

Raman Scattering of Inorganic Fibers

著者	Sasaki Yoshiro, Sato Mitsuhiko, Okamura Kiyohito, Nishina Yuichiro
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	32
number	2
page range	111-115
year	1985-03-26
URL	http://doi.org/10.50974/00043334

Raman Scattering of Inorganic Fibers *

Yoshiro Sasaki, Mitsuhiko Sato, Kiyohito Okamura and Yuichiro Nishina

The Research Institute for Iron, Steel and Other Metals

(Received December 25, 1984)

Synopsis

We have examined evolution of Raman spectra of carbon fibers and SiC fibers through structural transformations caused by heat treatment. Raman spectra of the SiC fibers indicate that the fibers consist of amorphous or microcrystalline SiC and graphitic microcrystals. We discuss the correlation between the tensile strength of the fibers and their microscopic structure deduced from the Raman data.

I. Introduction

During the last two decades, various kinds of inorganic fibers, such as those made from carbon, SiC, alumina and etc., have been developed and they are used for structural components in industrial as well as consumer products.¹⁾ These fibers have common features, i.e. light in weight, high tensile strength and high modulus. They usually consist of amorphous clusters or microcrystals. In this paper, we report Raman spectra of SiC fibers and carbon fibers heat-treated at various temperatures. The Raman study on the fabrication process of carbon fibers has been reported in ref. 2. SiC fibers show the comparable mechanical strength to carbon fibers and they have an advantage that they can maintain such strength at temperatures up to ~ 1200 °C even in oxidizing environment.³⁾ It is the primary purpose of this paper to show the correlation between the Raman spectra and the tensile strength of SiC fibers.

II. Experimental

The SiC fibers have been made from polycarbosilane.³⁾ The final heat treatment temperature (hereafter denoted as HTT) is in the range

* The 1776th report of the Research Institute for Iron, Steel and Other Metals.

from 1000 °C to 1700 °C. We use carbon fibers made from pitch by heat treatment at temperatures up to 2400 °C. The Raman spectra are taken with a standard equipment. An Ar⁺-laser beam (488 nm, 20 mW) is focused on a spot of $\sim 50 \mu\text{m}$ in diameter on the fiber placed in air. The scattered light is collected by an $F = 1.4$ lens.

III. Results and Discussion

Figure 1 shows the Raman spectra of the SiC fibers and a 6H-SiC single crystal. For the fibers of $\text{HTT} \leq 1400 \text{ }^\circ\text{C}$, the Raman spectra consist of four broad peaks. The peaks at $\sim 1350 \text{ cm}^{-1}$ and $\sim 1600 \text{ cm}^{-1}$ are attributed to the vibrations of graphitic microcrystals because the Raman spectra of the SiC fibers between 1000 and 2000 cm^{-1} are

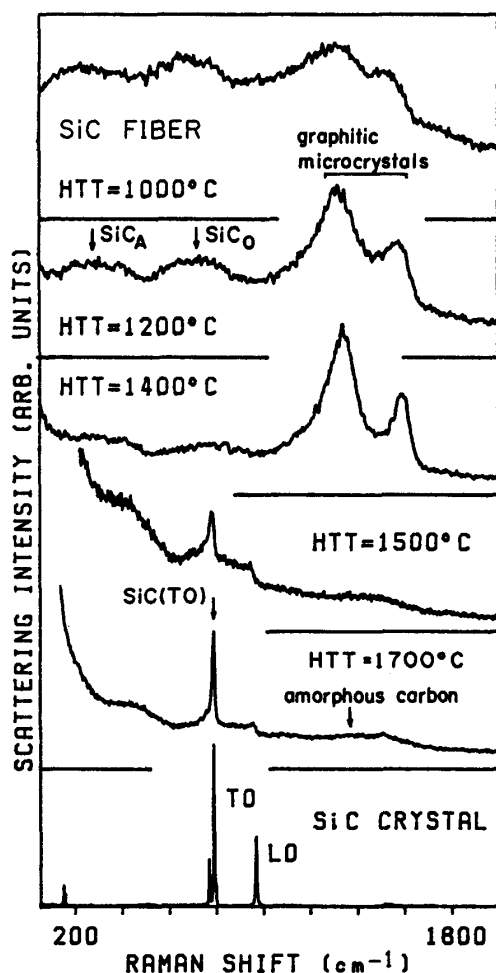


Fig. 1 Raman spectra of the SiC fibers made from polycarbosilane and 6H-SiC single crystal.

