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# High-performance SiC-polycrystalline fiber with smooth surface

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**Abstract:** Polymer-derived SiC-polycrystalline fiber (Tyranno SA) shows excellent heat-resistance up to 2000°C, and relatively high strength. Up to now, through our research, the relationship between the strength and residual defects of the fiber, which were formed during the production processes (degradation and sintering), has been clarified. In this paper, we addressed the relationship between the production condition and the surface roughness of the obtained SiC-polycrystalline fiber, using three different raw fibers (Elementary ratio: $Si_1Al_{0.01}C_{1.5}O_{0.4\text{-}0.5}$) and three different types of reactor (Open system, Partially-open system, and Closed system). With increase in the oxygen content in the raw fiber, the degradation during the production process easily proceeded. In this case, the degradation reactions ($SiO+2C=SiC+CO$ and $SiO_2+3C=SiC+2CO$) in the inside of each filament become faster, and then the CO partial pressure on the surface of each filament is considered to be increased. In consequence, according to Le Chatelier's principle, the surface degradation reaction and grain growth of formed SiC crystals would be considered to become slower. That is to say, using the raw fiber with higher oxygen content and closed system (highest CO content in the reactor), much smoother surface of the SiC-polycrystalline fiber could be achieved.

**Keywords:** SiC-polycrystalline fiber; Defect; Strength; Surface roughness

## 1. Introduction

Since the first precursor ceramics using polycarbosilane was developed, lots of polymer-derived SiC-base fibers have been developed. Present commercial polymer-derived SiC fibers are shown in Table 1. Through these developments, the heat-resistances of the SiC-based fibers were remarkably increased from 1300°C to 2000°C as can be seen from this table. Of these fibers, SiC-polycrystalline fibers (Tyranno SA, Hi-Nicalon Type S, and Sylramic) show the highest heat-resistance up to 2000°C, and then have been actively evaluated for aerospace applications as SiC/SiC composites [1-5]. However, to extend the application field, increase in the fiber's strength is eagerly required. Up to now, through our research, the relationship between the strength and the residual defects contained in the fiber, which were formed during the production processes, has been clarified [6-9]. In these researches, we have proposed several new methods for reducing the residual defects, and also demonstrated them using the conversion process from amorphous Si-Al-C-O fiber to SiC-polycrystalline fiber (Tyranno SA). Tyranno SA is produced by heat-treatment processes of amorphous Si-Al-C-O fiber which is synthesized from polyaluminocarbosilane [1]. During the heat-treatment processes, a degradation of the Si-Al-C-O fiber and a subsequent sintering of the degraded fiber proceed as well, accompanied by a release of CO gas and compositional changes, to finally obtain the dense structure. Since these structural changes proceed in each filament, a strict control should be needed to minimize residual defects. As mentioned above, to reduce the residual defects, we proposed new conversion processes and demonstrated them [7-9].

Table 1. Commercial Polymer-derived SiC Fibers

| | Fiber's Grade | Manufacturer | |
|---|---|---|---|
| First Generation ~1300°C | Nicalon NL 200 | NGS(~2012) (Nippon Carbon) | Amorphous |
| | Tyranno Lox M | UBE | |
| | Tyranno S | UBE | |
| Second Generation ~1500°C | Hi-Nicalon | NGS(~2012) (Nippon Carbon) | Amorphous |
| | Tyranno ZMI | UBE | |
| Third Generation ~2000°C | Hi-Nicalon Type S | NGS(~2012) (Nippon Carbon) | SiC-Polycrystalline |
| | Tyranno SA | UBE | |
| | Sylramic | COIC | |

And then, using these new processes, the inside defects were remarkably reduced. As the result of these research, the present maximum strength of the improved fiber is ~4GPa. However, this strength is remarkably low compared with a theoretical strength (46GPa) of SiC crystal which can be calculated using Orowan's equation [10]. Accordingly, further improvement will be needed. In the above research, by controlling the advantageous degradation-reaction and preventing the disappearance of gaseous SiO from each filament, residual carbon (one of residual defects) was remarkably reduced along with prevention of abnormal surface grain growth. In consequence, the surface roughness was relatively improved compared with that of previous fibers. By the way, the surface roughness was very sensitive depending on the atmospheric condition during the degradation process, and then obtaining much smoother surface was a relatively difficult problem. Smoother surface of the fiber is very important for obtaining good fibrous fracture behavior of ceramic matrix composites (CMCs) [11]. Accordingly, it should be important to clarify the relationship between the process condition and the surface roughness of the obtained fiber. Here, we describe the formation mechanism of the surface structure and the relationship between the process condition and the surface roughness of the obtained SiC-polycrystalline fiber.

