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β-SiC production by reacting silica gel with hydrocarbon gas

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A novel synthesis process, developed for producing high purity, submicron, non-agglomerated and low cost β-SiC powders. The process is based on carbothermal reduction reaction of a novel coated precursor. The precursor is derived from a silica gel and a hydrocarbon gas and provides high contact area between reactants. This yields a better distribution of carbon within the silica gel and results in a more complete reaction and a purer product. The powders produced in this process have a low oxygen content (less than 0.8 wt.%), very fine particle size (0.1–0.3 μm), narrow particle size distribution, non-agglomerated and are low cost. The sintering tests demonstrated that these powders can be pressureless-sintered to near theoretical density at about 2100°C in an inert atmosphere. No decarburization and no acid purification process was required before sintering.

1. Introduction

SiC is the leading advanced engineering ceramic used in metal working, electrical, and ceramic industries. This is due to its high temperature strength retention, excellent oxidation resistance, low thermal expansion coefficient, high wear resistance, and light weight. Fabrication of SiC involves a series of process steps that are designed to produce dense components. Processes include production of the SiC powder (powder synthesis); mixing and milling (powder preparation for consolidation); shaping (consolidation to engineering shape); sintering (densification/microstructural development) steps. Each step has the potential for introducing a detrimental heterogeneity, which persists or develops a new one during further processing. If reliable SiC component is to be fabricated, powder synthesizing methods must be developed to ensure that heterogeneities are eliminated from SiC powders.

The ideal powders for fabricating SiC components should have fine particle size, spherical uniform shape, high purity, and no agglomeration. In addition, the cost of high quality (high purity, high surface area, etc.) powder should be low. Present methods of synthesizing these powders require expensive steps that yield only small quantities of product. It is therefore apparent that a need is present for producing SiC powders with uniformity, speed and economy. In accord therewith, a primary object of the present work is to provide a process for synthesizing SiC powders possessing high purity, narrow particle size distribution, and stoichiometry for use in making components and composites for structural and electronic applications.

A number of processes exist for producing SiC powders. Among them is a method that exploits the reaction between the elemental Si metal and carbon [1]. This method requires 5–10 hours to complete, produces strongly agglomerated powders. The product requires extensive milling to yield fine powders and must be subjected to chemical purification to remove impurities from mill wear. In addition, the high cost of the elemental Si metal source leads to a relatively expensive product. Other methods, such as processes that rely on reactions between silanes and hydrocarbons do produce high quality powders, (but they) are much more expensive because of the high cost of the starting material [2].

An inexpensive technique for producing SiC powders involves the reaction between silica (SiO_2) and carbon particles in a controlled atmosphere (argon gas) at high temperatures (e.g. 1700°C–2100°C) [3]. Because the reactants exist in separate particles, the extent of this reaction is limited by the contact area between the reactants and the distribution of the carbon within the silica. These limitations result in a SiC product that contains unacceptable quantities of unreacted silica and carbon. Reaction time is typically very long (10–20 hours), and powders produced generally have non-uniform particle sizes (therefore requiring subsequent milling) and undesirable inhomogeneities.

The described process is patented and is a two-step method [4]. In the first step, a hydrocarbon gas is heated in the presence of silica gel. At temperatures about 600°C, the hydrocarbon gas decomposes and deposits a carbon coating on the silica particles. In the second step, the composite particles of silica gel and carbon react to form SiC powder. There are three advantages of using silica gel coated with carbon instead of a simple mixture of carbon black and silica powder. First, carbon coated silica gel forms an intimate mixing of the reactants. Second, it provides high surface contact between silica and carbon. Third, it produces a high-purity SiC powder at a comparatively low temperature, because the carbon source is a hydrocarbon gas. Consequently, the developed process results in a very complete reaction and yields a high-quality SiC powder that meets the exacting requirements for the manufacture of ceramic components: the powder has very fine, uniform spherical particles; contains very few impurities (particularly oxygen, iron, and free silicon); and it is presureless sinterable.

This paper concentrates primarily on the carbothermal synthesis of submicron β-SiC powders using carbon coated silica gel and the relations between powder quality and process variables.

