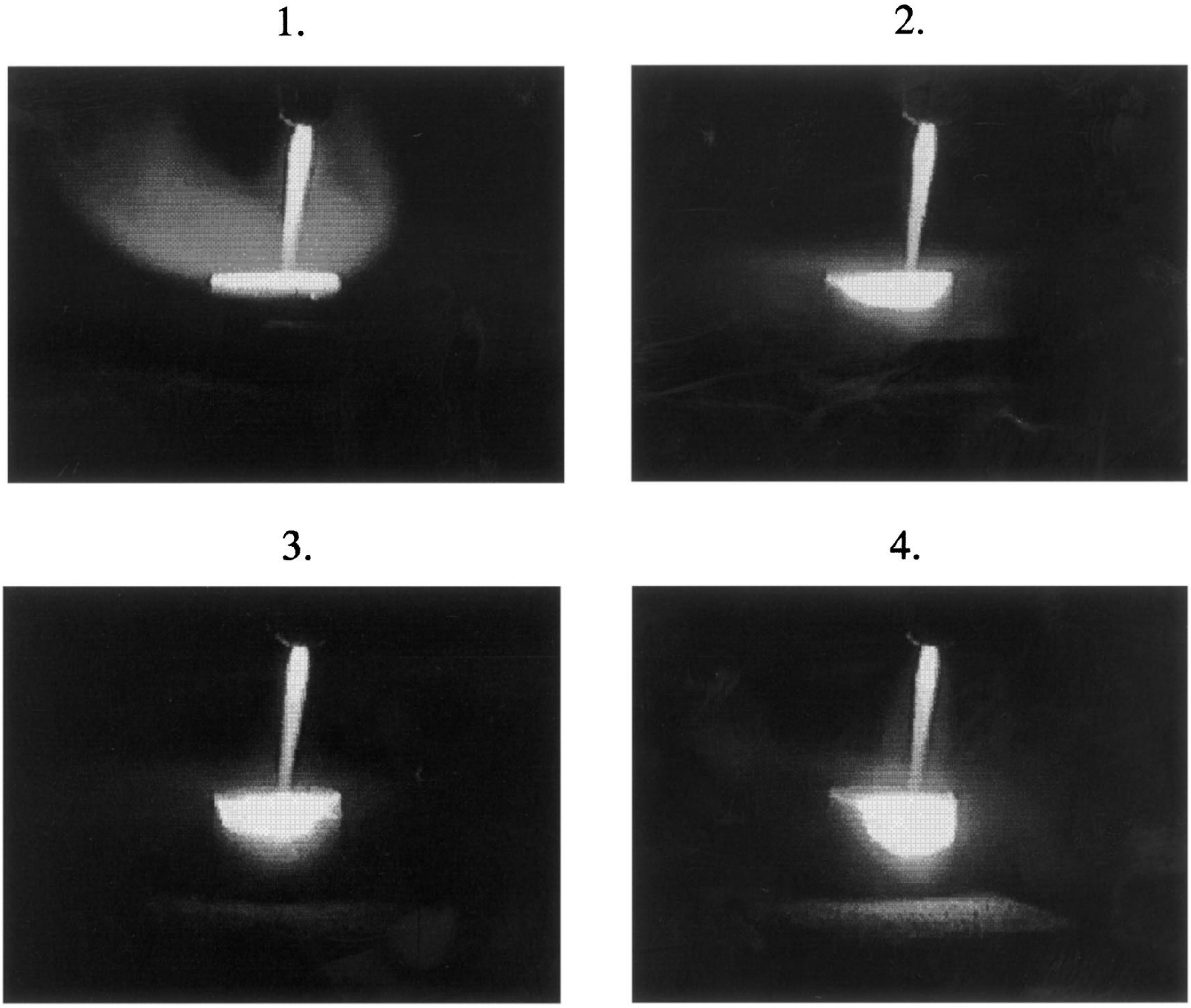

Figure 2 Snapshots of the reaction between Si and carbon black with time (reaction initiated by an oxy-acetylene torch). 1–4: burning of the first heated surface; 5–10: burning of the flipped surface. (*Continued*).

