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STRUCTURAL ANALYSIS IN CONTINUOUS SILICON CARBIDE FIBER OF HIGH TENSILE STRENGTH

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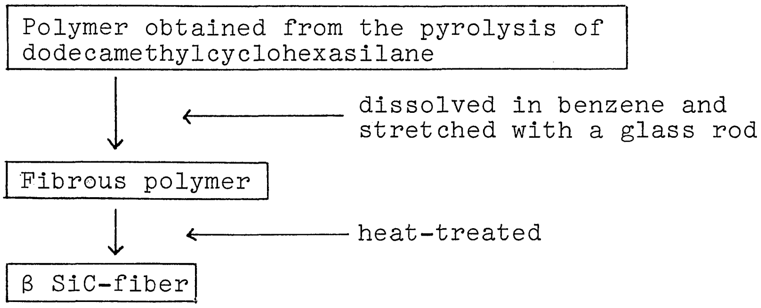
The starting material of a continuous silicon carbide fiber with very high tensile strength is a polycarbosilane. It begins to decompose from 300°C in vacuum and is gradually converted into a β-silicon carbide fiber by the heat-treatment at the temperature above 800°C.

The authors, S. Yajima, J. Hayashi, and M. Omori, have synthesized the continuous silicon carbide fiber with ultra fine crystallites and discovered that the tensile strength of the fiber was very high, about 350 kg/mm^2.[1)] The silicon carbide fiber could be obtained as follows;



In a previous paper, the fibrous polymer heat-treated at the temperature above 1200°C has been examined by the tensile test, the X-ray diffraction and the electron micrograph. It is very interesting that the polymer molecule is destroyed and shrinked by heat-treatment, finally, converted to the β-silicon carbide with high tensile strength.

In this paper, the formation process from the organosilicon polymer to the silicon carbide fiber was examined by the X-ray diffraction and the infrared analysis.

The polymer obtained from the pyrolysis of dodecamethylcyclohexasilane is a white powder which has the mean molecular weight of about 1500. The infrared analysis was made to examine the structure of the polymer. The infrared spectra of the polymer measured in KBr is shown in Fig.1. Absorption bands are observed at 2950, 2890, 2100, 1400, 1350, 1250, and 1050-700 cm^{-1}. It is significant that the bands at 2100 cm^{-1} and 1050-700 cm^{-1} show the presence of Si-H and Si-CH$_2$-Si bonds, respectively. The characteristic Si-O band is considered to be present in the vicinity of 1050 cm^{-1}. Thus, the structure of this polymer is believed to be a polycarbosilane.[2)] The structural change of the polycarbosilane begins gradually above 300°C under reduced pressure, and that is clearly observed from the decrease of

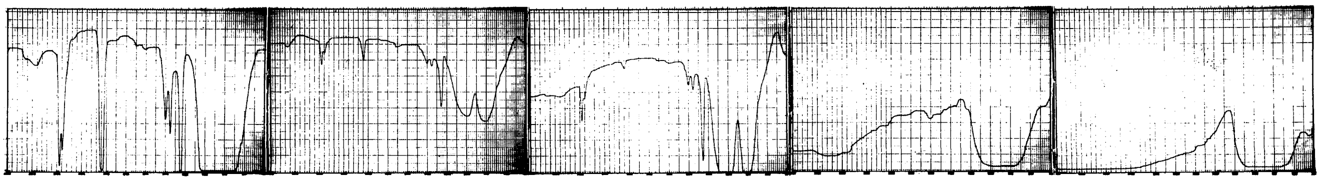

(1) (2) (3) (4) (5)

Fig.1 Infrared spectra of polycarbosilane (1) and polycarbosilene heat-treated at each temperature; (2) 300°C, (3) 400°C (4) 750°C, and (5) 1100°C.

the infrared absorption band at 2100 cm^{-1} due to Si-H linkage. The cleavage of the Si-H bond is completed at about 450°C. The fact suggests that the cleavage of the Si-H bond leads to the cross-linking of the polycarbosilane. In fact, the polycarbosilane heat-treated at 400°C under reduced pressure was completely insoluble in common organic solvents, which was consistent with the infrared analysis. In the polycarbosilane heat-treated at 750°C, the infrared analysis indicates that common organic bonds such as $Si-CH_3$ or $-CH_2-$ are almost absent. The infrared absorption bands at 1050-700 cm^{-1} due to Si-C and Si-O linkages only are present.

