A new process for creating a solid-phase sintered body using a unique densification process between powders

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Abstract
SiC-polycrystalline fiber (Tyranno SA) had been developed using a conversion process from amorphous Si-Al-C-O fiber to SiC-polycrystalline fiber via carbothermal reduction (~1700°C) and sintering processes (~2000°C). In the conversion process, the carbothermal reduction (SiO + 2C → SiC + CO and SiO₂ + 3C → SiC + 2CO) of the oxide phase and residual carbon contained in the raw Si-Al-C-O fiber and the subsequent sintering proceed inside each filament. Here, we describe a new densification process of SiC powder that optimally uses the conversion process from Si-Al-C-O fiber to SiC-polycrystalline fiber. In this new process, we adopted the densification process, that occurred in each filament of the Si-Al-C-O fiber, for the development of a dense SiC sintered body using partially oxidized SiC-powder with surface oxide layer and polymer-derived pyro-carbon containing a considerable quantity of aluminum as sintering aid for SiC crystals. Herein, the reactions and sintering, which occurred in each filament of Si-Al-C-O fiber, proceeded in the interstices of SiC powder to create a dense SiC body. In this paper, we will describe the new densification system of SiC powder.

KEYWORDS
SiC powder, SiC-polycrystalline fiber, solid-phase sintering

1 | INTRODUCTION

Silicon carbide has been researched for comprehensive applications in the field of aerospace, aeronautics, biomedical, automotive, nuclear-reactor, and mechanical industries, owing to its excellent strength, oxidation resistance, and chemical stability. To consolidate its position for these applications, a simplified production process to obtain an excellent sintered body with higher strength and toughness is desired.¹⁻⁴ To develop the excellent SiC sintered body with higher mechanical properties compared with that prepared by powder-mixing and previous sintering processes, some new processes such as reaction sintering (RS) and spark plasma sintering (SPS) have been developed.¹⁻⁵,⁶ For RS, a significantly high strength (over 1 GPa) has been achieved. However, some large residual defects (over 100 nm) composed of metallic silicon were observed, and its high-temperature strengths were problematic.⁶ And SPS is not applicable to complicated shapes because of its high-pressure process, and also an existence of some residual pores was reported.¹⁻⁸ Furthermore, most present production processes of SiC sintered body contain mechanical milling process such as a ball-mill in a preparation of the mixed raw powders. The mechanical milling process requires relatively long preparation time and can
be contaminated in the preparation process. Accordingly, suppose simple pressureless solid-state sintering process without mechanical milling was developed, it would be significantly useful. Here, we describe a new process using SiC raw powder and aqueous organic polymer containing aluminum (sintering aid) and aqueous silica (filling element of the interstices), that can be converted into SiC by carbothermal reduction, without the ball-mill process. Figure 1 shows the schematic concept and outstanding feature of our new process. Because our new process uses aqueous additives, the powder mixing process is relatively easy, and thus, the ball mill process is not required. Accordingly, incorporation of contamination can be effectively prevented. Furthermore, small quantity of aluminum contained in the raw material plays an important role as a sintering aid to result in an effective solid-state sintering in the interstices of SiC raw powders under the pressureless condition. Thus far, a dense SiC-poly crystalline fiber (Tyranno SA) has been synthesized via carbothermal reduction and subsequent solid-state sintering in each filament under pressureless conditions.\(^9\) In this case, the pressureless sintering process between SiC crystals in each filament effectively resulted in a dense structure with high strength. In the proposed process discussed in this paper, the densification process, that occurred in each filament (the raw fiber of Tyranno SA), was adopted to create the dense interstices between SiC raw powders. As mentioned above, in our new process, since the SiC raw powder and aqueous additives, that can form the dense SiC interstices, were used, a remarkable simple process was achieved. We discuss the detailed preparation process of the modified SiC powders and the subsequent sintering process for developing the dense SiC sintered body by pressureless solid-state sintering process.

2 | EXPERIMENTAL PROCEDURE

Commercially available raw materials were used in this study. SiC powder with a mean size of 400 nm (~99%) was obtained from Wako Pure Chemical Corporation, Japan. An aqueous organic polymer containing aluminum and silica was prepared via the condensation reaction (100°C, 1 h) of tetra-ethoxy silane (Wako Pure Chemical Corporation) with ethylene glycol (Wako Pure Chemical Corporation) and subsequently adding aluminum nitrate (Wako Pure Chemical Corporation).