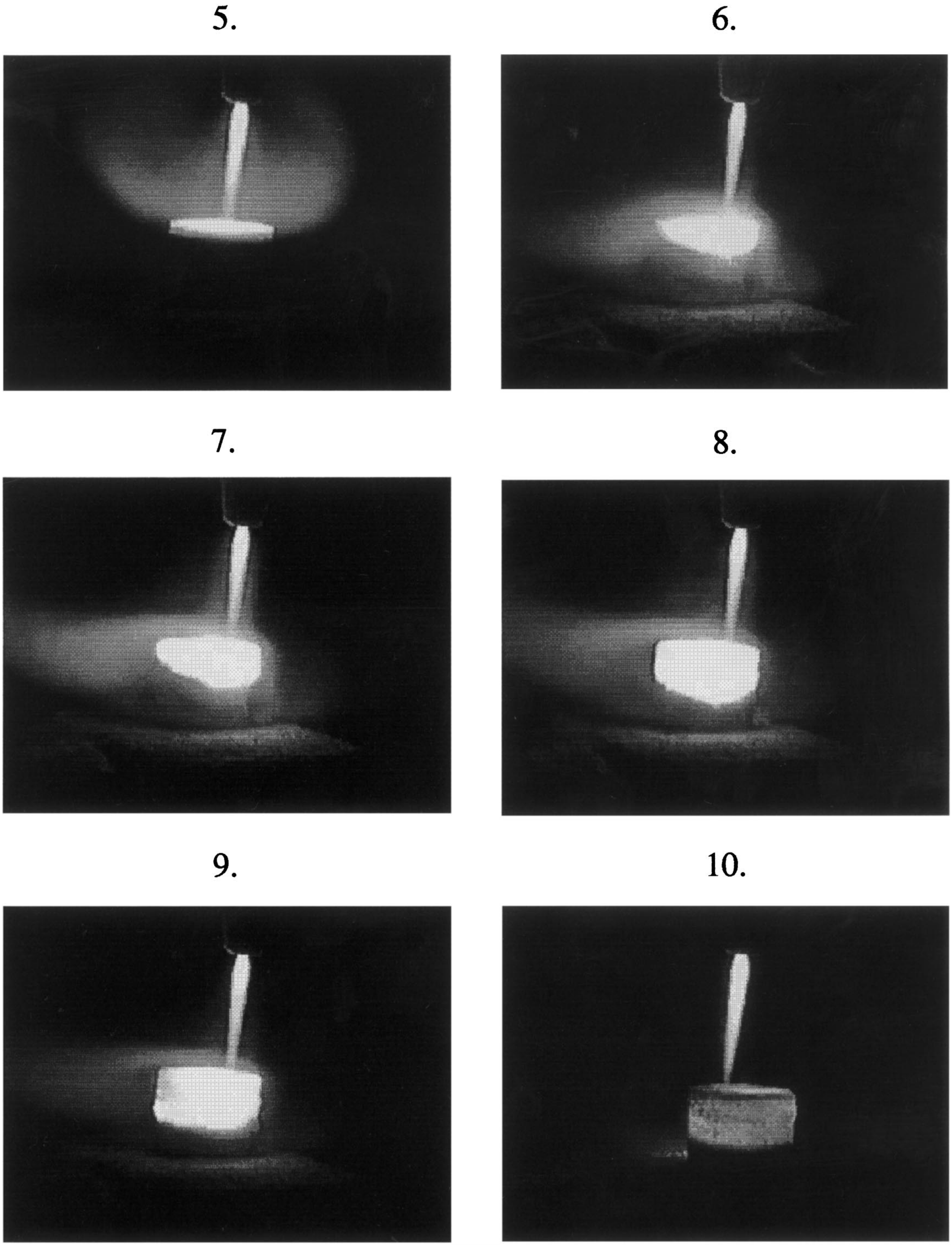

Figure 2 (*Continued*).

carbon black, and the reactivity of the ceramic reaction was dramatically increased.