Thermogravimetric analysis of the polycarbosilane is shown in Fig.2. It indicates that the decomposition occurs from 300°C and finishes at about 800°C. The weight residue, 60% suggests that the polycarbosilane will be converted into the material containing mainly Si-C bonds.

In order to examine the structural formation process from polycarbosilane to silicon carbide fiber, five samples were prepared. They are summarized in Table 1. The X-ray diffraction studies were made on powders of the polycarbosilane and a bundle of fibers using the CuKα radiation (Ni filter).

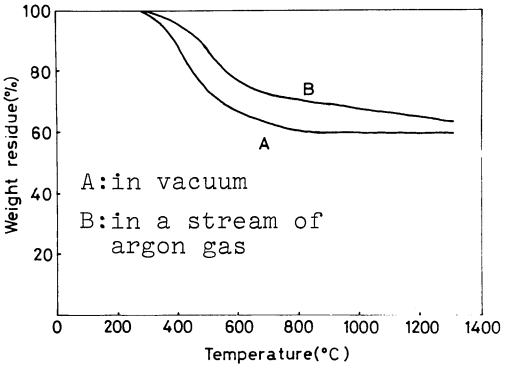
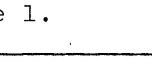


Fig.2 Thermogravimetric analysis of polycarbosilane. Heating rate, 5°C/min.

Table 1.

number	sample
I	polycarbosilane  $(-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{C}}-)_n$
II	polycarbosilane fiber
III	polycarbosilane fiber heat-treated up to 750°C at the heating rate of 10°C/3 min in vacuum
IV	up to 1000°C at the same condition
V	up to 1100°C at the same condition

The broad patterns are shown in Fig.3 and the pattern of the fiber heat-treated at 1500°C is also shown for comparison. As the polycarbosilane fiber is heated at successively higher temperature, the peak at position (a) decreases and completely disappears at the temperature above 1000°C. However, the peaks at positions (b)