## 2. Materials and Methods

The SiC-polycrystalline fiber (Tyranno SA) was synthesized by heat-treating an amorphous Si-Al-C-O fiber up to 2000°C in argon gas atmosphere. The Si-Al-C-O fiber was produced from polyaluminocarbosilane which was synthesized by a reaction of polycarbosilane with tetra-butoxyaluminum at 300°C in nitrogen atmosphere. A spun fiber was obtained by melt-spinning of the polyaluminocarbosilane, and then the spun fiber was cured at around 200°C in air. The cured fiber was fired at 1300°C in nitrogen atmosphere to obtain the amorphous Si-Al-C-O fiber which was composed of SiC fine crystals, oxide phases (estimated forms: $SiO_2$, $AlO_x$), and excess carbons. By the way, as mentioned above, since in this synthesis we used polyaluminocarbosilane which was synthesized by the reaction of polycarbosilane and tetra-butoxyaluminum, we presumed that the aluminum existed as some oxide forms in the Si-Al-C-O fiber. In the next step, the amorphous Si-Al-C-O fiber was heat-treated up to 1500°C in argon gas atmosphere. During the heat-treatment, by the existence of the oxide phase and excess carbon in the fiber, the amorphous Si-Al-C-O fiber was degraded accompanied by a release of CO gas to obtain a porous degraded fiber. The porous degraded fiber was composed of a nearly stoichiometric SiC composition containing small amount of aluminum. In this case, since a part of the aluminum contained in the amorphous Si-Al-C-O fiber might be disappeared as some oxide

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materials during the heat-treatment process, consequently a very small amount of aluminum (less than 1wt%) was contained in the degraded fiber. By the existence of the small amount of aluminum, at the next step, an effective sintering proceeded in each degraded filament composed of the nearly stoichiometric SiC crystals during further heat-treatment up to 2000°C in argon atmosphere. The production scheme of the polymer-derived SiC-polycrystalline fiber using the Si-Al-C-O fiber as the raw fiber is shown in **Fig.1**.

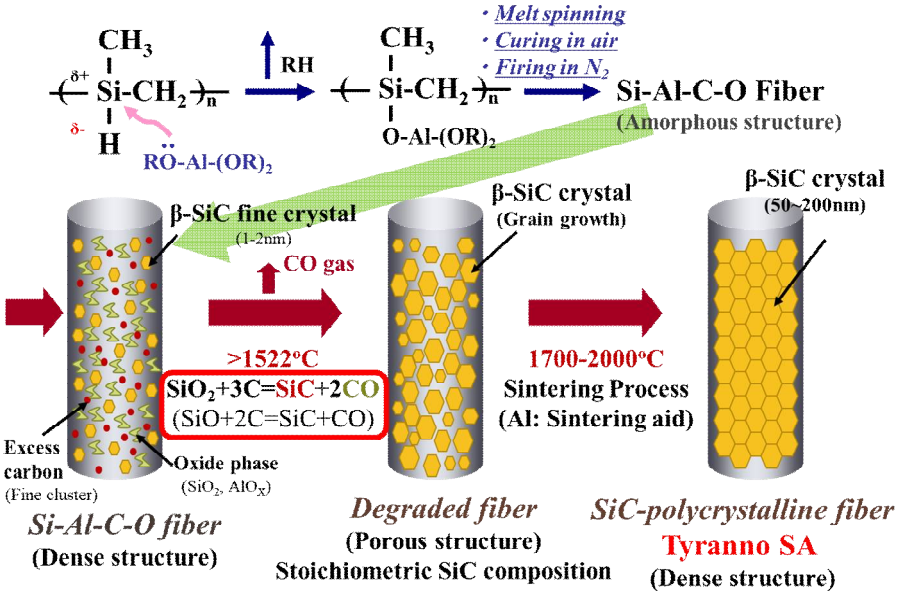


Fig.1 The production scheme of the SiC-polycrystalline fiber using a raw Si-Al-C-O fiber

As mentioned in our previous papers, degradation reactions of the amorphous Si-Al-C-O fiber enclosed in red frame in this figure (Fig.1) strongly affects the final fine-structure (inside structure and surface roughness) of the SiC-polycrystalline fiber. Especially, reaction condition concerning CO gas content during the degradation process is most important [6, 9]. Accordingly, in this research we adopted three types of reaction vessel (Open system, Partially-open system, and Closed system) made of carbon shown in **Fig.2**.

