STRENGTH DEGRADATION OF SiC FIBER BY HYDRO-THERMAL TREATMENT AND ITS APPLICATION TO THE SURFACE MODIFICATION OF SiC FIBER

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ABSTRACT

A composite material of SiC/SiC is a promising combination from the point of view of heat resistance and anti-oxidation properties. One of the problems of the combination is brittleness due to easy crack propagation to the matrix from the fiber. Forming a thin carbon film on the fiber is promising method to control the interfacial condition. In this experiment, two kinds of SiC fibers of NICALON and HI-NICALON made by Nippon Carbon Co. Ltd., were used. A thin carbon film was formed on the SiC fibers by hydro-thermal treatment. The treatment was performed in water at 150• 700• under 0.5• 22.0MPa for 4 hours. Tensile test revealed that the fiber maintained the original strength after hydro-thermal treatment at 300• for 4 hours. No damage was observed at the surface, and the strength of both fibers was maintained after hydro-thermal treatment up to 300• . From these results, hydro-thermal treatment at 300• for 4 hours is appropriate to form a thin carbon film without deterioration of the fiber.

INTRODUCTION

Inorganic fibers such as SiC fiber have excellent properties such as high strength, high modulus and high heat resistance. Especially a composite material of SiC/SiC is promising combination from the point of view of high heat resistance and anti-oxidation properties. Then various trials to utilize the fiber as the reinforcement in composites have been attempted[1)]. One of the problems of the composite is brittleness due to easy crack propagation to the matrix from the reinforcement. The bonding strength at the interface should be strong enough to transfer the stress between the matrix and the reinforcement. It should, however, not be too strong to propagate the crack from the reinforcement to matrix, so that the crack splits along the interface, which can avoid the stress concentration. Controlling the characteristics by forming a thin film at the interface can improve the strength of the composite.

As is known, there are various methods to form a thin film on a fiber, e.g. PVD, CVD, or plasma spraying. They are usually performed at a higher temperature than 1000• . Then the fiber is easily deteriorated during the coating process because of the high temperature. On the other hand, forming a thin film by hydro-thermal treatment can be carried out at much lower temperature, therefore serious deterioration may be avoided.

EXPERIMENTAL PROCEDURES

In this experiment, two kinds of SiC fibers, NICALON and HI-NICALON, made by Nippon Carbon Co.Ltd., were used as the fibers. The properties of the as-received fibers are listed in Table 1.

TABLE 1 Typical Properties of the low oxygen SiC fiber

Property	HI-NICALON	NICALON
Fiber diameter (ìm)	14	14
Number of filament (fil./ yarn)	500	500
Tex (g/ 1000m)	200	210
Tensile strength (GPa)	2.8	3.0
Tensile modulus (GPa)	270	220
Elongation (%)	1.0	1.4
Density (g/ cm^3)	2.74	2.55
Specific resistively (ohm-cm)	1.4	103• 104
Chemical composition Si(wt.%)	62.4	56.6
C(wt.%)	37.1	31.7
O(wt.%)	0.5	11.7

A thin carbon film was formed on the SiC fibers by hydro-thermal treatment. The instrument was the THP-AII type made by Nikkiso Co. Ltd., which had a test tube. 10 yarns of 7cm in length were set in the test tube. The test tube was filled with pure water. The treatment was performed in water at 150• 700• under 22.0MPa for 4 hours.

Strength of the single fiber before and after treatment was examined. The diameter of a fiber was determined by using He-Ne laser. Diffraction fringe was observed by applying the laser to the fiber on a cardboard mount. The diameter of the fiber(d) was precisely determined from the wave length of the laser(ë=633nm), distance between the diffraction fringes(ä) and the distance from the fiber to the screen(s) as follows;

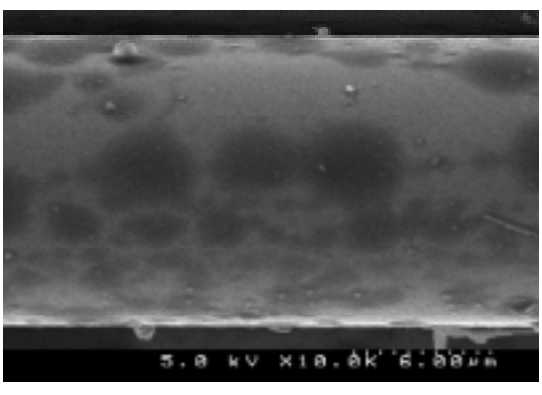
$$d=2ës/ä \quad (1)$$

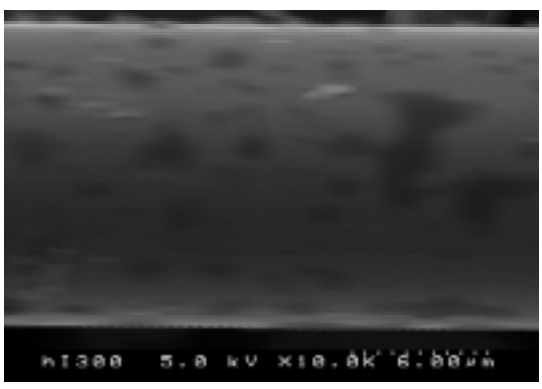
The load was detected when the fiber was fractured. The strength was determined from the load and the cross sectional area from “d”. 30 fibers were examined for each condition[2)].

Observation of the surface was performed by FE-SEM, EDX, XRD and Raman spectroscopy.