2. Experimental procedure

Rotating coating apparatus, consisting of a 10 cm ID × 35 cm long stainless steel vessel was used for preparing low density, pyrolitic carbon coated silica gel utilizing propylene (C_3H_6) as the coating gas at 600°C. The silica gel about 100 gram (W. R. Grace, Sylox 2) were placed in the vessel and it was evacuated. Then the propylene (C_3H_6) gas was filled into the vessel to initiate the deposition of a low density pyrolytic carbon coating. The vessel was heated to 600°C while it was rotating. Thermal cracking of propylene increased the internal vessel pressure upon initiation of the carbon coating. A gas pressure sensor with digital readout allowed monitoring of the internal vessel pressure. The coating step was continued until the desired amount of carbon was deposited. The coating time was varied as a function of amount of silica gel and its surface area, deposition temperature and propylene pressure.

The amount of carbon deposition in the coated silica gel was determined by using thermogravimetric analysis (TGA). The samples with about 38 wt.% carbon were subjected to second step. SiC powders were produced by promoting a reaction within the carbon coated silica gel at temperatures of 1400°C to 1650°C for 2 hours in flowing argon gas (1LPM). This step was performed in an atmosphere controlled tube furnace with ID 70 mm.

The characterization of the produced powders involved determination of free and total carbon and oxygen, X-ray diffraction to identify the crystalline phases and determination of BET surface area. Oxygen and total carbon determination was conducted at Coors Analytical Laboratory at Golden, CO. Oxygen was analyzed by infrared detection on a LECO N/O induction furnace. Total carbon was determined by ignition in a LECO induction furnace and analyzing the evolved CO_2 coulorimetrically. SEM and TEM were used to reveal the morphology of powders.

For sintering tests; produced SiC powders with 0.5 wt.% Boron, 2 wt.% phonelic resin, 5 wt.% α-SiC, 0.5 wt.% Tamol and 4 wt.% PEG were placed in plastic jars with 40 ml of 88% isopropyl alcohol and 12% water and two 1/4″ SiC balls, milled for one hour. These samples were pan dried in a vacuum oven overnight and then dry milled for three hours with four 1/4″ SiC balls. A compaction pressure of 2500 kg/cm^2 yielded 2.5×0.5 cm pellets with density of about 55% theoretical. These pellets were sintered at 2090°C in an argon atmosphere for 30 minutes with ten-hour cycle at Coors Ceramics Company. Bulk densities of compositions were measured by the liquid (freon) displacement technique.

3. Results and discussion

The reaction between carbon and silica provides an inexpensive technique for producing silicon carbide.

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)\ [T_{eq} = 1514°C] \tag{1}$$

Because the reactants exist in separate particles, the extent of this reaction is limited by the contact area between the reactants and the distribution of the carbon within the silica. These limitations result in a silicon carbide product that contains unacceptable quantities of unreacted silica and carbon.

Although the reaction (1) involves both reactants in solid form, the carbothermal reduction of silica consists of gas-solid reactions. The reduction of silica by carbon may take place through the following gas-solid reactions:

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) \tag{2}$$

$$C(s) + CO_2(g) = 2CO(g) \tag{3}$$

$$SiO(g) + 2C(g) = SiC + CO(g) \tag{4}$$

The solid-solid reduction takes place before any other reaction does in the system and this reaction provides the initial CO gas for solid-gas reactions. Once the reaction is initiated, carbon regenerates CO gas through reaction (3). In these reactions, carbon is either a CO_2 getter or a CO generator, which keeps the CO_2/CO ratio low enough to make the reduction of SiO_2 possible by gas phase CO. Therefore, the intimate contact of carbon with SiO_2, SiO and CO_2 is essential during the reduction reactions for complete conversion of SiO_2 into SiC. Full conversion using a stoichiometric ratio of SiO_2/C requires an additional contact between C and SiO_2 particles as the intimate contacts of carbon with SiO and CO_2 can be easily achieved in the process.