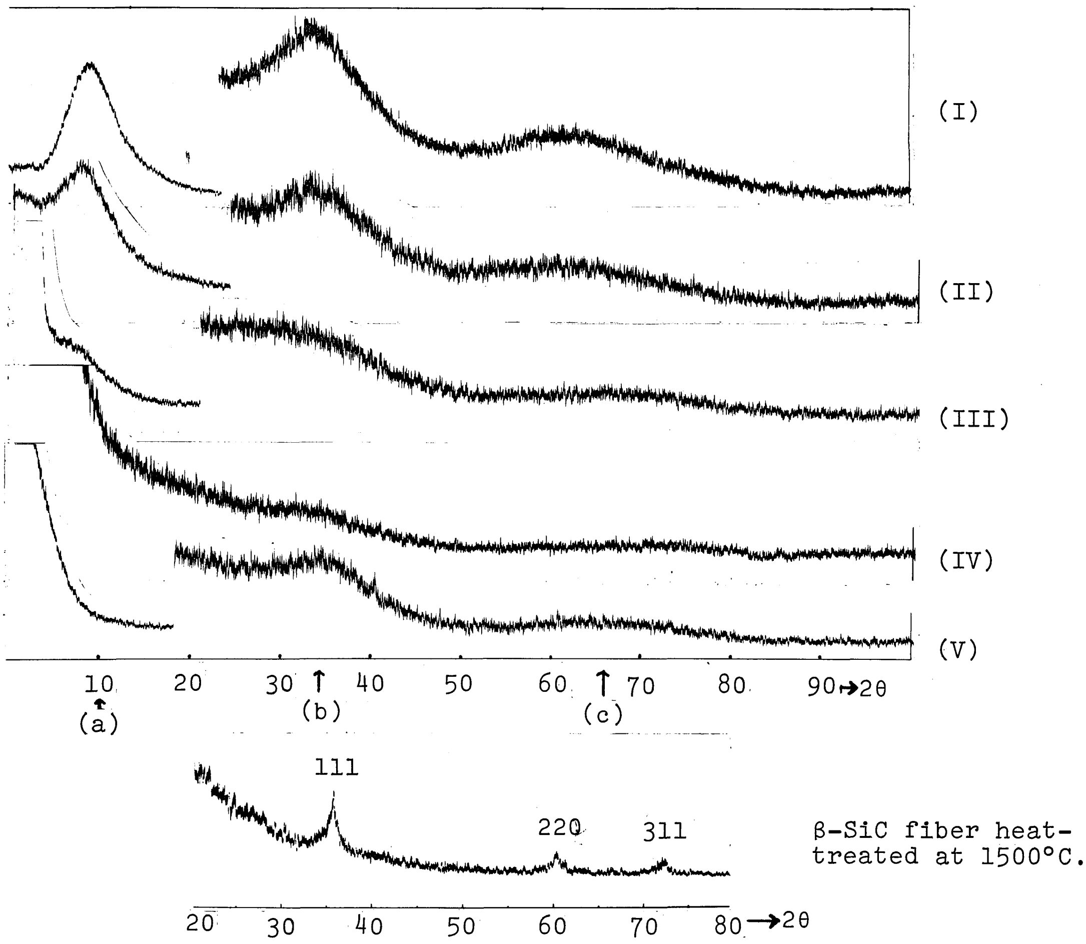


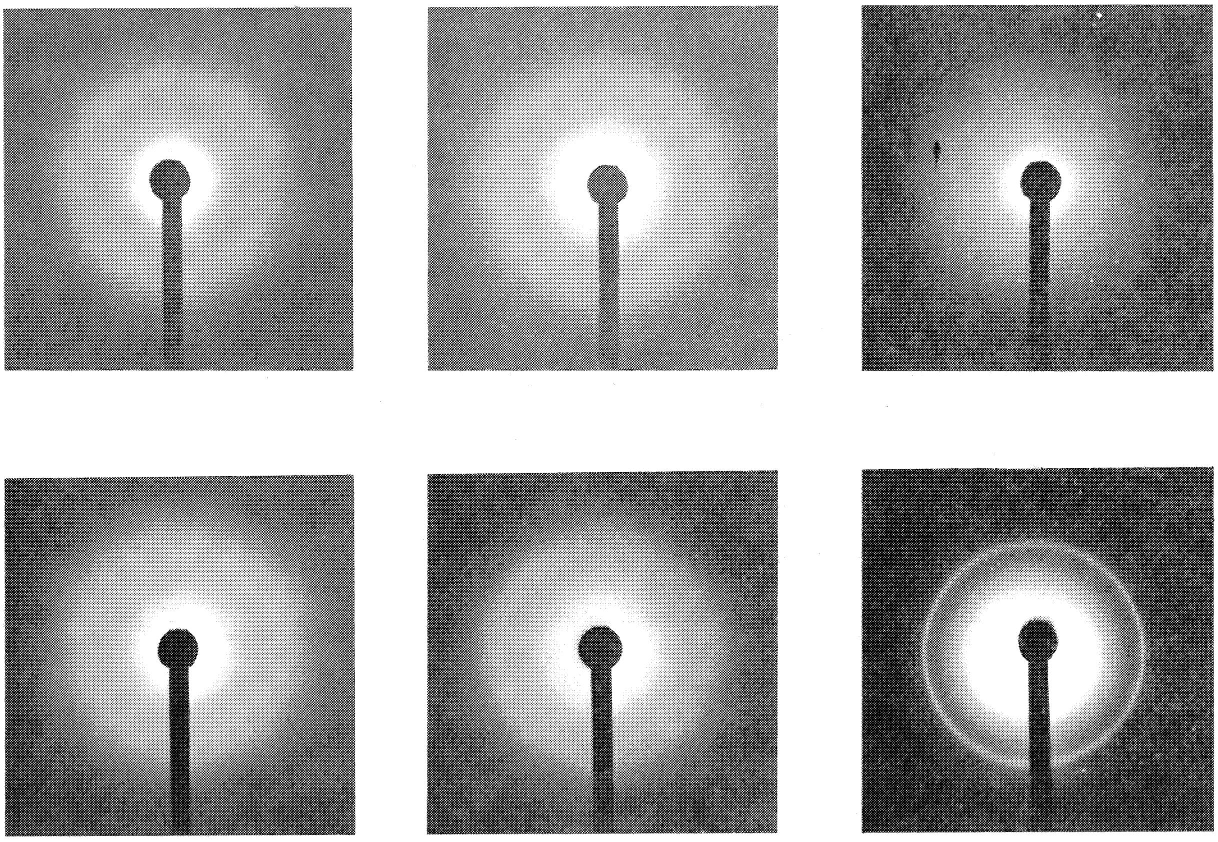
Fig.3 X-ray diffraction patterns of samples in Table 1. (I)-(V) correspond to the number of Table 1. The intensity full scale range of the low angle side below about 20° is 4 times that of the high angle side above 20°.