A mixture of the SiC raw powder and the aqueous organic polymer containing aluminum and silica was performed using a simple aqueous mixing. Thereafter, the mixed compound was freeze-dried, and then heat-treated up to 500°C in nitrogen atmosphere to obtain the precursor mixture. After the preliminary molding, the precursor was heat-treated up to various temperatures in argon atmosphere.

For the heat treatment (degradation reactions and sintering) of the precursor materials, we used “Super High Temperature Inert Gas Furnace (NEWTONIAN Pascal-40, Produced by NAGANO)” under nitrogen gas flow (1 L/min) or argon gas flow (1 L/min). The size of the heating zone (made of graphite and C/C composites) was 35 mm in diameter and 40 mm in height. The programming rate and the maximum temperature were 400°C/min and 2000°C, respectively.

The fine structure of the heat-treated materials was observed using a field emission scanning electron microscope (FE-SEM), model JSM-700F (JEOL, Ltd.). Parts of several samples were sharpened by an etching machine using focused ion beam (FIB), and then, the fine structures were observed by a transmission electron microscope (TEM), model JEM-2100F (JEOL, Ltd.).
3 | RESULTS AND DISCUSSION

3.1 | A general concept of our new densification process

We adopted the in situ conversion process that occurred in each filament for preparing SiC-poly crystalline fiber, to develop the dense interstices between SiC powders. The schematic of our thought (process extension of the SiC-poly crystalline fiber) is shown in Figure 2. In the production process of the SiC-poly crystalline fiber, a degradation process of an amorphous raw fiber (Si-Al-C-O fiber) and a subsequent sintering process led to the SiC dense structure. The raw fiber was composed of SiC fine crystals, oxide phases (SiO$_2$, AlO$_x$), and excess carbons as can be seen from Figure 2. The amorphous raw fiber was heat-treated up to 1500°C in Ar gas atmosphere. In the heat treatment, owing to the existence of the oxide phase and excess carbon in the fiber, the amorphous raw fiber was degraded accompanied by a release of CO gas to obtain a porous degraded fiber. This degradation of the raw fiber proceeds mainly via the following reactions.

1. $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$ ($\Delta G < 0$ over 1522°C)
2. $\text{SiO} + 2\text{C} = \text{SiC} + \text{CO}$ ($\Delta G < 0$ at all temperatures range)

The porous degraded fiber was composed of a nearly stoichiometric SiC composition containing small amount of aluminum (less than 1 wt%). By the existence of considerable quantities of aluminum, at higher temperatures, an effective sintering proceeded in each degraded filament composed of the nearly stoichiometric SiC crystals. Thereafter, the dense SiC-poly crystalline fiber was obtained. We extended this process to a powder-densification process. That is, the proposed concept creates the same compositional interstices between SiC powders using the aforementioned carbothermal reduction.

The proposed concept (a general densification system using carbothermal reduction in the interstices) is shown in Figure 3. Herein, we used the surface oxide layer of the pre-oxidized SiC raw powder and pyro-carbon caused by aqueous polymer containing aluminum and silica. The surface oxide layer plays an important role for creating the combine-structure with the dense SiC interstices. Accordingly, significantly thin oxide layer is acceptable for the process. As can be seen from Figure 3, by heat treatment in nitrogen atmosphere, we prepare the same compositional interstices as the Si-Al-C-O fiber. This type of interstice is formed by a pre-heat-treatment of oxidized SiC powders and aqueous polymer containing aluminum and silica. By this pre-heat treatment, the interstices composed of silica and pyro-carbon containing aluminum are created. After preliminary molding, at higher temperatures, the degradation and subsequent sintering (solid-phase sintering process) proceed to produce nearly stoichiometric SiC interstices, that is, to result in the SiC sintered body.
3.2 Carbothermal reduction on each pre-oxidized SiC powder covered with pyro-carbon

In the proposed system, the initial important step is the carbothermal reduction proceeding in the interstices (pyro-carbon) and on the surface region (oxide layer) of each SiC powder according to the following reactions.

1. \( \text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO} \quad (\Delta G < 0 \text{ over } 1522^\circ\text{C}) \)
2. \( \text{SiO} + 2\text{C} = \text{SiC} + \text{CO} \quad (\Delta G < 0 \text{ at all temperatures range}) \)

The surface oxide layer was formed by pre-oxidation, and the pyro-carbon was formed by pre-heat treatment of aqueous organic polymer existing on each SiC powder. The image of the initial step of the proposed system (carbothermal reduction on the pre-oxidized SiC powder) is shown in Figure 4.