3.2. Si and carbon black

When the green pellet made of Si and carbon black was synthesized in the tungsten-coil reactor, there were tiny cracks formed at the pellet surface and the volume was slightly dilated as the electric power turning on. Twenty seconds after switching the power on, the heated surface was ignited and a combustion wave started to propagate. Because part of the heated layer was separated from the rest of the unreacted pellet at this moment, the combustion wave traveled only about 0.5–1 mm and then paused. The reason of separation of the top layer from the pellet was as the absorbed water vapor

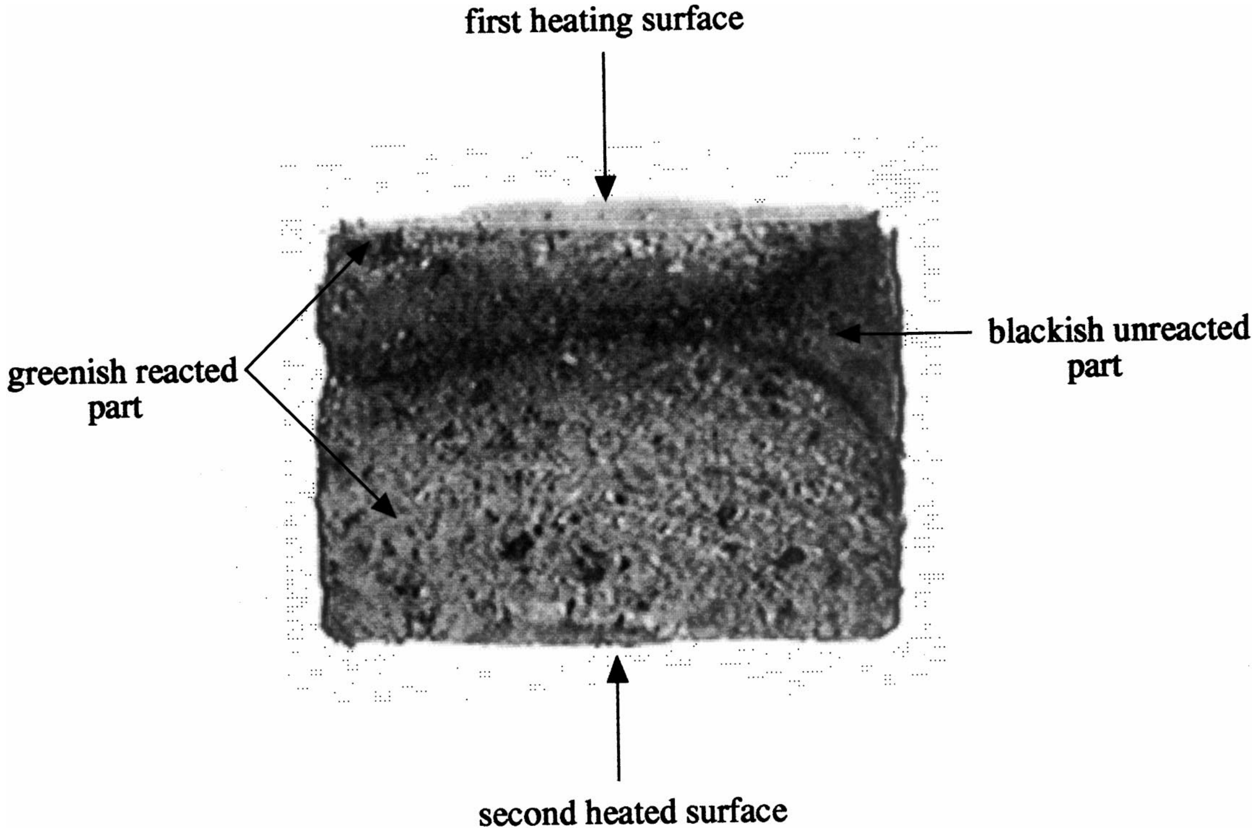

Figure 3 The longitudinal cross section of the reacted pellet synthesized by an oxy-acetylene torch.

