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Development of stable supports consisting of SiC–Si composite for high temperature combustion catalysts

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Abstract

SiC–Si composite, that is stable in oxidizing atmosphere at 1300°C and has thermal shock resistance, was prepared from a powder mixture of porous β-SiC, which was prepared from rice hulls, and Si metal. To use an SiC–Si composite as a structural support for a high temperature combustion catalyst, the foaming SiC–Si composite form with continuous bubbles was prepared from foaming SiC form and the mixture of the porous β-SiC and Si metal. The foaming SiC form was prepared from the foaming polyurethane form and a β-SiC fine particles. The β-SiC fine particles having an average diameter of 0.3 μm was coated on the foaming polyurethane form. The polyurethane part of the form was burned out and the coating β-SiC was sintered to form the foaming SiC form. The SiC form was coated on the porous SiC and Si metal powder mixtures and was heated at 1500°C in argon to prepare the foaming SiC–Si composite. The foaming composite was stable in an oxidizing atmosphere at 1300°C and was highly resistance to thermal shock. The compression stress of the foaming SiC–Si composite form ($175\ \mathrm{kg/cm^2}$) was about twice that of the a-axis of honeycomb-shaped cordierite ($>85\ \mathrm{kg/cm^2}$).

Keywords: Combustion; Silicon carbide; Stable supports; SiC–Si composite; Rice hulls

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1. Introduction

High temperature combustion catalysts need the properties for heat resistance in an oxidizing atmosphere, thermal shock resistance and high surface areas at the temperatures over 1000°C. $BaO \cdot 6Al_2O_3$ [1] and La_2O_3. $11Al_2O_3$ [2] have been reported as promising catalyst supports for high temperature combustion catalysts. A practical catalytic combustion system needs structural support to have good catalyst contact with fuel and oxygen gases and the low pressure dropping gas stream. Generally, the honeycomb-shaped cordierite is used as a structural support. However, the cordierite can not be used for a long term at the temperatures over 1000°C and the production process of honeycomb-shaped cordierite consists of troublesome steps to control the orientation of kaolinite crystal [3].

SiC is physically and chemically stable in inert gases at temperatures up to 1650°C with good thermal shock resistance. In the previous paper [4], we have reported that SiC–Si composite had heat resistance in an oxidizing atmosphere at the temperature of 1200°C and thermal shock resistance. In this report, the structural support of a high temperature combustion catalyst which has heat resistance in oxidizing atmosphere and thermal shock resistance was synthesized from porous β-SiC powder prepared from rice hulls and Si metal powder. Instead of honeycomb-shaped

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structural support, the foaming SiC–Si composite form having continuous bubbles with a low pressure dropping gas stream through a catalyst bed was synthesized.

2. Experimental procedure

2.1. Porous β-SiC powders

Pyrolyzed rice hulls (mixture of $SiO_2 + C$; SiO_2 content 38.5 wt.-%), the product of rice hulls heated in flowing argon (Ar) at 500°C for 1 h, were heated in flowing Ar at 1400°C for 3 h to prepare the porous β-SiC and C mixture. Unreacted C in the product was removed by heating in air at 700°C for 1 h and then the powder was washed in an HF solution to remove SiO_2. Commercial β-SiC produced by carbonization of Si metal powder was compared with the rice hull SiC.

2.2. SiC–Si composite pellets

Porous β-SiC powder was mixed with Si metal powder (purity: 98%) using a planetary ball mill (P-10, Fritsch) for 15 min. The paste consisting of porous β-SiC and an Si metal powder mixture with SiC/Si weight ratios varying from 0.5 to 2.0 and methanol was molded into a 5mmϕ×5mm bar, and was treated in flowing Ar at 1500°C for 6 h to prepare the porous β-SiC–Si composite pellets. The commercial SiC powder was also used for a comparison of the porous β-SiC powder.