and (c) in Fig.3 decrease in case of the sample heat-treated at about 750°C, but are observed in all samples. As the polycarbosilane fiber is heated at higher temperature, those peaks are shifted to a slightly higher angle side and change to 111 pattern and both 220 and 311 in β-SiC, respectively.

The X-ray (CuKα) transmission pinhole photographs of these samples are shown in Fig.4. The patterns corresponding to position (b) in Fig.3 show no fiber texture patterns and show diffuse halos characteristic of an amorphous state, but especially the pattern of No.III is very broad. The atomic arrangement of the specimen heat-treated in the vicinity of 750°C is considered to be very random. The polycarbosilane ceases to decompose in the vicinity of 750°C and is gradually changed into β-silicon carbide with the heat-treatment above 800°C.

Values of the tensile strength of the fibers heat-treated at 750°C, 1100°C and 1300°C are shown in Fig.5. The value of the tensile strength is higher with heating, but that of fiber heat-treated at 1500°C is lower, 100 kg/mm^2.$^{1)}$ The strength of the fiber at 1300°C is the highest among fibers heat-treated at several temperatures.

In the infrared spectrum of the polycarbosilane heat-treated at the temperature above 750°C, common organic bonds except for the Si-C bond are absent, in the



(IV) (V) β-SiC fiber heat-treated at 1500°C

Fig.4 X-ray transmission pinhole photographs of samples in Table 1.

thermogravimetric analysis the weight loss ceases at 750-800°C and in the X-ray diffraction analysis the diffraction patterns at (b) and (c) change to those of β-SiC, so the Si-C skeleton in the polycarbosilane is considered to be converted to the atomic arrangement of the β-SiC structure with the heat-treatment.

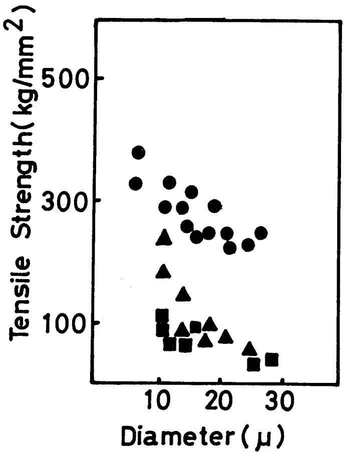


Fig.5 Tensile strength of the silicon carbide fiber heat-treated at 750°C (■), 1100°C (▲) and 1300°C (●).

References

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