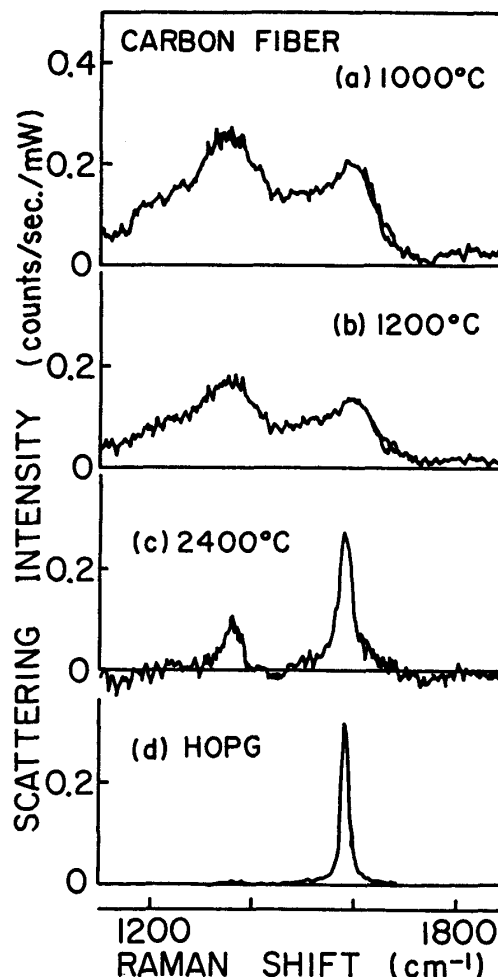


Fig. 2 Raman spectra of carbon fibers made from pitch in several heat treatment temperatures, and that for highly oriented pyrolytic graphite (HOPG).

similar to those of carbon fibers of $\text{HTT} = 1000\text{ }^\circ\text{C}$ or $1200\text{ }^\circ\text{C}$ as shown in Fig. 2. The existence of excess carbon in the SiC fiber has been confirmed by chemical analyses.⁴⁾ The peaks at $\sim 300\text{ cm}^{-1}$ (SiC_A) and at $\sim 750\text{ cm}^{-1}$ (SiC_O) are assigned to acoustic and optical phonons in amorphous SiC, respectively, because the phonon density of states of cubic SiC shows peaks at around 350, 550, and 850 cm^{-1} , among which the 550 cm^{-1} peak is weak compared with the others.⁵⁾ The peak positions of the SiC_A and SiC_O lines shift by 100 cm^{-1} toward higher frequency as HTT increases from $1000\text{ }^\circ\text{C}$ to $1400\text{ }^\circ\text{C}$, i.e. from 210 to 320 cm^{-1} for SiC_A and from 680 to 780 cm^{-1} for SiC_O . Such a frequency shift of the $700 \sim 800\text{ cm}^{-1}$ line has been reported on the crystallization process of amorphous SiC by thermal annealing as low as $850\text{ }^\circ\text{C}$.⁶⁾ The crystallization, therefore, is the cause of the observed increase in Raman shift. Since the peak shift in the SiC fiber occurs at a temperature much higher than that in the amorphous SiC, the crystallization is rather suppressed in the fiber. Transmission electron microscope images of the fiber suggest that the graphitic microcrystals and the SiC microclusters distribute uniformly in the fiber of $\text{HTT} = 1300\text{ }^\circ\text{C}$.⁴⁾ Aggregation of the same species, or growth of the microcrystals, therefore, is hindered by the other kind of the constituent clusters.

Following analyses of the X-ray diffraction line width ($\text{SiC}(111)$), one can estimate the average size of the SiC microcrystals to be 25 \AA after the heat treatment at $1400\text{ }^\circ\text{C}$ as shown in Fig. 3. In the case of microcrystalline Ge, the Raman spectra is quite similar to those of amorphous Ge if the crystal size is smaller than 100 \AA .⁷⁾ Thus it is reasonable, in spite of the crystallization of the SiC cluster on account of $\text{HTT} = 1400\text{ }^\circ\text{C}$, that we have found amorphous-like Raman spectra rather than crystalline-like sharp lines.

The Raman spectra of $\text{HTT} \geq 1500\text{ }^\circ\text{C}$ samples are considerably different from those of $\text{HTT} \leq 1400\text{ }^\circ\text{C}$; namely the graphitic lines quench and the sharp line takes place, corresponding to the TO-phonon of SiC single crystals. Furthermore, the gas evolution analyses during the heat treatment process show the loss of carbon atoms from the SiC fiber in a form of CO gas at around $1500\text{ }^\circ\text{C}$. The oxygen is included in the precursor fiber.⁸⁾ These experimental observations indicate that aggregation (or growth) of SiC microcrystals, which have been isolated from each other by the graphitic clusters, occurs rapidly due to decomposition of the graphitic clusters incurred by the CO gas evolution. In fact, an average SiC crystal size in the fiber increases abruptly at a temperature between $1400\text{ }^\circ\text{C}$ and $1500\text{ }^\circ\text{C}$ from 25 \AA to 190 \AA as plotted in Fig. 3. Figure 3 also shows that HTT

dependence of the tensile strength of a SiC fiber. The tensile strength decreases to virtually zero by the heat treatment above 1500 °C. The experimental evidences mentioned above suggests that the graphitic microcrystals distributing uniformly in the fiber play important roles for the high tensile strength and high modulus of the SiC fiber. The graphitic microcrystals hold SiC clusters together, which are either amorphous or microcrystalline, and furthermore, they prevent aggregation of the SiC clusters.