and other gases inside the pellet were heated, the large pressure gradient quickly expelled the vapor and gases and caused cracks in the pellet, owing to the vacuum surrounding. About 30 s later, the combustion wave continued to propagate toward the unreacted portion. But, as the reaction was in progress, the outer surface of pellet broke apart. The volume of the remaining final product was only about 50% of the green pellet. As shown in Fig. 1, XRD analysis shows that the remaining integral product mainly consisted of β-SiC with a small amount of residual Si and a trace of α-SiC.

Next, if the torch was used instead, the combustion phenomena were quite different from those observed in the tungsten-coil reactor. As the torch started to burn the green pellet, the heated surface was not ignited in the first three or four seconds. The green pellet was then moved so that torch fire could reach any edge of the pellet, the ignition started right away at that heated spot and the combustion wave propagated. However, the combustion wave was not planar and was propagated radially with the ignited spot as a circle center, because the torch was considered to be a point heat source. The maximum propagation length was only about 2–3 mm measured from the ignition spot. The pellet was then continually moved such that all the upper portion of pellet could be converted into product via this local combustion. The time needed for the upper part to be reacted was very short. Next, the pellet was flipped upside down and the unburned portion was heated by the torch. As long as the torch touched this unburned part, the ignition started in no time and the combustion wave traveled to the unreacted part in a SHS way, in which the combustion phenomenon was completely different from the first headed surface. Sometimes, spin combustion was observed. The maximal longitudinal propagation length was found to be about 5 or 6 mm. The detailed experimental progresses are shown in Fig. 2. Because the propagation lengths of combustion waves initiated from the top and bottom surfaces were both limited, there existed a slim unreacted middle layer with a blackish color, compared to the greenish product shown in Fig. 3 (the reacted portion was very hard while the unreacted part was loose). The cylindrical shape of final product was maintained and was only slightly changed due to dilation. This is because the reacting environment, the ambient pressure reduced the pressure gradient across the pellet boundary. The trapped vapors and gases did not expel violently so that there were visible pores produced in the product portion (Fig. 3). Fig. 4b shows that the product compositions were similar to that synthesized in the tungsten-coil reaction, but with a slightly higher yield. As shown in Fig. 5, SEM analysis of the fractured surface reveals that the morphology of SiC product was aggregated fine particles.

3.3. Ground Si and carbon black

It is well known that finer reactant will have a better reactivity because of larger contact area. Thus, the Si powders were ground because we could not obtain Si powders with smaller particle size in the course of this study. The experimental results could be classified into two completely distinct categories. Sometimes, the reactivity of pellet consisting of ground Si and carbon black was similar to the previous case. Compared to