The new process provides intimate contact of carbon with SiO_2, SiO and CO_2, which is essential for complete conversion of SiO_2 into SiC. The starting raw materials were silica gel (Sylox 2) and hydrocarbon gas (propylene, C_3H_6). Silica gel (Sylox 2) is mainly used as an absorbent for the chemical industry. Propylene is a commodity chemical and polymerized to make rubber for tires. It easily decomposes and it is easily stored and transported. These properties of starting materials make this process economically very attractive. Received Sylox 2 was subjected to BET surface area measurements and it was measured to be 130 m^2/g as compared to the 225 m^2/g reported by the supplier. This silica gel was loaded into the rotating coating reactor and carbon deposition was performed at 600°C for about 7 hours. The BET surface area of the carbon coated silica gel precursor was directly determined by multi point BET analysis and found to be 56 m^2/g. This result confirmed that the carbon coating on silica gel instead of the formation of individual carbon particles was taking place in the coating process. Fig. 1 shows the X-ray diffraction pattern of the precursor, which consists of amorphous silica gel and carbon.

By reaction of the carbon coated silica gel at 1400–1650°C, β-SiC powder was produced. Depending on the carbon content in the coated silica gel precursor, SiC powder was produced with a different amount of oxygen and free carbon. Table I shows the influence of the initial carbon content on the oxygen and free carbon content in resulting SiC powders. At a stoichiometric ratio of carbon and silica corresponding to the reaction $SiO_2 + 3C = SiC + 2CO$, the SiC obtained contained 0.71 wt.% of oxygen (temperature of synthesis was 1650°C, holding time was 2 hours in flowing argon of 1LPM). With increase in the silica content in the coated precursor, a significant increase in the concentration of oxygen in resulting SiC powder was observed. From a coated precursor with a >10% excess of carbon, compared with the standard ratio, SiC was produced with an oxygen content of 0.64 wt.%, but it contained excessive free carbon. Further increase in the carbon content in the precursor did not lead to a substantial decrease in the oxygen content in SiC powder, while the content of free carbon increased. The optimal amount of carbon in the precursor was determined to be 37.9 wt.% which was slightly higher than stoichiometric amount (37.5 wt.%). In the subsequent experiments, SiC synthesis was conducted with the precursor containing 37.9 wt.% carbon.

TABLE I The influence of the initial carbon content on the oxygen and free carbon in the SiC powder produced at 1650°C for 2 hours in flowing argon

Carbon content in the precursor (wt.%)	Oxygen content in the resulting SiC powder (wt.%)	Free carbon in the resulting SiC powder (wt.%)
36.9	4.42	2.5
37.9	0.71	3.2
39.3	0.64	6.8

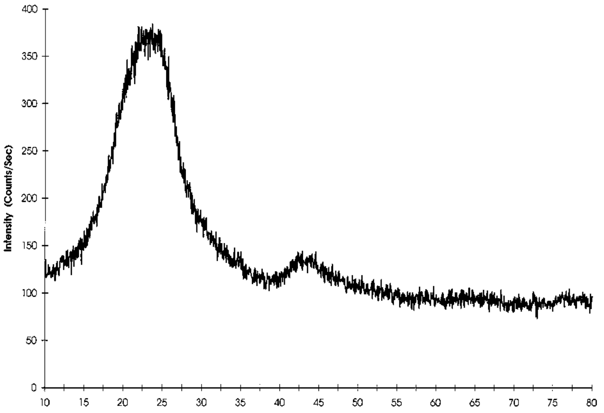

Figure 1 X-ray diffraction pattern of carbon coated silica gel precursor.

TABLE II The percent weight loss and oxygen content in the resulting SiC as a function of temperature (theoretical weight loss = 58.284 wt.%; residence time is 1 hour in flowing argon; precursor contains 37.9 wt.% of carbon)

Reaction temperature (°C)	Weight loss (%)	Oxygen content in the resulting SiC powder (wt.%)
1400	21	—
1450	38	8.1
1500	59	3.8
1600	59	2.6
1650	60	1.01

From Equation 1, the percentage weight loss for the stoichiometric reaction is calculated to be 58.284%. A weight loss less than this amount indicates an incomplete reaction, whereas greater weight loss indicates either the presence of volatile species in the silica gel or loss of silicon in the form of SiO(g). Weight loss calculations were made to determine the completion of the conversion and the yield. Table II shows the percent weight loss and oxygen content in resulting SiC powder as a function of reaction temperature for residence time 1 hour in flowing argon atmosphere (1LPM). The weight loss determinations indicated that the formation of SiC started at temperatures of <1500°C, only partial conversion to SiC occurred, the remainder being unconverted SiO_2 and C. Complete conversion occurred at temperatures above 1500°C. The oxygen content in the produced SiC powder as a function of reaction temperature was also included in Table II. The SiC powder from the precursor containing 37.9 wt.% carbon had 1.01 wt.% oxygen and 3 wt.% free carbon when they were reacted at 1650°C for 1 hour in flowing argon atmosphere (1LPM).