2.3. Foaming SiC–Si composite form having continuous bubbles

The foaming SiC–Si composite form having continuous bubbles (foaming SiC–Si composite form) was prepared from foaming SiC form and the powder mixture of the porous β-SiC and Si metal. The foaming SiC form was prepared from foaming polyurethane form (HR-08, Bridgestone) and the commercial β-SiC powder. The foaming polyurethane form was dipped in the SiC paste prepared by kneading the commercial β-SiC powder with methyl cellulose, methanol and water. The SiC coated foaming polyurethane form was heated to 600°C in air at an adequate heating rate to remove the polyurethane, and heated at 1800°C for 3 h in Ar to prepare the foaming SiC form.

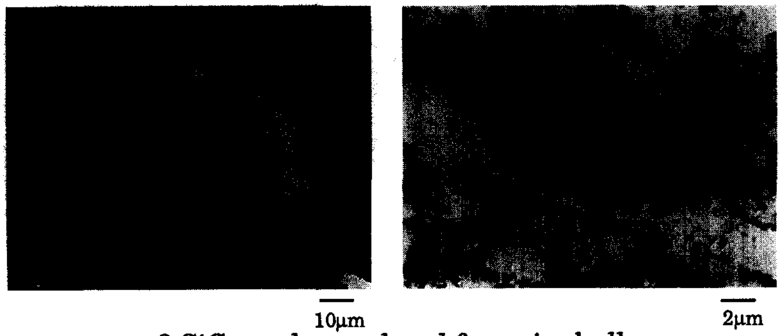
The foaming SiC form was coated with Si metal-methanol paste or porous β-SiC–Si metal (SiC/Si = 0.5 (wt./wt.))-methanol paste and was air-dried and then heated at 1500°C for 5 h in Ar to prepare the foaming SiC–Si composite form.

2.4. Foaming SiC–Si composite form coated with $BaO\cdot 6Al_2O_3$

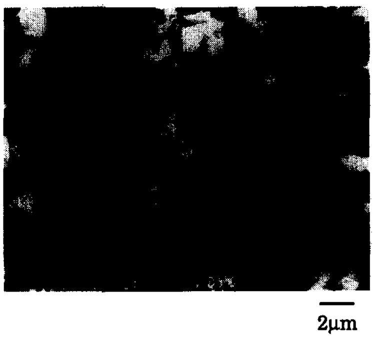
$BaO\cdot 6Al_2O_3$ powder was prepared by the sol-gel method using alkoxides reported by Machida et al. [1]. The surface area of $BaO\cdot 6Al_2O_3$ was 14 m^2/g at 1300°C. The foaming SiC–Si composite form coated with $BaO\cdot 6Al_2O_3$ was prepared by dipping them in a $BaO\cdot 6Al_2O_3$-methanol paste.

2.5. Characterization

The weight changes of SiC and SiC–Si composite samples after treatment in air at various temperatures were measured. The increase in weight change shows the degree of oxidation of SiC and Si to SiO_2 ($SiC + 2O_2 \rightarrow SiO_2 + CO_2$, $Si + O_2 \rightarrow SiO_2$). Crystalline phases were identified using X-ray difractometer (XRD). C and O contents were measured by a carbon and an oxygen analyzer, EMGA-510 and -550 (Horiba). Specific surface area was measured using the single-point BET method. Morphology of the samples and qualitative microanalysis of the section of sample for Si, O and Ba were performed using JXA-8600M (Jeol). The section of the sample was prepared by polishing using an alumina abrasive. Thermal shock resistance of these samples was examined by the observation of the surface of the sample after cooling, by dropping the sample heated at 1300°C to a 20°C water bath, using scanning electron microscope (SEM).



ß-SiC powder produced from rice hulls



Commercial ß-SiC powder

Fig. 1. SEM photos of β-SiC powder produced from porous and commercial β-SiC powder.