The TEM image of the surface region surrounded by quadrangular solid line in Figure 4 is shown in Figure 5. The pyro-carbon can be observed on the surface of the pre-oxidized SiC powder. The enlarged TEM image of the pyro-carbon existing on the pre-oxidized SiC powder is shown in Figure 6. As can be seen from Figure 6, this pyro-carbon was composed of turbostratic structure.

At the next step, this type of pre-oxidized SiC powder covered with pyro-carbon was heat-treated in argon atmosphere at 1600°C for 10 min. By this heat treatment, the formation of some products containing whisker could be observed on the SiC powder (Figure 7). These products are considered to be formed by the carbothermal reduction between the pyro-carbon and the surface oxide layer of the pre-oxidized SiC powder.

Figure 8 shows the STEM-image of the whisker-like product with the analytical results of the electron beam diffraction.
The formed whisker was composed of beta-SiC crystal with lots of twin boundaries. These SiC whisker was considered to be formed by the gas phase reaction according to the following reaction \( \text{SiO} + 2\text{C} \rightarrow \text{SiC} + \text{CO} \). Effective formation of this type of whisker-like SiC is expected for filling interstices at the initial stage of our new process.

Figure 9 shows the STEM-image of the crystal-like products on the SiC powder with the analytical results of the electron beam diffraction. These products were found to be beta-SiC crystals that were considered to be formed by the following reaction \( \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \). These reactions are similar to the in-situ reaction which proceeded in the inside of the raw fiber for preparing the SiC-polycrystalline fiber.

### 3.3 | Formation of the dense interstices (formation of the dense SiC sintered body)

In the proposed concept, the most important thing in the first step is to create the preliminary dense structure of SiC crystals. The concept for obtaining the dense product is shown in Figure 10. By controlling the oxidation of SiC powder and the quantity of the aqueous organic polymer containing aluminum and silica, equivalent carbothermal reduction proceeds, and then, this type of dense structure can be obtained. The image structure shown in Figure 10 is a green body that can be sintered at high temperatures under the pressureless condition. Accordingly, the composition of the interstices is important for obtaining the stoichiometric SiC composition after sintering. However, it is relatively difficult to strictly control the equivalent carbothermal reduction only by the surface oxide layer and the formed pyro-carbon.

Next, we show the differences in the fine structure of the interstices caused by the mismatching of the composition, that is, differences in the ratio of carbon and silica existing in the interstices (Figure 11). If large quantities of pyro-carbon (C/Si > 1.5) exist in the interstices before the carbothermal reduction, large quantity of residual carbon can be observed in the interstice after sintering. In contrast, in case thicker oxide layer (over 200 nm) on each SiC powder exists, after sintering large quantity of pore can be observed. Using equivalent composition \( \text{Si}_{1.01}\text{Al}_{0.01}\text{C}_{1.5}\text{O}_{0.5} \), we could obtain the desirable structure shown at the center of Figure 11. Regarding the composition of the interstice, we have another solution to prevent the above undesirable phenomena. That is, aqueous silica-compound containing equivalent carbon with aqueous aluminum compound is useful.
We explain the abovementioned aqueous silica compound containing equivalent carbon as an organic polymer with aqueous aluminum compound. This basic concept is shown in Figure 12. This type of compound can be converted into the precursor material for producing the SiC sintered body by solid-phase sintering. Using this type of aqueous material as an additional choice, we can control the composition of the interstices to create the desirable sintered structure. In the next section, we describe the sintered structure along with other important point (aluminum concentration).

3.4 Formation of the SiC sintered body (Effect of the aluminum concentration)

To achieve our new process, aluminum plays an important role as a sintering aid for the SiC crystal. In general, aluminum had been well-known as a liquid-sintering aid for SiC crystal. However, after that, we developed a solid-state sintering process of SiC crystals using small amount of aluminum less than 1 wt%.

According to our previous information, we strictly controlled the aluminum concentration in the proposed process.
SiC-polycrystalline fiber (Tyranno SA), we developed a new densification process of SiC powder to create a pressureless SiC sintered body. In the proposed process, an effective carbothermal reduction between the oxide layer existing on the surface of pre-oxidized SiC powder and pyro-carbon caused from the aqueous polymer containing aluminum and silica. When we used equivalent pyro-carbon containing considerable quantity of aluminum (0.5 wt%) to the silica element in the interstices between SiC powders, desirable dense SiC sintered body showing trans-crystalline fracture behavior could be successfully obtained.

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4 | CONCLUSIONS
Making the best use of our previous densification process which proceeded in each filament in preparation of...