The holding time at the synthesis temperature had also influence on the oxygen and free carbon content. Increase in the duration of the holding time to two hours at the synthesis temperature of 1650°C resulted in the formation of SiC powders with oxygen content 0.71 wt.% and free carbon less than 2 wt.%. The results showed that the produced SiC powder does not require a decarburization by oxidation and an acid treatment to remove oxygen for sintering.

The X-ray diffraction patterns in Fig. 2 shows the formation of the SiC powder as a function of reaction temperature (the holding time at reaction temperature was 1 hour in flowing 1LPM argon gas). At 1500°C silica phase disappeared and single phase β-SiC formed. The amount of the unreacted silica and carbon decreased with the reaction temperature. At 1600°C β-SiC with traces of α-SiC was obtained with no presence

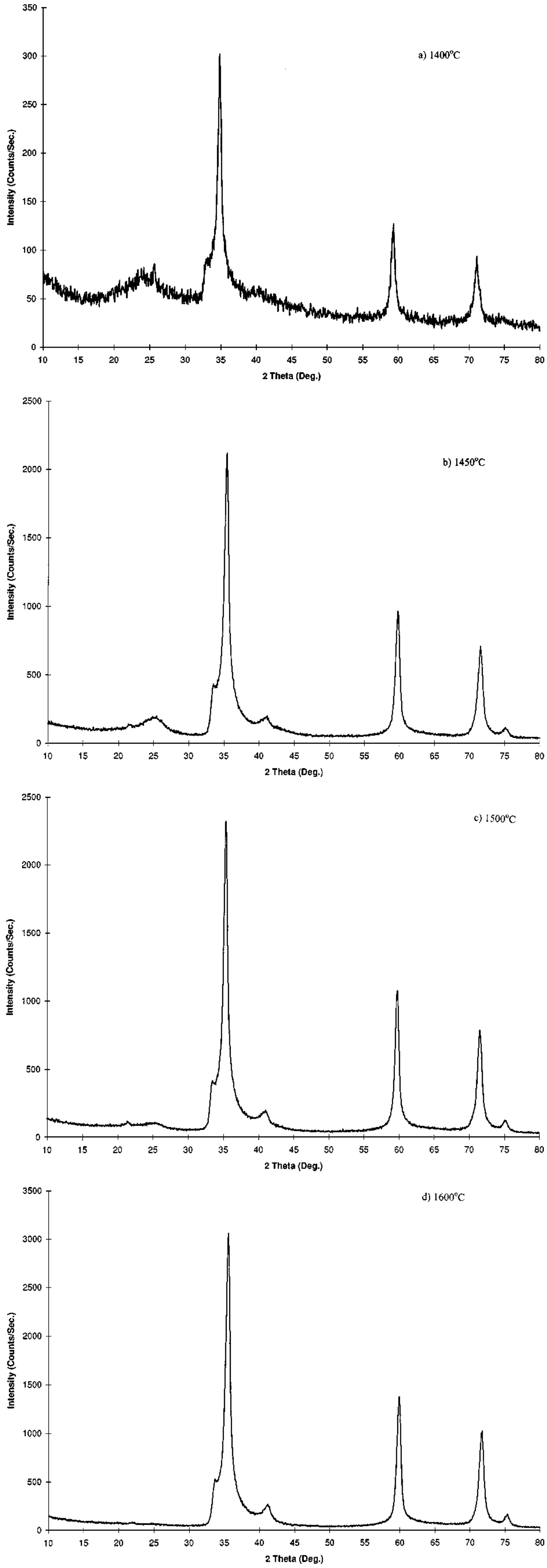

Figure 2 X-ray diffraction patterns of the reaction products as a function of temperature. (a) 1400°C, (b) 1450°C, (c) 1500°C, (d) 1600°C.

of unreacted carbon and silica. The degree of crystallinity of the β-SiC powder also increased with reaction temperature.