3. Results and discussion

3.1. Behavior of SiC powders in air

The particle surfaces of the porous β-SiC and commercial SiC powders are shown in Fig. 1. The porous β-SiC powder consists of an aggregate of microgranules with a diameter of less than 1 μm and whiskers and the surface area is 60 m^2/g. Commercial SiC powder consists of particles having a median diameter of 0.3 μm with a surface area of 7 m^2/g. The oxidation of porous β-SiC started at temperatures over 700°C and the surface area decreased as the oxidation temperature increased. The oxidation of commercial SiC started at a higher temperature than that of porous β-SiC. All of SiC was oxidized into SiO_2 finally. The morphology and surface area of SiC affected the oxidation behavior. SiO_2 was formed on SiC surface at a temperature over 700°C by the oxidation of SiC. SiO_2 was sintered at a temperature over 700°C, so that the surface area decreased.

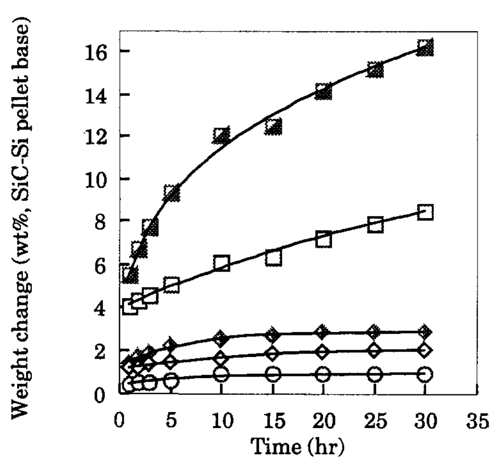


Fig. 2. Weight change of SiC–Si composite pellets treated in flowing air at 1300°C vs. time. ○: Porous β-SiC/Si metal = 0.5 (wt./wt.), ◇: Porous β-SiC/Si metal = 0.67 (wt./wt.), □: Porous β-SiC/Si metal = 1.0 (wt./wt.), ◆: Commercial β-SiC/Si metal = 0.5 (wt./wt.), ▨: Commercial β-SiC/Si metal = 0.67 (wt./wt.).

3.2. Behavior of SiC–Si composite pellets in air

The weight increases of an Si metal block of 5 × 5 × 5mm treated at 1300°C for 1 and 5 h in air were constant at 0.7 wt.-%. When an Si metal block is oxidized at temperatures less than the

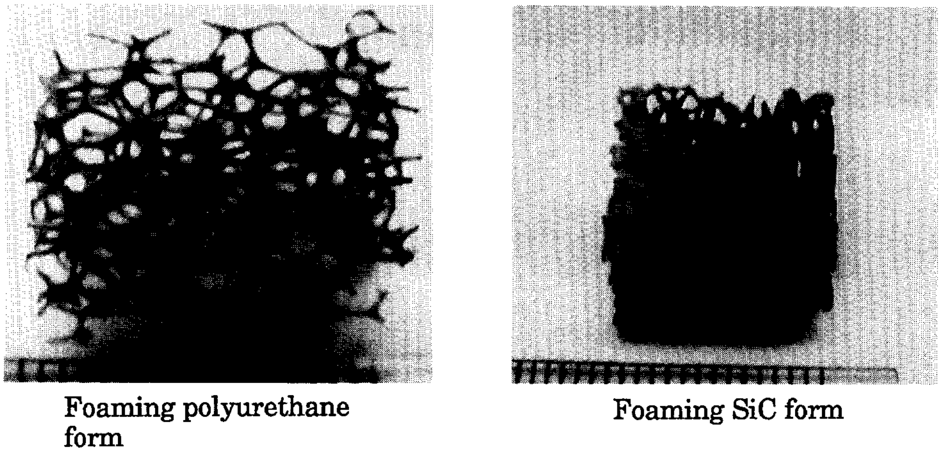


Fig. 3. Foaming polyurethane and SiC form (1 mm/div.).

