Original

Synthesis of Silicon Carbide by High Temperature Flame

by

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Abstract

An approach to the synthesis of silicon carbide (SiC) ultrafine (u.f.) particles using silica (SiO₂) powders by high temperature flame was briefly introduced. Calculations including Gibbs free energy of different reaction systems showed the possibility of SiC formation. The SiO₂ u.f. particles (5-10 nm) could be formed from the SiO₂ powders (50-100 μ m) by high temperature CH₄-O₂ flame around 2500 K. β -SiC u.f. particles including reticular membrane could be synthesized by an electric furnace at about 2018 K through Si + CH₄, SiO + CH₄ and SiO₂ + CH₄ reaction systems, respectively. The effects of H₂, CO, CO₂ and H₂O on the SiC percentage of synthesized u.f. particles were tested.

Key Word : Silicon carbide ; Ultrafine particle ; Flame synthesis

I. Introduction

One of the important counter measure to CO₂ problem is to develop a significant energy saving technology. Ceramic gas turbine or ceramic engine is one of the key technologies in this field. The development of these technologies is mostly dependent on the low energy input and low cost production of non-oxide fine ceramic powders such as SiC and silicon nitride (Si₃N₄) etc.. For these reasons, the studies of SiC formation process have been intensively carried out by many researchers for a long time. The most representative work among them is SiC formation by the chemical vapor deposition (CVD) process^{[1]-[4]} which has been presented so far. However, because of using expensive and ignitable Si source gases such as SiH₄ and CH₃SiCl₃ etc., the CVD-SiC process is high-cost and not safety.

A low-cost and safe synthesis process of SiC u.f. particles using SiO₂ powders as Si source and a CH₄-O₂ flame around 2500 K as a high temperature reactor was proposed and its possibility was investigated mainly in our laboratory. The advantages of the flame method are as follows :

- 1) A cost of Si source in the synthesis process is exceedingly low, compared with SiH₄ and CH₃SiCl₃ etc.;
- 2) This method is a most economical way to realize high temperature field, since it does not require

Received August 31, 1995

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an electric power like the plasma^[5] [6] or laser;

3) A high speed production of u.f. particles by a reaction between Si vapor and CH_x radical is carried out under an atmospheric pressure region ;

4) It is unnecessary to use expensive refractory materials for the reactor wall, because the high temperature zone can be formed by the flame itself in the space.

The SiC formation process has two stages. At the primary stage, SiO₂ vapor are formed from SiO₂ powders in high temperature CH₄-O₂ flame. At the secondary stage, SiC u.f. particles are synthesized by the reaction of SiO₂ vapor and CH₄. Because the combustion of CH₄-O₂ has a complex reaction mechanism which includes more than one hundred elementary reactions and a lot of species such as CO, CO₂, H₂O, OH, H, CH₃, CH₂, CH₂O, CHO etc.,^[7] the possibilities of SiC formation by the flame must be investigated fundamentally by using a simple reaction system at first.

In the present study, thermodynamic calculations including Si/CH₄, SiO/CH₄ and SiO₂/CH₄ systems were carried out at first, in order to examine the possibility of SiC formation from the thermodynamic point of view. Then, as a first experimental step, it was examined whether SiO₂ powders could be evaporated into the gas phase and changed to u.f. particles after passing the high temperature CH₄-O₂ flame. The experiments of SiC formation from Si + CH₄, SiO + CH₄ and SiO₂ + CH₄ were performed by an electric furnace as the second experiment. Furthermore, the effects of stable species in CH₄-O₂ flame such as H₂, CO, CO₂ and H₂O on the SiC percentage (SiC/(Si + SiC)) of synthesized u.f. particles were examined.

II. Thermodynamic Calculation

The Gibbs free energy ($\Sigma \Delta G$)^[8] of Si/CH₄ reaction in Eqs. (1), $\Sigma \Delta G$ of SiO/CH₄ reactions in Eqs. (2), (3) and $\Sigma \Delta G$ of SiO₂/CH₄ reactions in Eqs. (4), (5), (6) under the various reaction temperature were calculated respectively.

Fig. 1 shows that $\Sigma \Delta G$ versus temperature plot for these reactions. All of them tend to negative with an increase of temperature. $\Sigma \Delta G$ of SiO/CH₄ reactions or SiO₂/CH₄ reactions also tend to negative with an increase of CH₄ molecular.

SiO₂ equilibrium vapor pressures was calculated by Kelley's experience equation^[9] where the size effect was estimated by Kelvin's equation. Fig. 2 shows that SiO₂ equilibrium vapor pressure is about 0.15-0.18 atm at around 2000 K. Through these calculations, it is known that SiO₂ powders can be vaporized in the temperature condition of up to 2000 K. Hence, it is expected that the gas phase synthetic reactions of Si/CH₄, SiO/CH₄ or SiO₂/CH₄ can proceed over a 2000 K temperature condition.

Figure 1. $\Sigma \Delta G$ versus temperature plot for SiC formation reaction : (1), (2), (3), (4), (5) and (6).