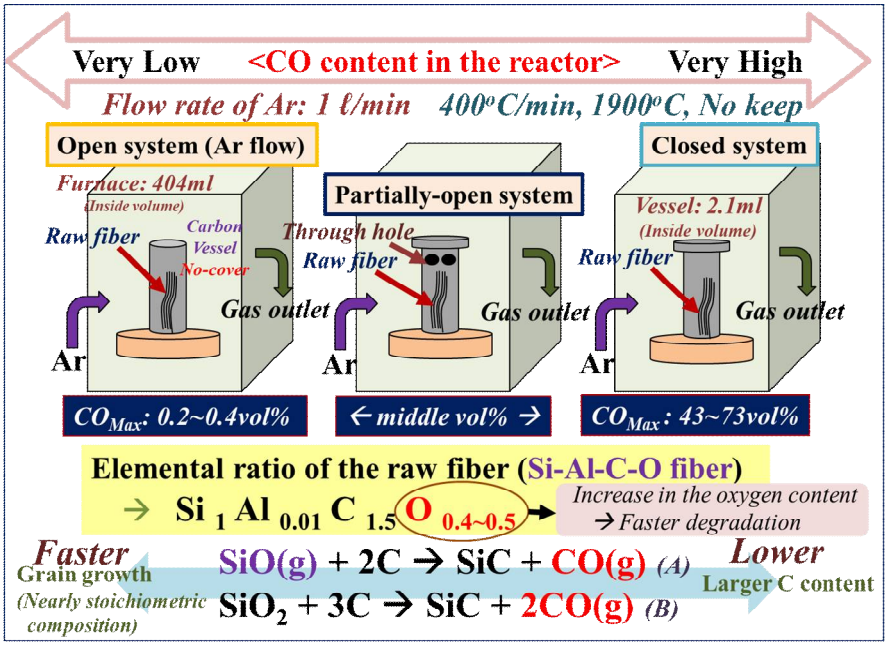


Fig.2 Experimental condition for research on fiber's surface roughness

For the heat-treatment (degradation reactions and sintering) of the Si-Al-C-O fiber, we used "Super High Temperature Inert Gas Furnace (NEWTONIAN Pascal-40, Produced by NAGANO)" under argon gas flow (1 L/min). The size of the heating zone (made of graphite and C/C composites) is 35 mm in diameter and 40 mm in height. Several types of raw fibers (about 10 mg) (Elementary ratio: $Si_1Al_{0.01}C_{1.5}O_{0.4\text{-}0.5}$) were used and located in each vessel. The programing rate and the maximum temperature were 400°C/min and 1900°C, respectively.

The surfaces and cross sections of the obtained fibers were observed using a field emission scanning electron microscope (FE-SEM), model JSM-700F (JEOL, Ltd.). Parts of surface region and inside of the several samples were sharpened by an etching machine using focused ion beam (FIB), and then the fine structures were observed by the transmission electron microscope (TEM), model JEM-2100F (JEOL, Ltd.). Surface roughness was observed using Atomic Force Microscope (AFM), model AFM 5000II (Hitachi, Ltd.).

## 3. Results and discussion

### *3.1. Morphological changes during the degradation process*

As mentioned before, for obtaining the SiC-polycrystalline fiber, at the first step, the amorphous Si-Al-C-O fiber was heat-treated up to 1500°C in argon gas atmosphere. During the heat-treatment process, by the existence of the oxide phase and excess carbon in the fiber, the amorphous Si-Al-C-O fiber was degraded accompanied by a release of CO gas to obtain a porous degraded fiber. This degradation of the Si-Al-C-O fiber proceeds mainly by the following two types of reactions.

(1) $SiO_2 + 3C = SiC + 2CO$ ($\triangle G < 0$ over 1522°C)

(2) $SiO + 2C = SiC + CO$ ($\triangle G < 0$ 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 the small amount of aluminum, at the next step, an effective sintering proceeded in each degraded filament composed of the nearly stoichiometric SiC crystals during further heat-treatment up to 1900°C in Ar gas atmosphere. And then, the dense SiC-polycrystalline fiber was obtained. The morphological changes of each filament during the heat-treatment process (degradation and sintering) are shown in **Fig.3**.