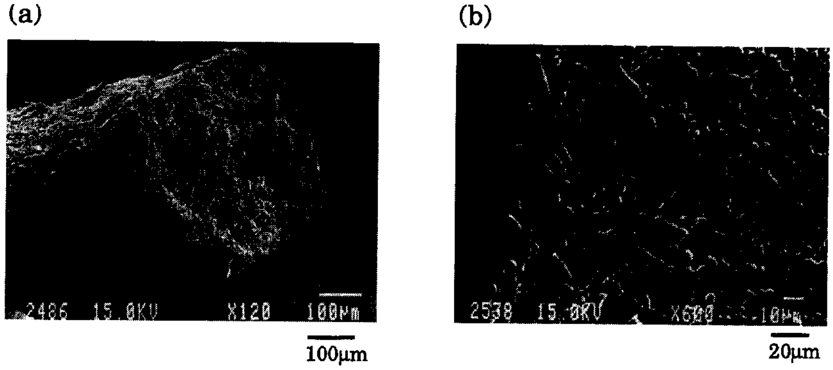


Fig. 4. SEM photos of fracture surface (a) and polished section (b) of the frame of the SiC form.

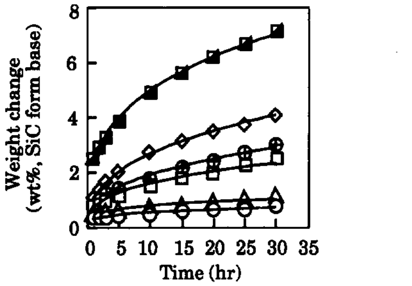
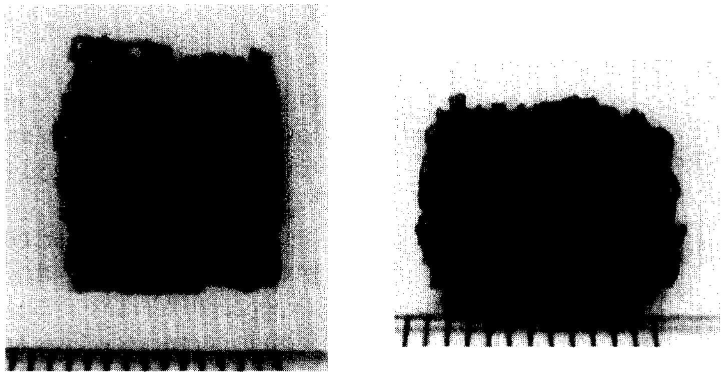


Fig. 5. Weight change of the foaming SiC form treated at various temperatures in flowing air in time. O: 800°C, Δ: 900°C, □: ⊕ 1000°C, : 1100°C, ◇: 1200°C, ◪ : 1300°C.

melting point (1414°C), a thin SiO_2 layer is formed on the surface of the Si block, halting any further oxidation into the Si block. SiC–Si composites in which SiC particles are covered by Si metal are expected to be stable in air at high temperatures and to have thermal shock resistance because of SiC in the composites. Such SiC–Si composites can be easily prepared by heat treatment of the powder mixture of SiC and Si metal at the temperatures over the melting point of Si metal in Ar because of the good wettability of SiC with molten Si metal [5].

Weight changes of SiC–Si composite pellets treated at 1300°C in flowing air for 1 to 30 h are shown in Fig. 2. Weight changes for rice hull SiC–Si composite pellets with SiC/Si weight ratios of 0.67 and 0.5 and commercial SiC–Si composite pellet with SiC/Si weight ratio of 0.5 are constant at 2.0, 1.0 and 2.9 wt.-%, respectively. These results show the oxidation of SiC–Si composite pellets is depressed at 1300°C in air and the porous β-SiC–Si composite is more difficult to oxidize than commercial SiC–Si composite. From the results of the SEM and qualitative microanalysis of the section of porous β-SiC–Si composite pellets after oxidation at 1300°C, Si metal permeated into the porous β-SiC particles and the SiC particles were covered by Si metal. In commercial SiC–Si composite pellets, fine SiC particles are



(a) Foaming SiC-Si composite form produced by the coating with Si metal

(b) Foaming SiC-Si composite form produced by the coating with porous SiC-Si metal

Fig. 6. Foaming SiC–Si form (1 mm/div.).

dispersed in Si metal. It was thought that the morphology of SiC in SiC–Si composite affected its ability to resist oxidation.

Porous β-SiC–Si composite pellets heated at 1300°C in air were dropped to a 20°C water bath to examine the thermal shock resistance of the pellets. No cracks were observed on the surface of the pellets. This result showed that the porous β-SiC–Si composite had good thermal shock resistance.

