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Sintering of ultrafine SiC powders prepared by plasma CVD

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Ultrafine SiC powders with a nanometre particle size were synthesized by r.f. plasma chemical vapour deposition (CVD) using a chemical system of SiH_4–C_2H_4–Ar. The powder was also ultrapure with a grade of 99.999% purity. The product was polytype 3C–SiC and black in colour, in spite of its high purity, because of its ultrafine size. Silicon carbide is a difficult ceramic to sinter; it is possible to sinter it to full density with the aid of sintering additives. Ultrafine and ultrapure SiC powders were hot-pressed without sintering additives in the present study, in order to investigate the sintering behaviour. The CVD powders proved sinterable to 88% theoretical density without sintering additives. The present experiments revealed that powder treatment before firing was a key technology when using ultrafine powders as starting materials in the sintering process. The sintering behaviour of the powder was characterized by a large shrinkage. Phase transformation was negligible after hot pressing at 2200° C for 30 min.

1. Introduction

Silicon carbide has high potential in applications for high-temperature structural materials, because of its good properties of thermal shock resistance, mechanical strength, chemical resistance, decomposition temperature, etc. In spite of these superior properties, silicon carbide cannot be used widely in industry. Some developments in the fabrication of SiC ceramics have been required in order to obtain high-quality ceramics with high reliability and good mechanical properties at high temperature. SiC is a typical material which is difficult to sinter because of its covalent bonding character. In order to densify SiC, sintering additives such as boron, carbon, aluminium and beryllium are necessary for present technology. A big technological barrier exist to producing a fully dense SiC without sintering additives in the present state of technology. Hence almost all sintering studies on SiC have been carried out with sintering additives, in order to densify SiC. In spite of the difficulty, the sintering of pure SiC was investigated using home-made ultrafine particles of SiC. Ultrafine powders are expected to decrease the sintering temperature and to be densified without sintering additives. Plasma chemical vapour deposition (CVD) is suitable to produce ultrafine powders with high purity and a narrow particle size distribution.

It has been attempted to produce ultrafine SiC powders by various methods such as gas phase reaction in the $(CH_3)_4Si$–H_2 system [1], gas evaporation method [2], plasma decomposition of CH_3SiCl_3 [3], and pyrolysis of polysilane [4]. Kondo and Saito [5] prepared SiC powders containing 0.8 to 1.0 wt % boron by plasma CVD using the chemical system of SiH_4–B_2H_6–CH_4–Ar. The SiC powders in the presence of boron were well sintered by normal sintering. Pure ultrafine SiC powders have not yet been reported to be densified without the use of additives. Ultrafine SiC powders were produced by the r.f. plasma CVD method using the chemical system of SiH_4–C_2H_4–Ar, in order to study their sintering behaviour without additives.

2. Experimental procedure

2.1. Powder preparation

SiC powders for use in sintering experiments should have the following characteristics [6]; ultrafine particles, ultrahigh purity both in the crystal phase and chemical elements, uniform particle size, and spherical particle shape. SiC powder having the above characteristics has not been available to date, and the commercially available particle size, for example, is of submicrometre order. The first step in the present experiment was to prepare SiC powder with ultrafine particle size and high purity. An inductively coupled thermal plasma was applied to the chemical vapour deposition method in order to obtain ultrafine and ultrapure SiC. A block diagram of the r.f. plasma CVD apparatus used here is schematically drawn in Fig. 1. Electric power was supplied by a radio frequency generator whose maximum capability was 15 kW plate output power. The frequency was about