The tensile strength reaches the highest value at $\text{HTT} = 1200$ °C. The Raman spectra of the fiber

suggest that it consists of amorphous SiC and graphitic microcrystals. The existence of SiC microcrystals (< 10 Å), however, is found in this fiber from the electron microscope image, although the number of microcrystals is very small. The SiC cluster in the $\text{HTT} = 1200$ °C fiber, therefore, is identified as the initial stage of its crystallization from the amorphous state.

The peak positions of the graphitic Raman lines are located ~ 30 cm^{-1} lower for the $\text{HTT} \leq 1200$ °C SiC fibers (Fig. 1) than the carbon fibers (Fig. 2) heat-treated at similar temperatures. Furthermore, the line widths are larger for the SiC fiber than those for the carbon fibers. We may speculate from these result that the bond angle in the graphitic cluster fluctuates and/or the cluster size is smaller than those of the carbon fibers (~ 30 Å).⁹⁾ The Raman spectra of the SiC fiber heat-treated above 1500 °C shows a trace of the amorphous carbon line at around 1400 cm^{-1} . Excess carbon, therefore, still exists in the fiber even after the loss of carbon by the CO gas evolution.

The upper limit of the temperature for the practical use of the SiC fiber may be related to the onset of the C-O reaction occurring in the fiber. The study of oxygen contained in the fiber, therefore, is very important for improving its mechanical properties.

IV. Conclusions

The Raman study of the SiC fiber shows that the fiber consists of;

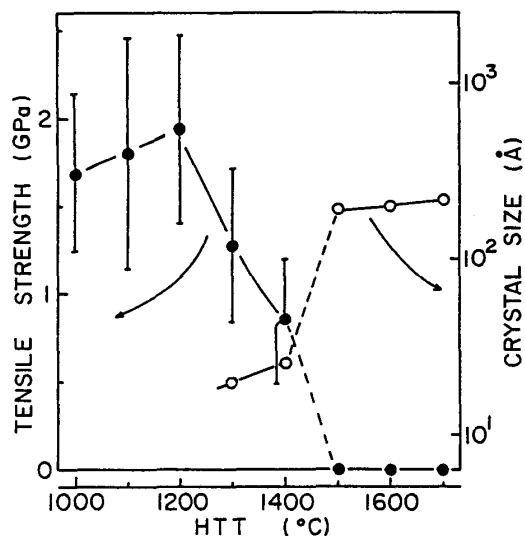


Fig. 3 The relationship between heat treatment temperature and the tensile strength (solid circles) and the crystal size of SiC (open circles) measured by the X-ray diffraction.

- 1) amorphous SiC and graphitic carbon for $HTT \leq 1200$ °C,
- 2) microcrystalline SiC and graphitic carbon $HTT \sim 1400$ °C, and
- 3) micro- and polycrystalline SiC and amorphous carbon for $HTT \geq 1500$ °C.

The strongest fiber may be obtained in the transition stage from 1) to 2). The existence of the graphitic carbon in the SiC fiber is very important for realizing its high tensile strength.

This work was supported in part by the Grant-in-Aid for the Special Project Research on the Properties of Molecular Assemblies (No. 58218002) from the Ministry of Education, Science and Culture.

References

- 1) "Strong Fibers and Composites", Phil. Trans. Roy. A294 (1980) 407.
- 2) Y. Sasaki and Y. Nishina, Proc. of 9th Int. Conf. on Raman Spectr., Tokyo (1984) p. 462.
- 3) S. Yajima, Phil. Trans. R. Soc. London A294 (1980) 419.
- 4) S. Yajima, K. Okamura, T. Matsunaga, Y. Hasegawa and T. Shishido, Nature 279 (1979) 706.
- 5) K. Kunc, M. Balkanski and A. Nusimovici, Phys. Status Solidi (b) 72 (1975) 229.
- 6) J.A. Bordes, S.T. Picraux and W. Beezhold, Appl. Phys. Lett. 18 (1971) 509.
- 7) S. Hayashi, M. Ito and H. Kanamori, Solid State Commun. 44 (1982) 75.
- 8) Y. Hasegawa and K. Okamura, J. Mater. Sci. 18 (1983) 3633.
- 9) F. Tuinstra and J.L. Koenig, J. Chem. Phys. 53 (1970) 1126.