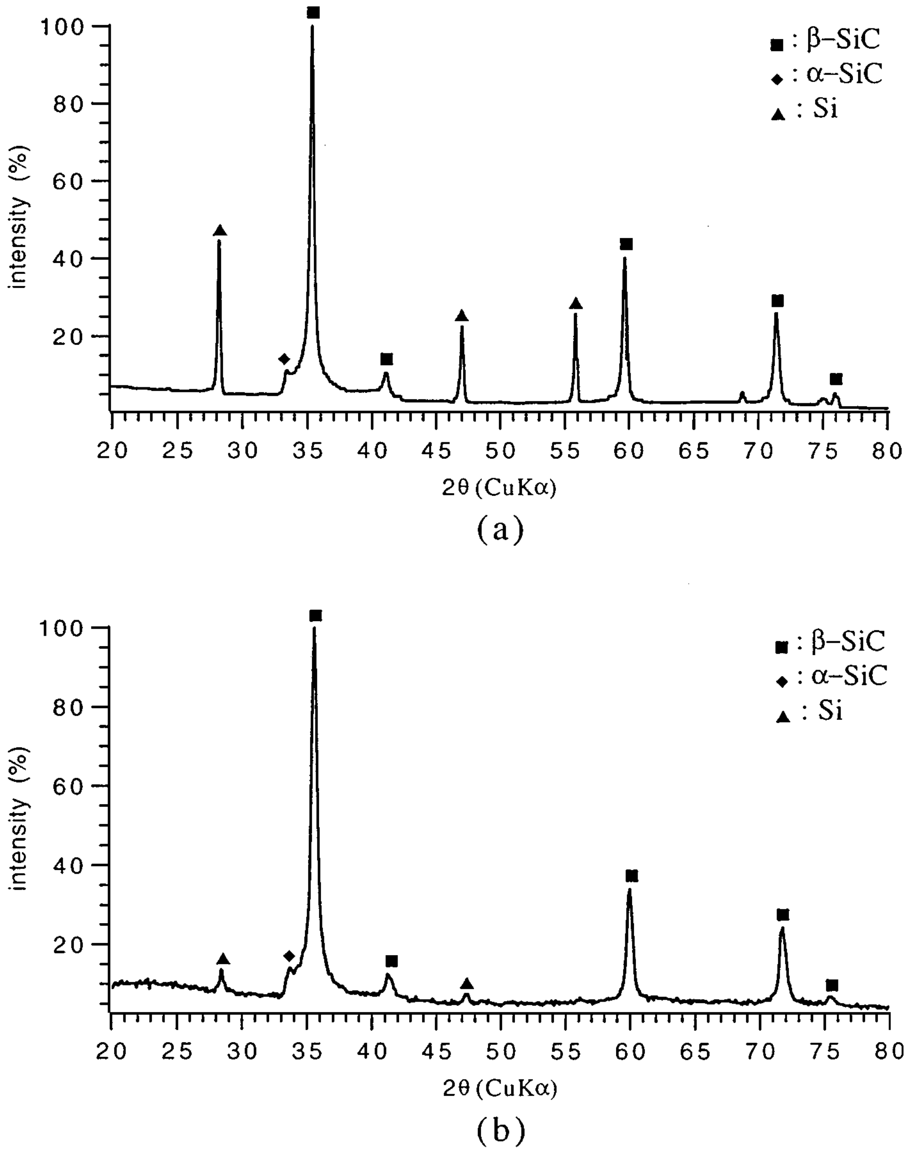

Figure 4 The XRD patterns of powders made from (a) the whole pellet in Fig. 1 and (b) the reacted part.

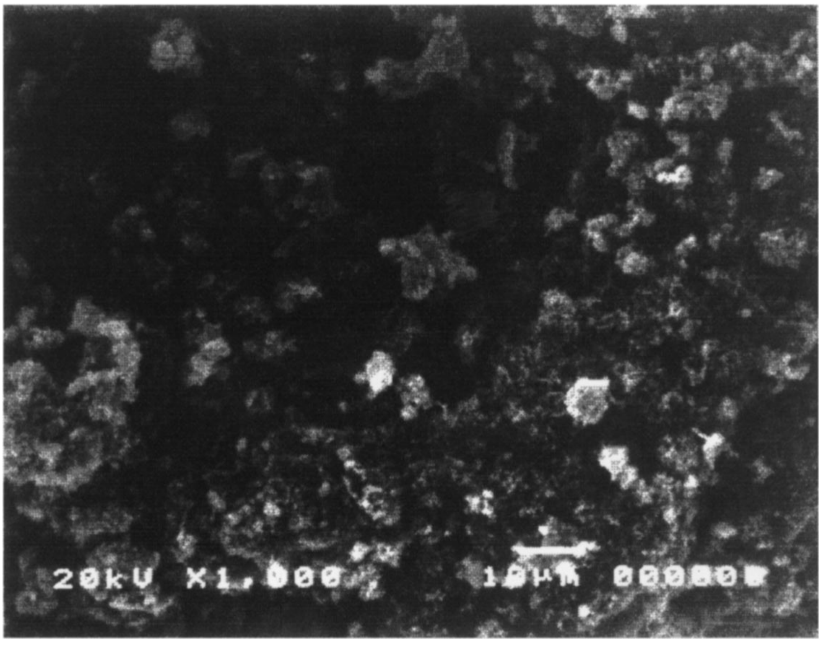

Figure 5 Scanning electron micrographs of the fractured surfaces of the product.