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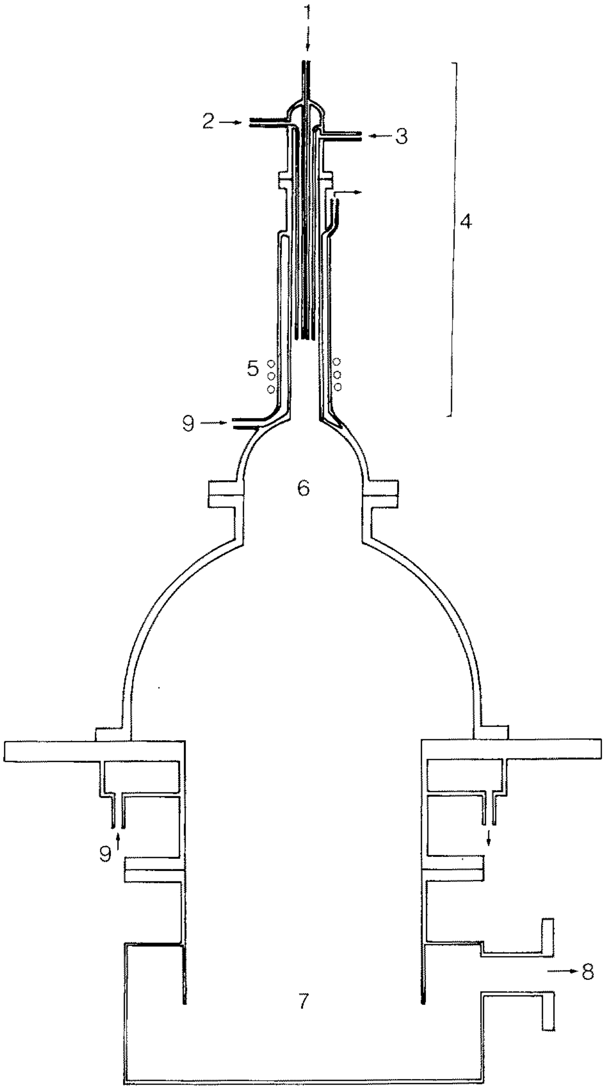

Figure 1 A schematic diagram of the r.f. plasma CVD apparatus. 1, Raw gas; 2, plasma gas; 3, sheath gas; 4, plasma torch; 5, r.f. coil; 6, reaction chamber; 7, collection chamber; 8, exhaust; 9, cooling water.

4 MHz when r.f. power inductively coupled with thermal plasma was passed through the work coil as shown in Fig. 1. The plasma CVD furnace basically consisted of a work coil and three concentric quartz tubes with three independent gas flow lines. Plasma working gas and sheath gas were independently introduced from an outer and an inner flow line. The reactant gas mixture was injected into the thermal plasma from a central gas line.

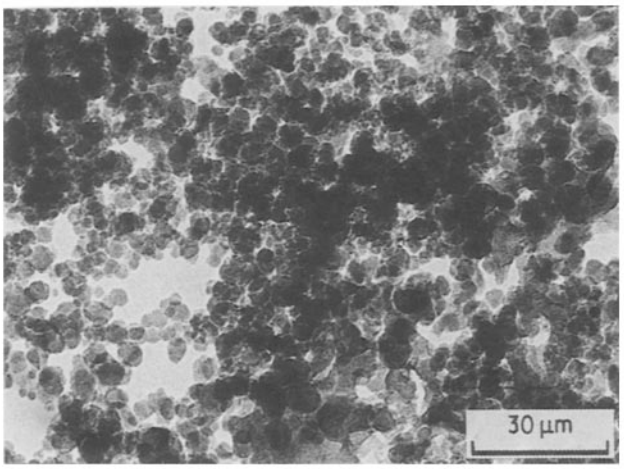

Figure 2 A microphotograph of ultrafine SiC.

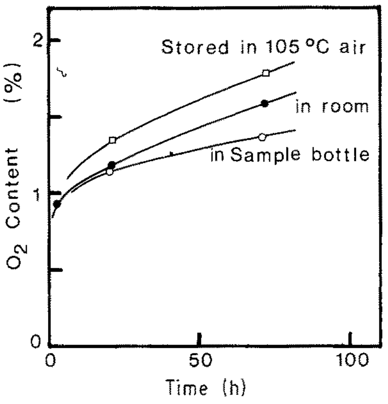

Figure 3 Change of oxygen content of ultrafine SiC powders on exposure to air.