3.3. Behavior of foaming Si composite form in air

The foaming polyurethane form (HR-08, Bridgestone) and the foaming SiC form, which was

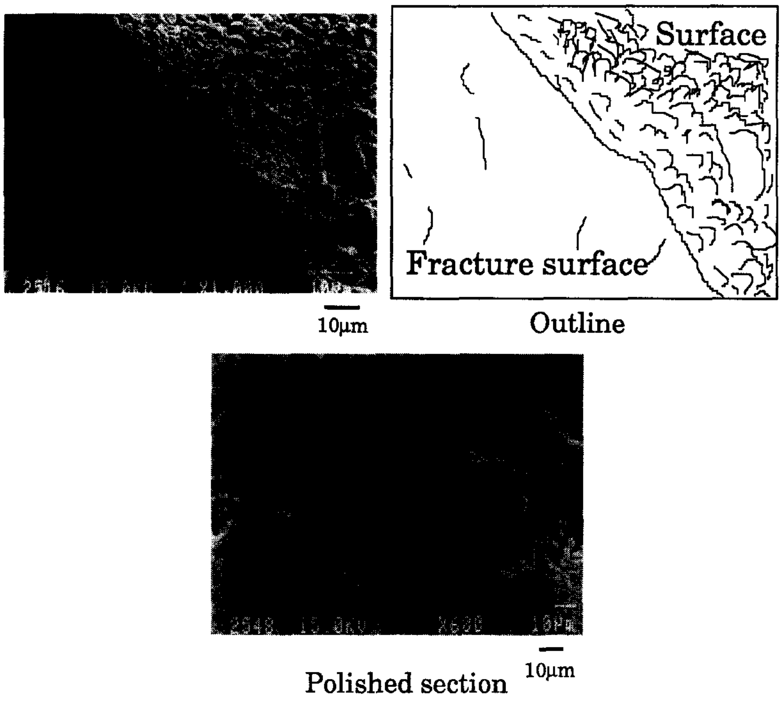


Fig. 7. SEM photos of a fracture surface, surface and polished section of a frame of the foaming SiC–Si composite with continuous bubbles produced by heat treatment at 1500°C in Ar of the foaming SiC form coated with porous β-SiC–Si metal powder mixture.

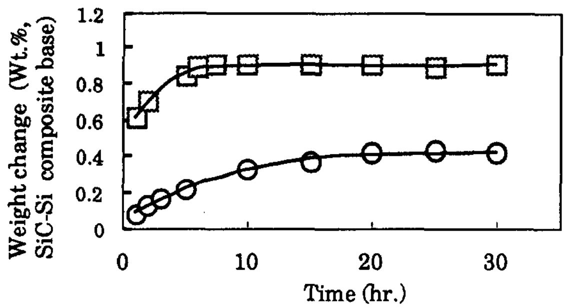


Fig. 8. Weight changes of the foaming SiC–Si composite forms, produced by heat treatment at 1500°C in Ar of foaming SiC form coated with a porous β-SiC–Si metal powder mixture and Si metal powder, treated at 1300°C in flowing air in time. ○: Foaming SiC–Si form produced by coating with Si metal, □: Foaming SiC–Si form produced by coating with porous β-SiC–Si metal.

made from polyurethane and the commercial β-SiC powder, are shown in Fig. 3. The vol.-% of bubbles in foaming SiC form was 85%. SEM photos of fracture surface and polished section of frame of the foaming SiC form are shown in Fig. 4. From the results of the SEM observation, the hole which is observed in the fracture of the frame of SiC form is the trace of polyurethane disappeared by the combustion. The foaming SiC form is composed of the aggregates of SiC particles with 1 to 50 µm diameter. This result shows that the foaming SiC form is not sintered enough and is assumed to have low mechanical strength.