Fig. 3 shows a TEM bright field image and electron diffraction pattern from a group of SiC particles synthesized at 1650°C for 4 hours in flowing argon gas. As it can be seen from Fig. 3, the produced SiC powder has fine particle size (0.2 μm), narrow particle size distribution, and are loosely agglomerated. Study of the electron diffraction pattern was conclusive to crystal structure of the produced powder, showing β-SiC with traces of α-SiC.

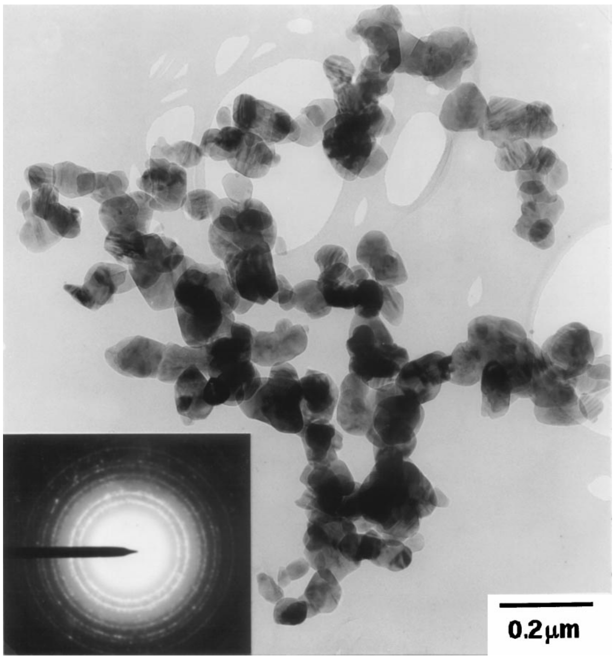

Figure 3 TEM bright field image and electron diffraction pattern from a group of SiC particles.

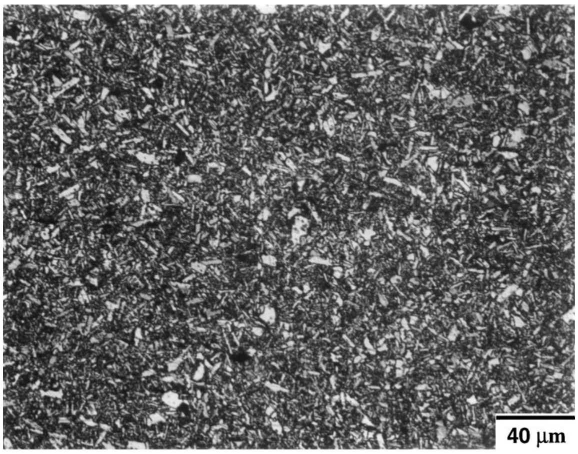

Figure 4 Microstructure of sintered SiC produced from the carbon coated silica gel precursor (400X).

In order to evaluate the sinterability of the synthesized powders, the density after sintering was measured to be about 90% of theoretical density. Fig. 4 is a micrograph of SiC powder sintered at 2090°C in an argon atmosphere for 30 minutes with 10 hours of cycle. This micrograph has a typical microstructure of sintered β-SiC, which consists of fine grains and a few pores. These initial investigations of densification showed that the produced SiC powder was highly sinterable.

4. Conclusion

β-SiC powders were synthesized by using a carbon coated silica gel precursors. The SiC powders produced in this process have a high purity (less than 0.8 wt.% oxygen), very fine particle size (0.1–0.3 μm), narrow particle size distribution, non-agglomerated and are low cost. The SiC powders were produced by promoting reactions within the carbon coated silica gel precursor at temperatures of 1400–1650°C in a flowing argon gas. The advantage of the process studied here is that synthesized SiC powders did not contain any residual silica and carbon if the carbon amount in the precursor was 37.9 wt.%. The sintering experiments showed that the produced SiC powders can be pressureless-sintered to near theoretical density at about 2100°C in an inert atmosphere.

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References

1. W. BOECKER, H. LANDFERMANN and H. HAUSNER, *Pow. Met. Int.* **11** (2) (1979) 83.
2. H. WU and D. W. READEY, *ACerS Transactions* **2** (1987) 35.
3. J. G. LEE, PhD dissertation, University of Utah, 1976.
4. G. GLATZMAIER and R. KOC, US Patent no. 5,324,494 (1994).

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