Reactants were SiH_4 and C_2H_4 whose flow rates were 12 to 18 standard cubic centimetre per minute (SCCM) and 18 to 38 SCCM, respectively. The molar ratio of C/Si in the reactants was controlled between 2 and 6 by adjusting the flow rates of C_2H_4 and SiH_4 gases. The plasma working gas, sheath gas and carrier gas were 300 SCCM, 2900 SCCM and 680 to 850 SCCM argon in the flow rates, respectively. The gaseous pressure in the reaction chamber was kept constant at 2.1×10^4 Pa by controlling the pumping speed of an exhaust line. Gas pressure and flow rate were strictly controlled because these parameters were important for the chemical species to effect a mean free path and staying time in the plasma.

The reactant gases were decomposed into atoms or ions by heating above 6000 K in thermal plasma and these activated chemical species recombined in the temperature zone below 3000 K to nucleate SiC. The hot SiC particles flowed down in a stream and were deposited on a vessel for powder collection.

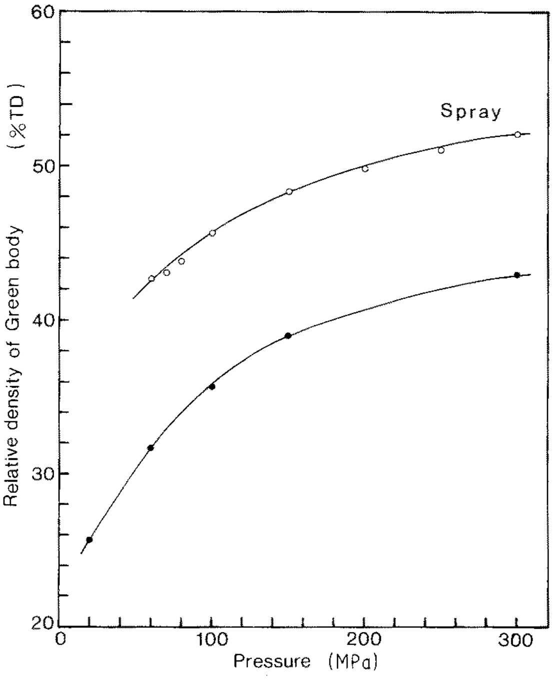

Figure 4 Relationship between green density and forming pressure uniaxially applied.

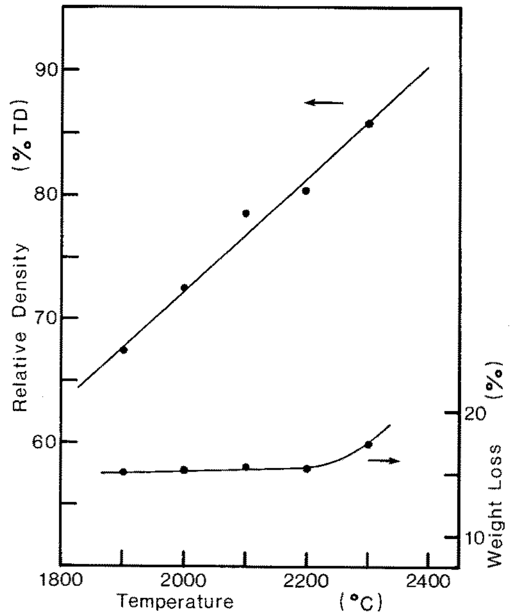

Figure 5 Relationship between sintered density and sintering temperature. (HP: 40 MPa, 30 min, Ar 1 atm).

2.2. Formation and hot pressing

Polyvinyl alcohol (PVA) was used to help form a powder compact of SiC ultrafine particles. After SiC mixed with PVA by a ball mill for 12 h in ethyl alcohol, the slurry was dried.

Ultrafine particles of SiC were granulated by two methods in order to produce a high green density after forming. In one method, the dried slurry was pulverized by a mortar. The pulverized powder was pressed into a disc under a pressure between 20 and 300 MPa. The disc was crushed again to obtain a granulated powder of ultrafine particles of SiC. In the other method, ultrafine particles were granulated by a spray drier.