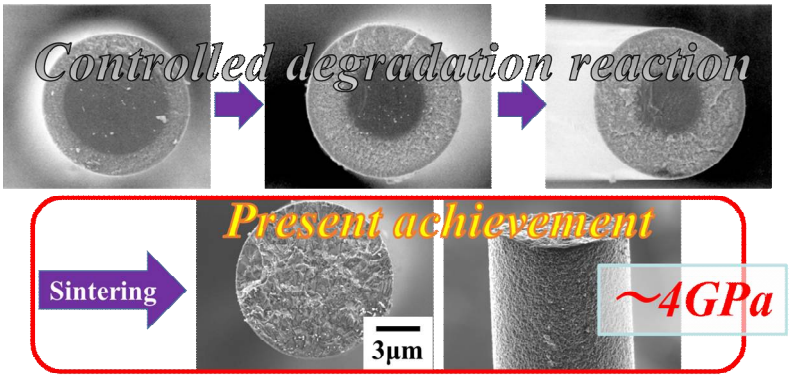


Fig.3 Morphological changes during the degradation and sintering processes

As can be seen from this figure (Fig.3), the degradation proceeded from outside to inside of the amorphous Si-Al-C-O fiber. And, regarding the SiC-crystalline size of the obtained sintered fiber, the surface SiC-crystals were relatively small compared with the inside crystals. This phenomenon was considered to be caused by the atmospheric condition (Especially: CO gas content) during the degradation process. That is to say, the degradation reactions ($SiO_2 + 3C = SiC + 2CO$ and $SiO + 2C = SiC + CO$) are strongly dominated by the CO gas content in the reactor. According to Le Chatelier's

principle, the higher the CO content becomes, the slower the reaction becomes. Anyway, the abovementioned degradation proceeds in the inside of each filament accompanied by a release of CO gas. So, the inside of each filament is saturated by the formed CO gas, and the surplus CO gas is ejected from the surface region to the outside. Furthermore, on the surface region of each filament, some boundary layer composed of CO gas must be formed. By these changes, in consequence, some CO gas distribution would be formed from the inside to the surface region of each filament. Accordingly, the degradation in the inside of each Si-Al-C-O filament was considered to proceed as shown in **Fig.4**.

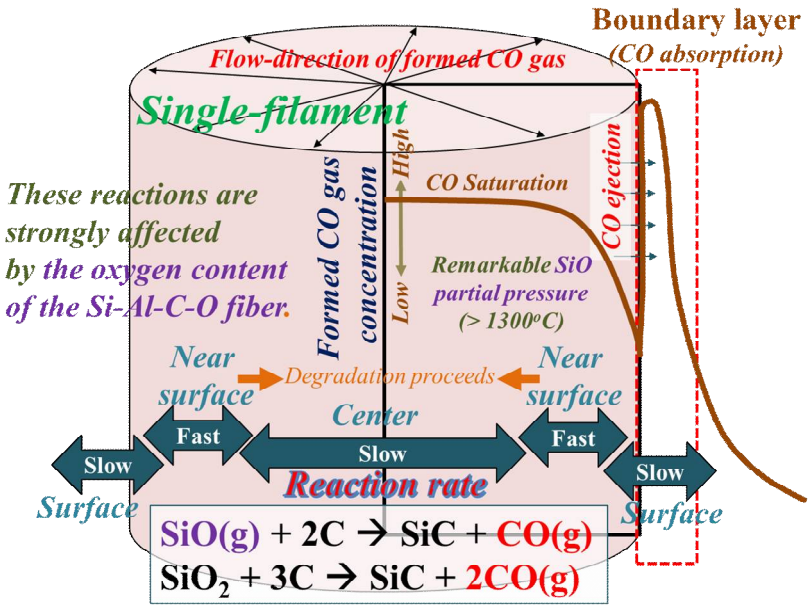


Fig.4 General degradation in the inside of each Si-Al-C-O filament

This figure shows general degradation reaction in the inside of the raw Si-Al-C-O filament. Degradation reaction proceeds according to the following reactions at high temperature:

(1) $SiO_2 + 3C = SiC + 2CO$

(2) $SiO + 2C = SiC + CO$

These reaction-rates are dominated by the partial pressure of the formed CO gas. When these reactions proceed in each filament, the inside of each filament is saturated by the formed CO gas. However, from the surface region, the formed CO gas is ejected. Accordingly, the CO partial pressure of the near-surface region becomes lower compared with that of the inside. So, the reaction rate becomes lower at the center of each filament, compared with that of the near surface region. On the other hand, on the surface of the raw fiber, a boundary layer composed of CO gas is formed. In consequence, at the surface, CO gas concentration becomes relatively higher compared with that of the inside. These CO gas-balance dominates the fine structures of the obtained SiC-polycrystalline fiber. Regarding the above phenomena, a TEM image of the sliced cross-section of the obtained SiC-polycrystalline fiber is shown in **Fig.5**. As can be seen from this figure, the grain size (white-dotted line shown in Fig.5) at each position was different from each other. As mentioned above, the degradation rate and the obtained grain-size are dominated by the partial pressure of the formed CO gas. That is to say, CO gas concentration of the near-surface region of the fiber is relatively low compared with that of the inside, so that the reaction rate becomes higher to lead to larger grain size compared with that of the inside. Furthermore, since the boundary layer composed of the ejected CO gas was formed on the surface, the partial pressure of CO gas on the surface