Figure 2. SiO_2 vapor pressure versus temperature.

III. Experimental Procedure

A flame reactor shown in Figure 3 was used for the evaporation of SiO_2 powders. It consisted of three parts those were a flame gas feed, a source powder supply and a reactor in an electric furnace. Gas flows including CH_4 , O_2 and Ar carrier gas were controlled by mass flow controllers. SiO_2 powders were fed into the reactor through a fluidized bed using 75 vol.% O_2 diluted by argon (Ar) as a carrier gas. The size range of supplied SiO_2 powders was 50- 100 μm . The outside of the reactor tube was heated by an electric furnace of silicon-knit heaters (Model: DSp-24, Siliconit Heater Industry Corp.). The temperature in the middle part of reactor tube was 1600 K. There

Figure 3. Schematic of the experimental apparatus of a flame reactor.

were four nozzles in the top of burner whose diameter was 0.88 mm and the gas linear velocity was 83 m/s which corresponds to Reynolds number of 3900. The equivalence ratio was 0.8- 1.4, and the temperature of CH₄-O₂ flame was around 2500 K. The formed particles were collected through a sample probe in a screen filter and were examined by TEM (Model : H-7000, Hitachi Co., Ltd.), XRD (Model : RAD-C, Rigaku Co., Ltd.) with Ni-filtered CuK_α and FT-IR (Model : FTIR-8600PC, SHIMADZU Corp.).

The possibilities for the synthesis of SiC using SiO₂ powders as Si source was investigated by an electric furnace system shown in Figure 4a. It consisted of an electric resistance furnace equipped by LaCrO₃ heaters (Nippon Kagaku Togyo Co., Ltd.) and a control unit (Okura Electronic Corp.). A maximum temperature capability of heaters was 2073 K and about 2018 K at the inside of the alumina reactor tube (ID : 30 mm). A heating rate was 4.0 K/min which was measured by a Pt40Rh20 thermocouple between the heaters and the reactor tube. An alumina crucible loading Si source powders (Av. size : 10 nm, Mizusawa Chemical Industry Corp.) was kept in the hot zone of the furnace. The CH₄ (Conc.: 0.5-3.0 vol.%) balanced by Ar was introduced into the top of the reactor tube and exhausted from the bottom. After the completion of the synthesis experiments, the specimens were collected from the crucible.

Furthermore, we prepared another method of collecting specimen shown in Figure 4b to collect the synthesized SiC u.f. particles from Si, SiO and SiO₂ powders (size range : 1-3 μm) as Si source. The CH₄ balanced by Ar was introduced into the bottom of the reactor tube and exhausted from the top. To prevent any possibility for oxidation of Si source or SiC by impurity oxygen during reaction, another Ar gas as a purge gas was fed along the wall of the reactor tube which ensured the

(a) Type 1.

Figure 4. Schematic of the experimental apparatus : (a) type 1 and (b) type 2 of an electric furnace.

inside pressure about 20-40 mm H₂O higher than an atmospheric pressure in the whole experimental process. A paper filter was directly put above the reactor tube to trap solid u.f. particles.

H₂ (Conc : 10.0 vol.%), CO (Conc.: 2.0 vol.%), CO₂ (Conc.: 10.0 vol.%) or H₂O (Conc.: 1.0 vol.%) diluted by Ar carrier gas were respectively fed into the hot zone of the reactor tube. The gas flow velocity was about 14.0 cm/s at 2018 K. All of the collected specimens were examined using XRD (Model : RAD-C, Rigaku Co., Ltd.) with Ni-filtered CuK α , SEM (Model : S-450DX, Hitachi Co. Ltd.) and TGA (Model : TGD-7000RH, Vacuum Science and Engineering Corp.).

IV. Results and Discussion

(1) Evaporation Experiment

The evaporation of SiO₂ powders in the CH₄-O₂ flame was conducted under the oxidizing condition. The experimental conditions were CH₄ : 10 l/min, O₂ : 25 l/min, Ar : 5 l/min ; feed time : 2 min. The white fine particles were collected from the filter. Figure 5 shows a TEM photograph of

(b) Type 2.

Figure 4. Schematic of the experimental apparatus : (a) type 1 and (b) type 2 of an electric furnace.

Figure 5. TEM photograph of u.f. particles formed from the evaporation of SiO₂ powders in a flame reactor.

them. The particle sizes observed by TEM were basically in the range 5-10 nm, confirming the evaporation and condensation mechanism of the supplied SiO_2 powders. The relative and accumulative distribution were determined by counting several hundreds particles from the TEM photographs. XRD of the particles shows only the peaks of SiO_2 (JCPDS N0.27-605^[10]). It shows that SiO_2 powders could be evaporated into the gas phase through the high temperature $\text{CH}_4\text{-O}_2$ flame.