Sintering experiments were carried in a hot-pressing apparatus using graphite dies. A graphite crucible containing the dies was heated by the r.f. induction method. A frequency of 20 kHz was used in order to produce a uniform temperature in the crucible, because a lower frequency causes a small skin effect in inductive coupling. Samples were heated in an atmospheric pressure of argon gas flow between 1900 and 2300° C for 30 min. The pressures were kept constant during hot pressing in the range 20 to 50 MPa.

2.3. Measurements

SiC powders used as starting materials were observed by transmission electron microscopy (TEM) and the crystal phase was identified by X-ray diffractometry. The green density of a powder compact was calculated from weight and volume. The shrinkage behaviour was measured by a ram displacement using a differential transformer. The density of the sintered body was measured by Archimedes' method, and its crystal phase was identified using X-ray powder diffractometry with nickel filtered Cu$K\alpha$ radiation. The microstructure was observed by scanning electron microscopy (SEM) and the oxygen content of the powder was analysed using an oxygen analyser (LECO TC-136 model).

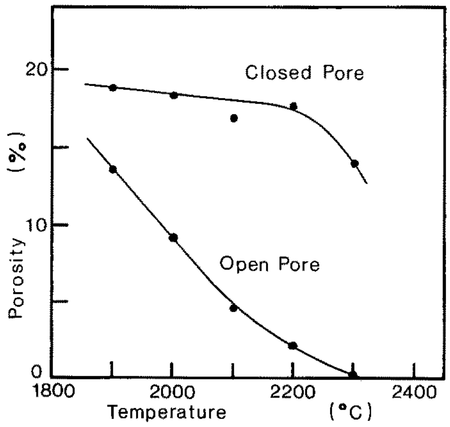

Figure 6 Relationship between porosity and sintering temperature. (HP: 40 MPa, 30 min, Ar 1 atm).

3. Results and discussion

Some problems still exist in powder synthesis by plasma CVD methods despite many trials. Almost all powders have been synthesized using an arc plasma or an arc jet plasma, which is well established in plasma generation and operation [7–11]. These kinds of plasmas, however, are difficult to obtain as high-quality powders. Reed [12] showed that inductively coupled plasma could be applied to ceramic synthesis. This kind of plasma has potential in the preparation of high-quality powder because of a capability of easy plasma control. Two big problems remain: plasma instability and reactant injection into the plasma flame. The problems have recently been overcome by Yoshida *et al.* [13] and by ourselves [14], independently. The features of the present powder preparation were high-speed production, high-quality powders and highly efficient production, because the reactants could pass through the centre of a plasma flame.

The particle size of the powder was 5 nm, which was controllable between 5 and 20 nm, and its aspect ratio was nearly one. A microphotograph of ultrafine particles of the present SiC is shown in Fig. 2. The product powder had a polytype of 3C-SiC and was pure in the crystal phase, containing no other SiC polytype, carbon or silicon. The powder was also ultrapure as shown in Table 1. The ultrafine powders were black, in spite of the purity. It is reported [15] that ultrafine metallic powders were grey in colour for diameters smaller than 0.1 μm and black for diameters smaller than 10 nm. The light absorption character

TABLE I Cation impurities by emission spectrochemical analysis (p.p.m.)

Element	Present powder*	Commercial powder
B	–	200
Al	–	800
Ca	–	50
Ti	–	50
Cr	–	20
Fe	5	300
Cu	–	40
Zn	–	30
Ag	–	1
W	–	1000
Mg	1	?

*A bar means that element is under the sensitivity limit by emission spectrochemical analysis.