Weight changes of the foaming SiC forms treated at various temperatures in air for 1 to 30 h

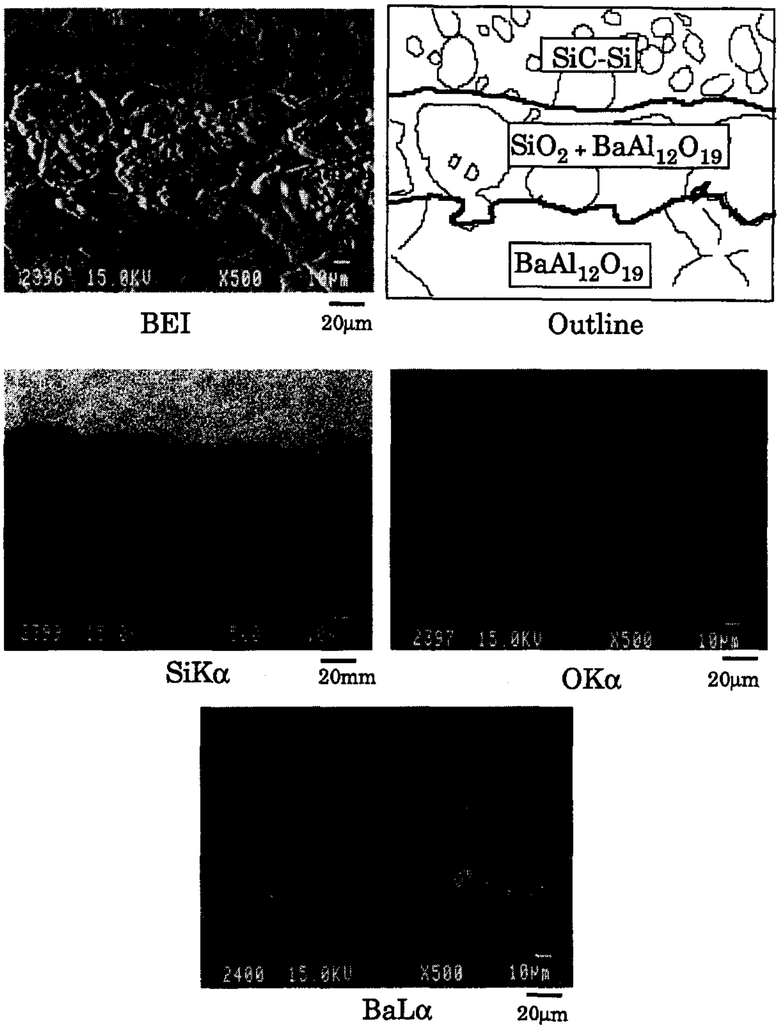


Fig. 9. BEI, SiKα, OKα and BaLα images and outline of the section of foaming SiC–Si composite form coated with $BaAl_{12}O_{19}$ in flowing air at 1300°C for 60 h.

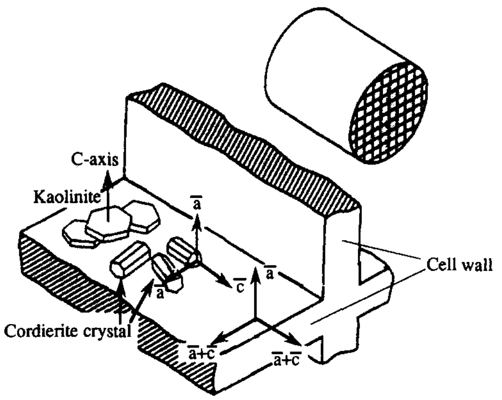


Fig. 10. Crystallographic axes of honeycomb-shaped cordierite.

are shown in Fig. 5. These weight changes increase with time at temperatures over 800°C. From the result of kinetic analysis of the oxidation of foaming SiC form, the reaction was fitted for the reaction model of Ginstling–Brounshtein's equation [6]. The result showed the diffusion of oxygen in the product layer, SiO_2, was the rate-limiting step and the small surface area of the foaming SiC form could depress the oxidation of SiC.