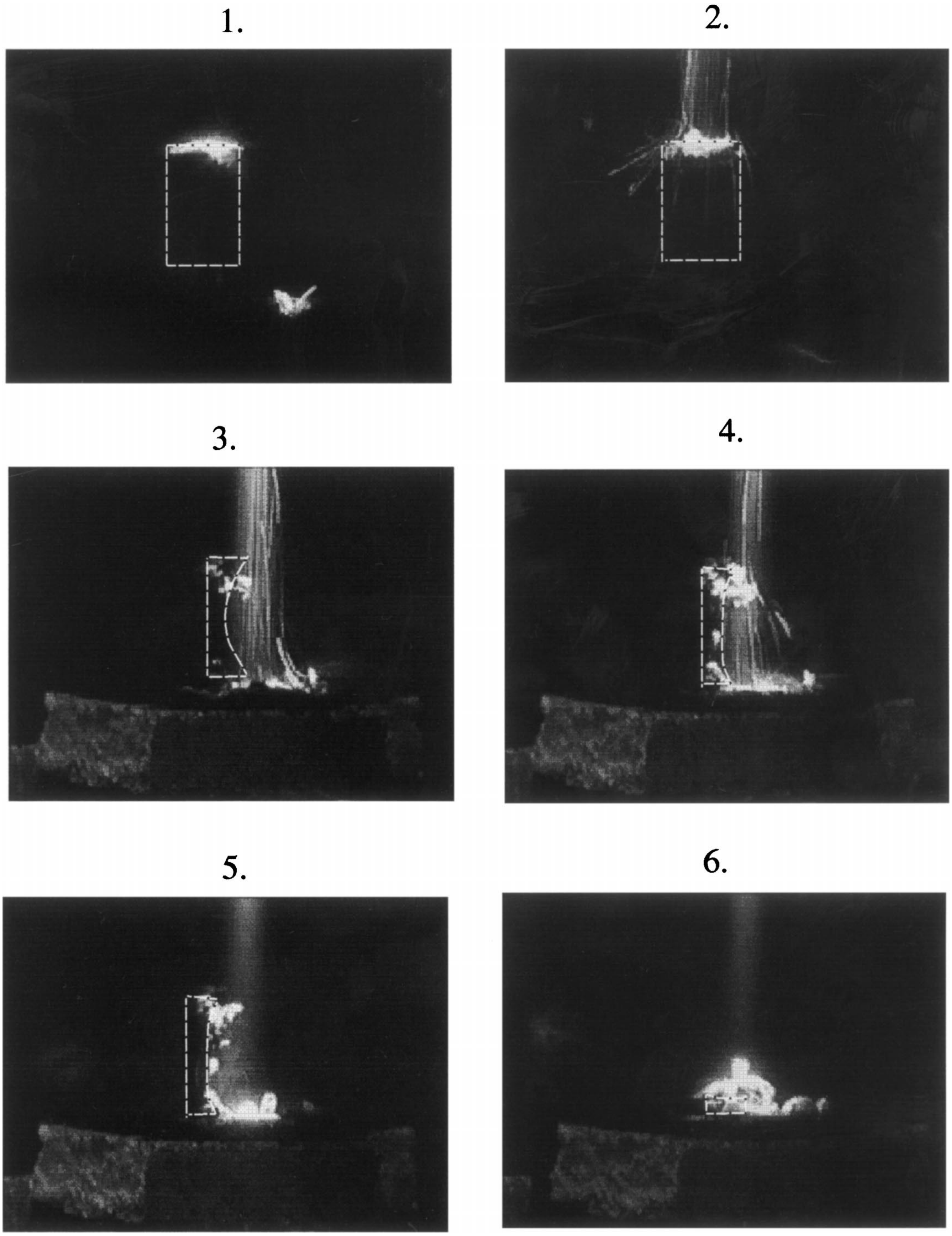

Figure 6 The fireworks scenario of pellet made of ground Si and carbon black burned by a torch in air.