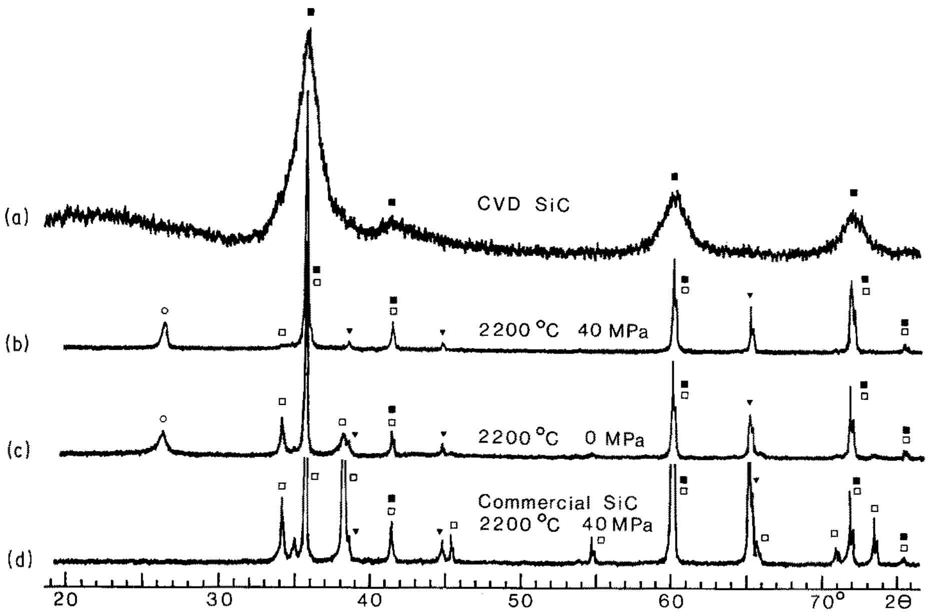

Figure 7 X-ray diffraction pattern. (a) Present ultrafine SiC powder. (b) Sintered body at 2200° C at 40 MPa for 30 min. Starting powder is as in (a). (c) Normal sintered body at 2200° C for 30 min. Starting powder is as in (a). (d) Sintered body at 2200° C at 40 MPa for 30 min. Starting powder is commercially available β-SiC with 0.3 μm particle size. (■) β-SiC, (□) α-SiC, (○) C, (▼) Al sample holder.

changes for ultrafine particles containing a limited number of atoms.

It is known that oxygen contamination retards densification during sintering and this behaviour was true for the present ultrafine SiC powder. Ultrafine particles are considered to be easily oxidized on the surface in air. The oxidation behaviour of oxygen was investigated and the change in oxygen content in the powder was analysed, as shown in Fig. 3. Oxidation velocity varied according to methods of storage. The oxygen content reached 1 wt % rapidly on exposure to air and gradually became saturated after 2 h. Ultrafine powders should be treated carefully in air to avoid surface contamination.

Another problem with ultrafine particles is difficulty in obtaining a high green density. Powder granulation and forming pressure were effective in increasing the density of a green powder compact. These effects are shown in Fig. 4, where granulation by a spray drier produced an increase in relative density by 10% in the green compact. The forming pressure was very effective on green density up to 100 MPa, the effect becoming saturated above 300 MPa. Cold isostatic pressing (CIP) after uniaxial pressing was also effective in increasing green density by about 10% of the theoretical density (TD). These processes made a green compact possible with a density exceeding 50% TD, and sintering experiments then became possible by using the powder compacts prepared according to these data. The densification during sintering was greatly affected by powder treatment before firing.

The effect of sintering temperature on densification is shown in Fig. 5, where hot pressing was carried out at 40 MPa pressing for 30 min in an argon gas flow of 1 atm pressure. Densification proceeded as the sintering temperature was increased in the range 1800 to 2300° C. The sintered density achieved about 85% TD at 2300° C. It should be noted that this densification was achieved for an SiC sample without any sintering additives. Weight loss was observed by evaporation at 2300° C as shown in Fig. 5. It is expected that the sintered density was decreased by evaporation at about 2400° C, thus the optimum sintering temperature is decided by balancing these opposite effects. The behaviour of open and closed pores was also investigated and their temperature effects are shown in Fig. 6. This figure also shows that open pores could not exist at 2300° C where the relative density was 85% TD. Closed pores also decreased drastically above 2200° C.