3.4. Behavior of foaming SiC–Si composite form in air

The foaming SiC–Si composite form was produced by heat treatment at 1500°C in Ar of the foaming SiC form coated with Si metal powder (Si metal content of 26wt.-% for foaming SiC–Si composite form) and with porous β-SiC–Si metal powder mixture with a SiC/Si weight ratio of 0.5 (porous β-SiC–Si metal powder mixture content of 33wt.-% for foaming SiC–Si composite form). The external views of the SiC–Si composite forms are shown in Fig. 6. The plugging of continuous bubbles by Si metal is observed in the foaming SiC–Si composite produced from the coating of the foaming SiC form with Si metal powder as shown in Fig. 6(a). The external view of the SiC–Si composite form produced from the coating of the foaming SiC form with porous β-SiC–Si metal powder mixture as shown in Fig. 6(b) is similar to that of the SiC form shown in Fig. 3. No plugging of continuous bubbles of the foaming SiC–Si composite form is observed. These results show that the porous β-SiC–Si metal powder mixture is good coating material to produce the foaming SiC–Si composite form.

SEM photos of the fracture surface and the polished section of the foaming SiC–Si composite form, produced from the coating of the foaming SiC form with the porous β-SiC–Si metal powder mixture shown in Fig. 7, shows a dense SiC–Si composite obtained by filling the space between the SiC particles of the foaming SiC form with porous β-SiC–Si metal.

The weight change of the foaming SiC–Si composite form treated at 1300°C in air in time is shown in Fig. 8. The weight change is constant at 0.9 wt.-% over 6 h for the foaming SiC–Si composite form produced by the coating with porous β-SiC–Si metal powder mixture and at 0.4 wt.-% over 20 h for the foaming SiC–Si composite form produced by the coating with Si metal powder. These results show the depression of the oxidation of the foaming SiC–Si composite form.

The thermal shock of the composite was examined by the same method as that of the SiC–Si pellets described above. The SiC–Si foaming composite form had good thermal shock resistance which was similar to that of the pellets.

The surface area of the foaming SiC–Si composite form was less than 0.5 m^2/g. To use the foaming SiC–Si composite form as a structural support of combustion catalyst, a catalyst having high surface area at high temperatures such as $BaO \cdot 6Al_2O_3$ should be coated on the composite. The foaming SiC–Si composite form, produced by the coating with porous β-SiC–Si metal, coated with $BaO \cdot 6Al_2O_3$ was treated at 1300°C for 60 h

Table 1
Compression stresses of foaming SiC–Si composite form, foaming SiC form and honeycomb-shaped cordierite

	Compression stress (kg/cm^2)
SiC–Si composite form	175
SiC form	19
Honeycomb-shaped cordierite	
a-axis (a)	>85
c-axis (c)	>1

in air. Secondary back electron image (BEI), SiKα, OKα and BaLα images of the section of the foaming SiC–Si composite form are shown in Fig. 9. $BaO \cdot 6Al_2O_3$ exists in the oxide (SiO_2) layer of 60 μm thickness formed on the surface of the foaming SiC–Si composite form. This result indicates that the strong coating layer of $BaO \cdot 6Al_2O_3$ was formed on the foaming SiC–Si composite form after heat treatment at 1300°C in air, because $BaO \cdot 6Al_2O_3$ permeated the SiO_2 layer formed on the foaming SiC–Si composite form.

The results of the compression stress of the foaming SiC–Si composite form, foaming SiC form and honeycomb-shaped cordierite [7] are shown in Table 1. On a honeycomb-shaped cordierite, the a-axis of the cordierite crystals orients vertically for a cell wall as shown in Fig. 10. The combined a- and c-axes orient horizontally for a cell wall. The compression stress of the foaming SiC–Si composite form is about twice that of the a-axis orientation of honeycomb-shaped cordierite which is a practical catalytic structural support.

4. Conclusion

The foaming SiC–Si composite form, that has a stable oxidizing atmosphere at 1300°C and has thermal shock resistance and high compression stress, was prepared from the foaming SiC form and porous β-SiC–Si metal powder mixture using a simple production process. Porous β-SiC was prepared from rice hulls. It is expected that the foaming SiC–Si composite form can be used as a structural support for high temperature combustion catalysts.

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