case (2), the ignition time was shorter and the combustion propagation area seemed to be a little bit larger. But more often, the experimental results were completely different. Once a certain point ignited, the combustion wave quickly propagated. The way of combustion wave behaved like it wrapped the outer surface of pellet in no time. There was no limitation on propagation length, contract to case (2). If the pellet was flipped and heated again, this flipped surface won't be ignited and this was again different from that of case (2). Also, XRD analysis of products showed that only a thin layer of product formed at the pellet surface and no product was found in the core of pellet. This means that the reaction took place in outer layers during the combustion wave wrapping the pellet surface. We believe that the contrast of the combustion mode was due to the mixing of ground Si and carbon black. If tiny pieces of Si particles, which were formed during Si powders being ground, were not evently distributed throughout the whole green pellet and were located mostly on the pellet surface (this was possible because these tiny particles were lighter), it was likely to have the second experimental scenario since the reactivity at the pellet surface was much higher due to large contact areas. Nevertheless, it seems to suggest that there is no extra benefit at all to have silicon ground from the observations of both experimental situations.

3.4. Ground Si and ground carbon black

The final reactant combination was prepared by grinding Si and carbon black powders in order to achieve better reactivity. The reaction rate of this mixture was faster than the previous cases, but the reaction did not go to completion. Either heated by an oxy-acetylene torch in air or by a tungsten coil in vacuum, the heated surface ignited so violently such that the reacted top surface exploded into tiny pieces and it was impossible for the combustion wave to be sustained and propagated, and so the remaining integral pellet did not react at all. If the heat source was supplied continuously, the new top layer of the pellet broke up into pieces, leaving unreacted material as shown in Fig. 6. From the observations of cases (3) and (4), it seemed that if the reactant powders were ground, the reactivity would be enhanced but the overall product conversion was reduced. Moreover, the structural strength of the pellet was also reduced by grinding. As the particles were ground, there were many tiny and irregular particles produced and the surface of particles would be roughly fractured. We believe that the peculiar particle characteristics and the large particle size variation would result in a relatively loose structure of pellet during cold press. Thus, the violent reaction, which resulted by increasing the contact surface area of the particles, and the relatively loose pellet structure would lead to the pellet breaking as the gases or vapors were expelled.

From the above experimental observations of four combinations of reactive mixtures under two different reacting environments, we can conclude that it is possible to directly synthesize SiC using green pellets made of Si and carbon black heated by an oxy-acetylene torch in the air. We now report the characteristics of the products synthesized by this arrangement. If the whole reacted pellet was ground into powders and was examined by XRD, Fig. 4a shows that there was some considerable amount of Si present, which was due to the unreacted middle layer shown in Fig. 3. If only the reacted parts was examined by XRD, Fig. 4b shows that the conversion was near perfect and there was no trace of oxides present.

Because unreacted Si remained, the amount of carbon black was increased to see if we can remove the unreacted Si. However, if molar ratio between C and Si in the green pellet was varied from 1 to 1.3, the combustion phenomenon, product morphology, and conversion did not have much difference. The final words are that it is possible to combustion synthesize high-purity SiC powders with no oxide present by an oxy-acetylene torch in air. The experimental results suggest that for large-scale production of SiC, one can make compact reactive mixtures with large surface and thin thickness, and then feed the reactants into a tunnel kiln equipped with oxy-acetylene torches firing from the top and bottom directions. In this manner, a continuous manufacturing process could be feasible. Also, we believe that advanced materials with weakly exothermic reaction could be synthesized in the similar manner.

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