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becomes higher to result in the smaller grain size. Considering these fundamental matters, we can control the surface roughness. In the next section, we will address the relationship between the degradation reaction at the surface and the surface roughness of the obtained SiC-polycrystalline fiber.

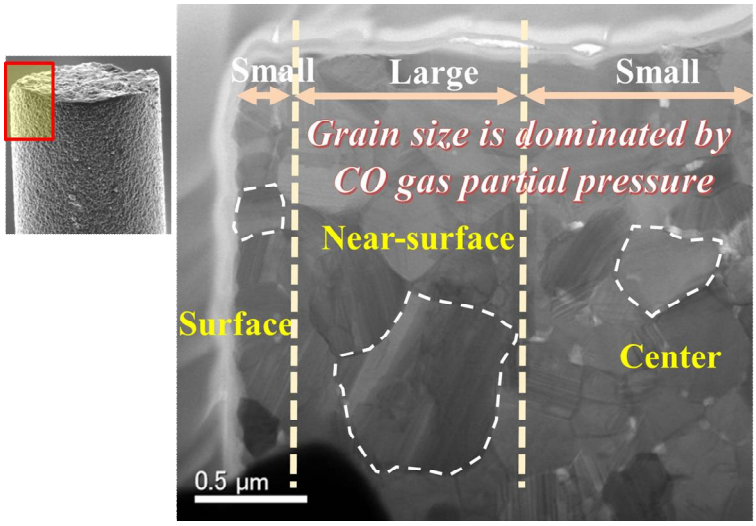


Fig.5 TEM image of the sliced cross-section of the obtained SiC-polycrystalline fiber

*3.2. Change in the surface roughness of the SiC-polycrystalline fiber*

As mentioned above, both the degradation reaction and the grain growth of the formed SiC crystals are strongly affected by the CO content in the reactor during the degradation reaction. As shown in Fig.2, we used three different types of vessel (Open system, Partially-open system, and Closed system) and several types of raw fiber (Elementary ratio: $Si_1Al_{0.01}C_{1.5}O_{0.4\sim0.5}$) for changing actual CO content in the reactor. Under our reaction condition, we calculated that the maximum CO content in the reactor was 73vol% when we used both the closed system and the raw fiber with highest oxygen content ($Si_1Al_{0.01}C_{1.5}O_{0.5}$), whereas the minimum CO content was 0.2vol% when we used both the open system and the other raw fiber with lowest oxygen content ($Si_1Al_{0.01}C_{1.5}O_{0.4}$). The surface structures (FE-SEM images) of the obtained SiC-polycrystalline fibers are shown in **Fig.6**.

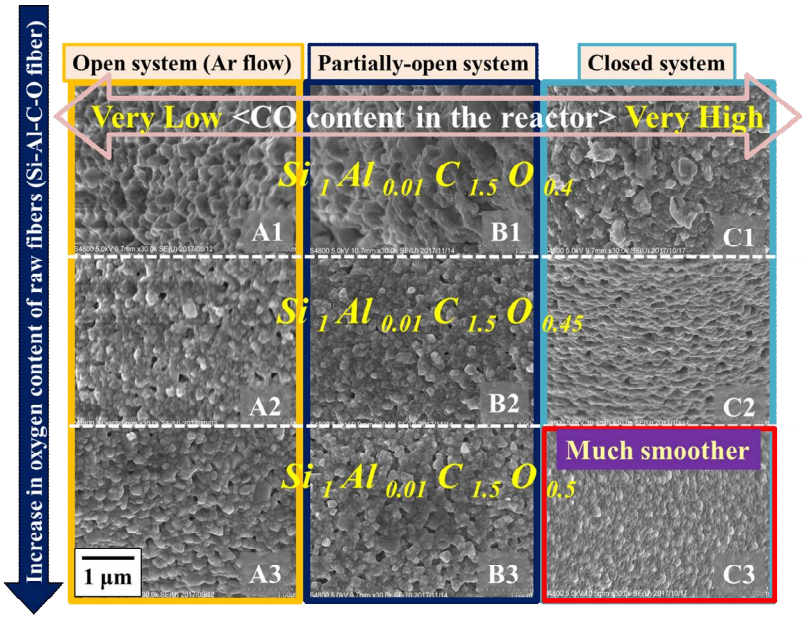


Fig.6 Changes in the surface structures obtained using different types of raw fiber and vessels