Fig. 7 shows changes in the X-ray diffraction patterns for ultrafine SiC powders effected by sintering temperature and pressure. A typical X-ray diffraction chart from the as-deposited ultrafine SiC powders is shown in Fig. 7a. The product was identified as 3C-SiC (β-SiC) and the particle size, produced under a C/Si molar ratio of 2.4 for example, was calculated to be 16 nm, using Warren's method. Changes in their widths and heights after sintering at 2200° C for 30 min are shown in Figs 7b and c. Graphite was crystallized and some α-SiC transformed from β-SiC

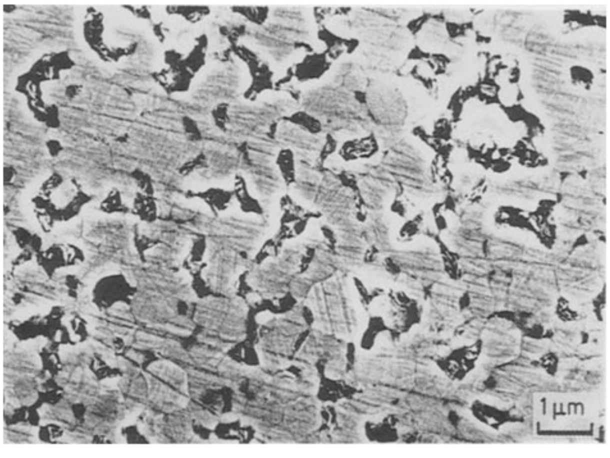

Figure 8 Scanning electron micrograph of etched surface of sintered body hot-pressed at 2200° C at 40 MPa for 30 min without sintering additives. The starting material is the present ultrafine SiC powder.

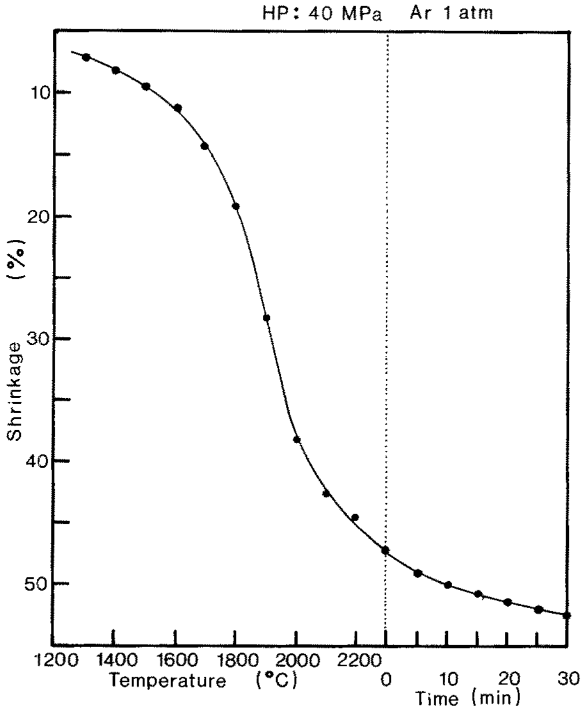

Figure 9 Shrinkage curve during hot-pressing.

could be observed as shown in Figs 7b and c. Pressure retarded the transformation of the powder during sintering, as shown in Fig. 7b. If commercial powder was used instead of plasma CVD powder, phase transformation could be observed after sintering under pressure, as shown in Fig. 7d.

SEM observation (Fig. 8) indicates that the grain size was 1 μm and that the aspect ratio of a grain remained at 1 after sintering. The microstructure of sintered SiC from ultrafine powders are fine and homogeneous, but the density was not high enough in this experiment. To obtain sufficiently densified bodies from these ultrafine SiC powders, the powder should be carefully treated without oxygen contamination and be formed with a high green density. A well sintered body with good mechanical and chemical properties at high temperature can be expected from this method because of preferable microstructures and high purity.

The shrinkage curve during hot-pressing is shown in Fig. 9. The sample began to shrink about 1600° C, and the rate of shrinkage was maximum at about 1900° C. The maximum shrinkage was sometimes observed to be 50% after sintering at 2300° C for 30 min.

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