(2) Synthesis of SiC Reticular Membrane

The SiC synthesis experiment was performed through the reaction of $\text{SiO}_2 + \text{CH}_4$. The murky grey membrane was collected from the alumina crucible wall. Figure 6 shows a SEM photograph and XRD patterns of the specimen. From the SEM photograph, it is noted that only reticular membrane specimen was observed but u.f. particles were not observed. From the XRD result, β -SiC (JCPDS N0.29-1129^[10]) and SiO_2 (JCPDS N0.27-605) patterns were observed mainly. It was clear that the β -SiC reticulation was successfully synthesized in the experiment system of Figure 4a. The percentage of SiC u.f. particles ($\text{SiC}/(\text{Si} + \text{SiC})$), which was determined from the calibration curves of the relative intensities, using the XRD patterns of the SiC-Si standard mixtures and TGA results, was about 66%. In addition, when the electric furnace was cooled down after CH_4 feed was

Figure 6. (a) SEM photograph and (b) XRD pattern of synthetic SiC using experimental system type 1.

Figure 7. XRD patterns of products for the reaction systems of (a) Si + CH₄, (b) SiO + CH₄ and (c) SiO₂ + CH₄ in an electric furnace.

stopped, surplus SiO₂ continues to evaporate and deposited on the synthetic SiC adhere in the alumina crucible wall. This is the reason why SiO₂ crystal was examined by XRD.

(3) Synthesis of SiC Ultrafine Particles

The synthesis experiments of SiC u.f. particles were performed through the reactions of Si + C H₄, SiO + CH₄ and SiO₂ + CH₄, respectively. Figure 7 shows XRD patterns of the specimen collected from the paper filters. The XRD results of specimens show the peaks for β-SiC (JCPDS N0.29-1129) and Si (JCPDS N0.27-1402^[10]). The scales of β-SiC crystallites calculated by Scherrer's equation were 18.3 nm, 27.4 nm and 28.9 nm for Si, SiO and SiO₂ source powders, respectively. It was clear that the β-SiC u.f. particles (size range : 18-29 nm) were successfully synthesized in the experimental system of Figure 4b. The percentages of SiC were 72%, 54%, 78% (shown in Figure 9) for Si, SiO and SiO₂ source powders, respectively. In addition, XRD peak of carbon (C) which might be formed from CH₄ decomposition and alumina (Al₂O₃) formed from a small impurity in SiO₂ powders were observed.

(4) Effect of H₂, CO, CO₂ or H₂O

The effects of H₂, CO, CO₂ and H₂O on the SiC percentage of synthesized u.f. particles were performed through the reactions of Si + CH₄ + H₂, Si + CH₄ + CO, Si + CH₄ + CO₂ and Si + CH₄ + H₂O ; SiO + CH₄ + H₂, SiO + CH₄ + CO, SiO + CH₄ + CO₂ and SiO + CH₄ + H₂O ; SiO₂ + CH₄ + H₂,

Figure 8. Change of SiC u.f. particle average size under different reaction systems.

Figure 9. SiC percentage of synthesized u.f. particles under different reaction systems.

$\text{SiO}_2 + \text{CH}_4 + \text{CO}$, $\text{SiO}_2 + \text{CH}_4 + \text{CO}_2$ and $\text{SiO}_2 + \text{CH}_4 + \text{H}_2\text{O}$, respectively. All of the XRD results of specimens showed the peaks for β -SiC (JCPDS N0.29-1129) and Si (JCPDS N0.27-1402). The scale range of β -SiC crystallites calculated by Scherrer equation was 10-30 nm shown in Figure 8. They showed that the β -SiC u.f. particles were successfully synthesized even if H_2 , CO, CO_2 or H_2O were added to the reaction systems.

Figure 9 shows the SiC percentage changes of synthesized u.f. particles with different reaction systems. It is noteworthy that the effects of CO, CO_2 or H_2O on $\text{Si} + \text{CH}_4$ and $\text{SiO}_2 + \text{CH}_4$ reaction systems are bigger than those on $\text{SiO} + \text{CH}_4$. For example, the addition of CO or CO_2 decreased the synthesized SiC percentages of $\text{Si} + \text{CH}_4$ and $\text{SiO}_2 + \text{CH}_4$ reaction systems from 72% and 78% down to 10% and 5% respectively, while those of $\text{SiO} + \text{CH}_4$ reaction system was not changed. It is also noteworthy that the percentage of SiC which was 54% in $\text{SiO} + \text{CH}_4$ reaction system is increased to 96% by adding H_2 .

V. Conclusions

The possibilities for the formation of SiC u.f. particles from SiO_2 powders were examined experimentally.

SiO_2 powders were evaporated into the gas phase after passing through the high temperature $\text{C} + \text{H}_2 + \text{O}_2$ flame at around 2500 K. The β -SiC u.f. particles including reticular membrane were successfully synthesized in three reaction systems including $\text{Si} + \text{CH}_4$, $\text{SiO} + \text{CH}_4$ and $\text{SiO}_2 + \text{CH}_4$ by an electric furnace at about 2018 K. Furthermore, the effects of H_2 , CO, CO_2 and H_2O on the SiC percentage of synthesized u.f. particles were examined.

Acknowledgment

The authors would like to thank Mr. Akihito Matsumoto of Hitachi Cooperation Limited for providing the supports on the evaporation experiments.

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