These fibers were obtained by heat-treatment of the different types of Si-Al-C-O fiber at 1900°C in Ar using the three different types of vessels. As can be seen from this figure (Fig.6), the higher the oxygen content of Si-Al-C-O fiber becomes, the smoother the surface becomes. These results are closely related to the CO content in the reactor during the degradation reaction. The much smoother surface was obtained using the raw fiber with highest oxygen content ($Si_1Al_{0.01}C_{1.5}O_{0.5}$) and the closed system. As can be seen from these results, the surface roughness is effectively controllable by changing the degradation conditions (Especially; CO content in the reactor). The most important factors for change in the CO content in the reactor are (1) Oxygen content of the raw Si-Al-C-O fiber, and (2) Reactor system (Open system, Partially-open system, and Closed system). By change in the combination of these factors, different degrees of the surface roughness could be effectively obtained as can be seen from Fig.6. Some phenomena caused by increase in the oxygen content of Si-Al-C-O fiber are shown as follows. As the oxygen content in the law fiber increases, the degradation reaction becomes faster. It easily leads to nearly stoichiometric composition of the degraded fiber. In this case, the partial pressure of CO gas on the surface of the fiber becomes higher compared with that of the other fiber with lower oxygen content. This leads to lower reaction rate at the surface of the fiber. Consequently, increase in the oxygen content of the raw Si-Al-C-O fiber led to decrease in the SiC crystalline size at the surface region. This means getting smooth surface. That is to say, the higher oxygen content of the raw Si-Al-C-O fiber and the closed system cause relatively higher CO content in the reactor during the degradation reaction, and then the consequently higher partial pressure of the formed CO gas at the surface region reduces the reaction rate to result in getting smooth surface.

Changes in the actual surface roughness of the obtained SiC-polycrystalline fibers, which were synthesized by heat-treatment at 1900°C in argon gas atmosphere using different raw fibers and different vessels, are shown in **Fig.7**.

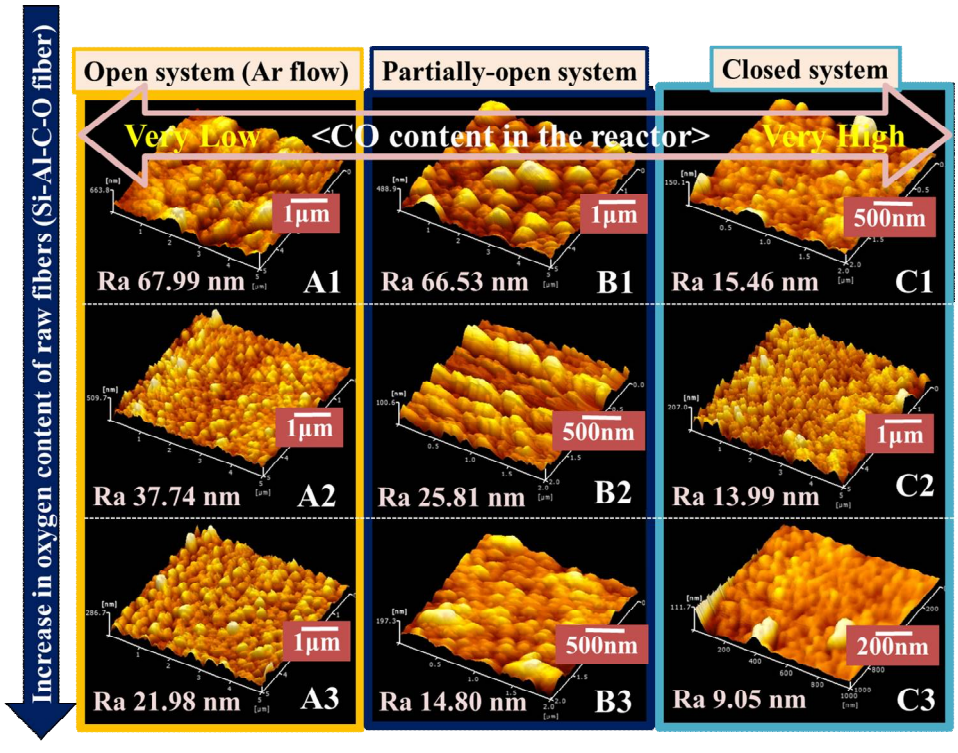


Fig.7 Change in the surface roughness of the SiC-polycrystalline fiber synthesized from different raw Si-Al-C-O fiber with different oxygen content at 1900°C in argon atmosphere. For obtaining A1, B1, C1, the raw fiber composed of $Si_1Al_{0.01}C_{1.5}O_{0.4}$ was used. For obtaining A2, B2, C2 and for obtaining A3, B3, C3, the raw fibers composed of $Si_1Al_{0.01}C_{1.5}O_{0.45}$ and $Si_1Al_{0.01}C_{1.5}O_{0.5}$ were used, respectively

As can be seen from this figure (Fig.7), the surface roughness could be controlled by changing both oxygen content of the raw Si-Al-C-O fiber and the reaction vessel. In this case, for obtaining A1, B1, C1 in Fig.7, the raw fiber composed of $Si_1Al_{0.01}C_{1.5}O_{0.4}$ was used for the synthesis. And, for obtaining A2, B2, C2 and for obtaining A3, B3, C3, the raw fibers composed of $Si_1Al_{0.01}C_{1.5}O_{0.45}$ and $Si_1Al_{0.01}C_{1.5}O_{0.5}$ were used, respectively. As can be seen from Fig.7, we could control the surface roughness from 67.99nm (maximum value) to 9.05nm (minimum value).

In this research, we used degradation process of the amorphous raw fiber (Si-Al-C-O fiber) accompanied by a release of CO gas and the subsequent sintering process, and also showed the controllable SiC crystalline size constructing the obtained SiC-polycrystalline fiber by changing the CO gas partial pressure in the reactor. In consequence, we could control the surface roughness of the SiC-polycrystalline fiber using CO gas released from the raw fiber. However, this means that an intentional change in CO gas partial pressure in the reaction vessel can lead to preferable crystalline structure.

**Fig.8** shows an improvement result regarding the surface roughness achieved by the adjustment of the CO gas partial pressure in the reactor during the degradation reaction. In this case, using Le Chatelier's principle, we accelerated the following reaction ($SiO_2+3C=SiC+2CO$) to consequently increase the CO gas partial pressure at the surface region of the fiber in the initial degradation process. Regarding this degradation condition, we reported the detailed content in the previous paper [6].

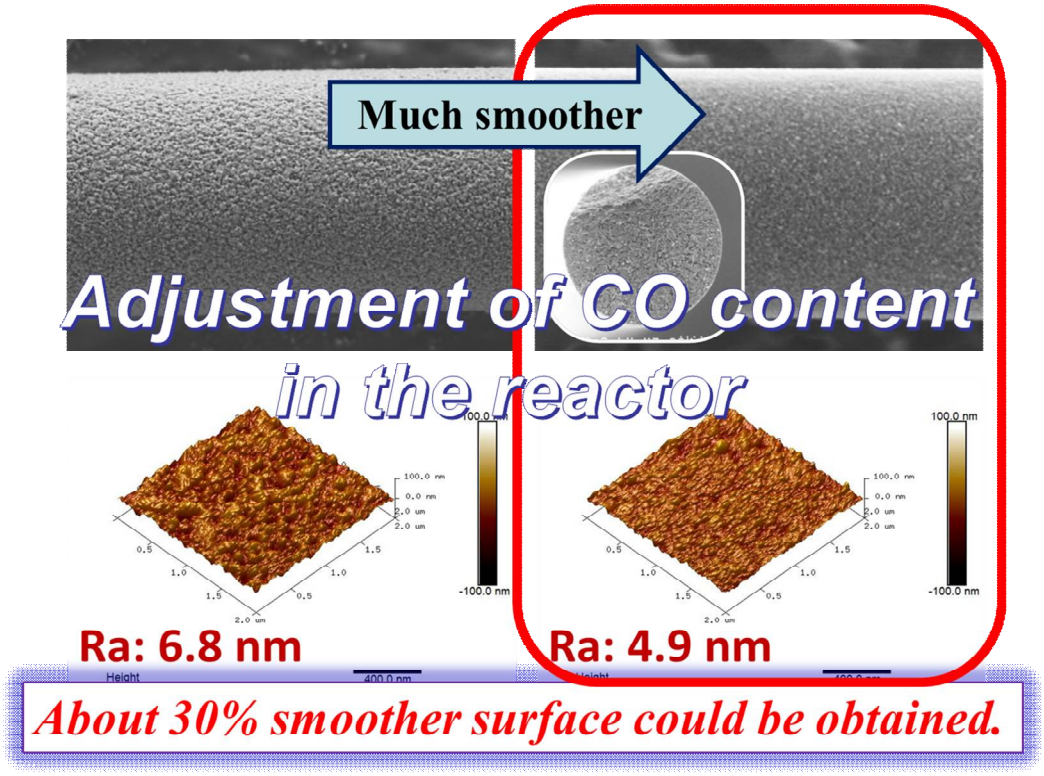


Fig.8 Improvement of the surface roughness by adjustment of CO content in the reactor

Finally, on the basis of our results, a perspective for developing the high-performance SiC-polycrystalline fiber is shown in **Fig.9**. Our target strength will be 6GPa, which is a similar strength to that of high-performance carbon fiber (T-800). To achieve the higher strength, the most important thing is to reduce the inside defects and surface roughness by controlling the partial pressure of CO gas in the reactor during the degradation reaction of the raw amorphous fiber.

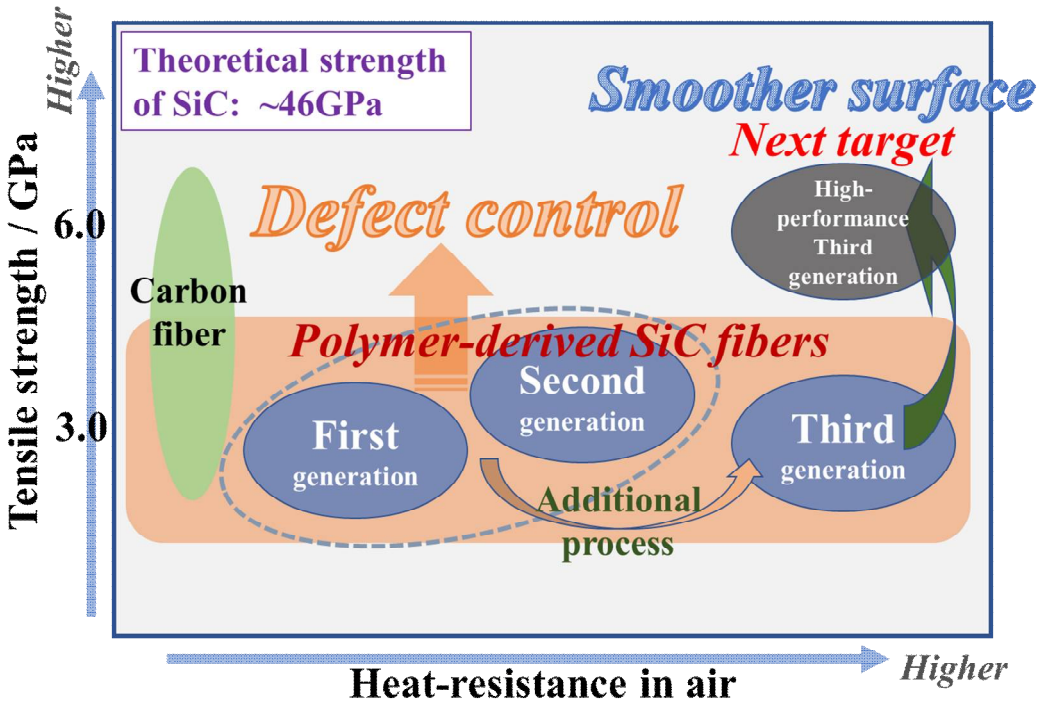


Fig.9 Perspective for the high-performance SiC-polycrystalline fiber

## 4. Conclusions

we clarified the relationship between the heat-treatment condition and the surface roughness of the obtained SiC-polycrystalline fiber, using three different raw fibers (Elementary ratio: $Si_1Al_{0.01}C_{1.5}O_{0.4\sim0.5}$) and three different types of carbon vessels (Open system, Partially-open system, and Closed system). With increase in the oxygen content in the raw fiber (Si-Al-C-O fiber), the degradation during the heat-treatment process easily proceeded accompanied by a release of relatively high concentration of CO gas. When we used the raw fiber composed of $Si_1Al_{0.01}C_{1.5}O_{0.5}$ and closed system, much smoother surface of the obtained SiC-polycrystalline fiber could be achieved. In this case, the degradation reactions ($SiO+2C=SiC+CO$ and $SiO_2+3C=SiC+2CO$) at the first stage in the inside of each filament became faster, and then the CO partial pressure at the surface region of each filament was considered to be increased. In consequence, according to Le Chatelier's principle, the surface degradation reaction and grain growth of formed SiC crystals would be considered to become slower.

## Acknowledgments

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