RESURTS AND DISCUSSION

The surface or the fiber was investigated by FE-SEM. Figure 1(a)(b) shows the morphology of NICALON and HI-NICALON after treated at 150• for 4 hours. Trace of size surface conditioner was remained on the surface of both of the fibers. PVA was used as the size for both fibers, which decompose at 200• . Then treatment at 150• was too low to decompose completely.

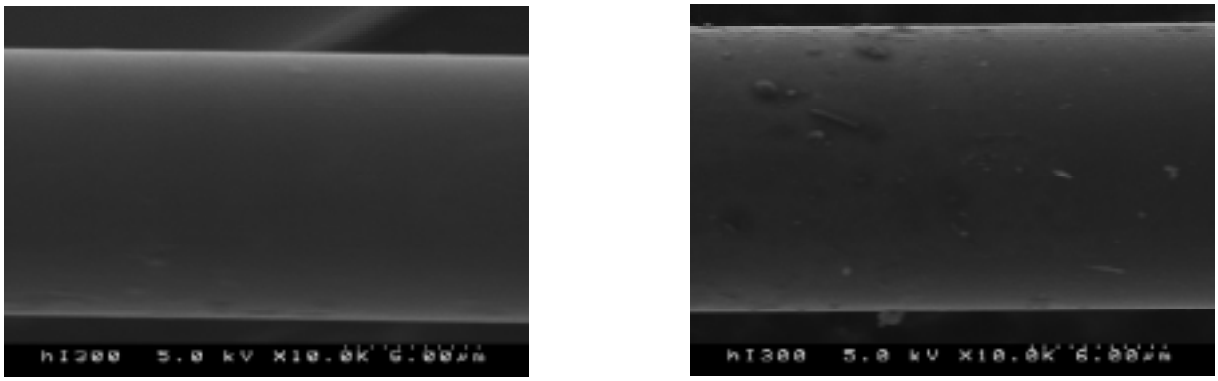




(a) NICALON (b) HI-NICALON

Figure 1 FE-SEM photographs of the surface of SiC NICALON (a) and HI-NICALON (b) fiber, hydro-thermally treated at 150• for 4hours.

On the other hand, both fibers, NICALON and HI-NICALON, showed the smooth surface without size as shown in Figure 2(a)(b). When the treatment temperature was elevated to 500• , foreign material or damage by corrosion was confirmed on the part of the surface, though photos are not shown hereafter. Projections or serious damage by corrosion were observed on both fiber after treatment at 700• .



(a) NICALON (b) HI-NICALON

Figure 2 FE-SEM photographs of the surface of SiC NICALON (a) and HI-NICALON (b) fiber, hydro-thermally treated at 300• for 4hours.

Compositional analysis was performed by EDX to determine the carbon film on the surface. In the case of HI-NICALON, the concentration of carbon on the surface after treatment at 300• was 2 times higher than as-received fiber. The concentration of carbon decreased, when treatment was performed at 500• .

In the case of NICALON, the carbon concentration increased after treatment at every temperature. The carbon concentration after treatment at 700• was lower than the others and oxygen concentration was higher. This result implies the fiber was oxidized at 700• .

X-ray profiles of NICALON and HI-NICALON after treatment are shown in Figure 3. Three peaks, (111), (220) and (311) of SiC are clearly seen in the figure. The peaks of the Hi-NICALON were higher and narrower than NICALON, which means the HI-NICALON was more highly crystallized. Generally speaking, highly crystallized material, such as HI-NICALON, has low reactivity, so it is preferable as the reinforcement for elevated temperature use. The thickness of carbon layer, however, should be very thin, as the peak of carbon was not observed in the profiles.

SiC: Moissanite-3C SiC: Moissanite-3C

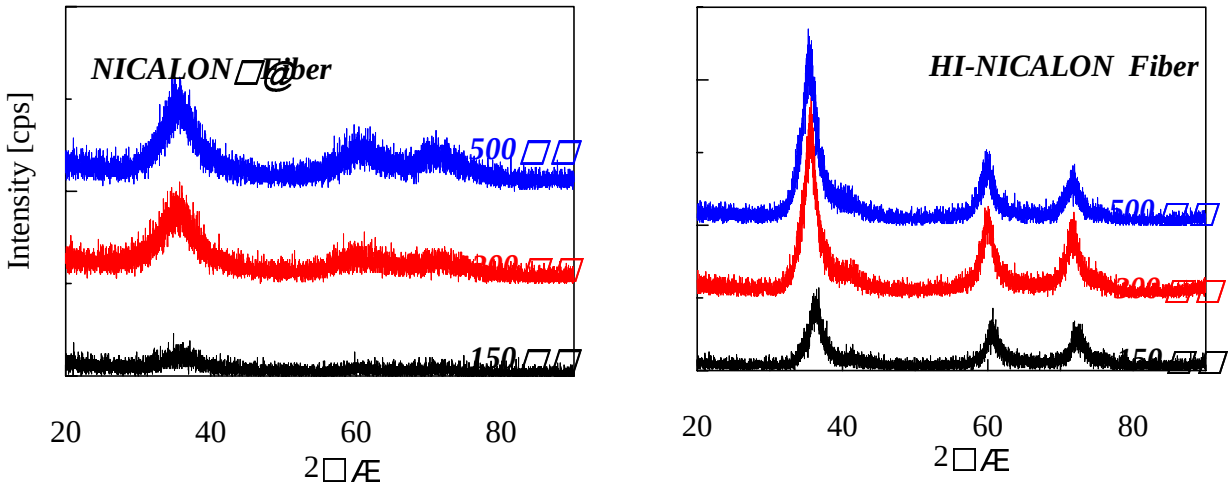


Figure 3 Results of XRD analysis

Figure 4 Results of Raman analysis

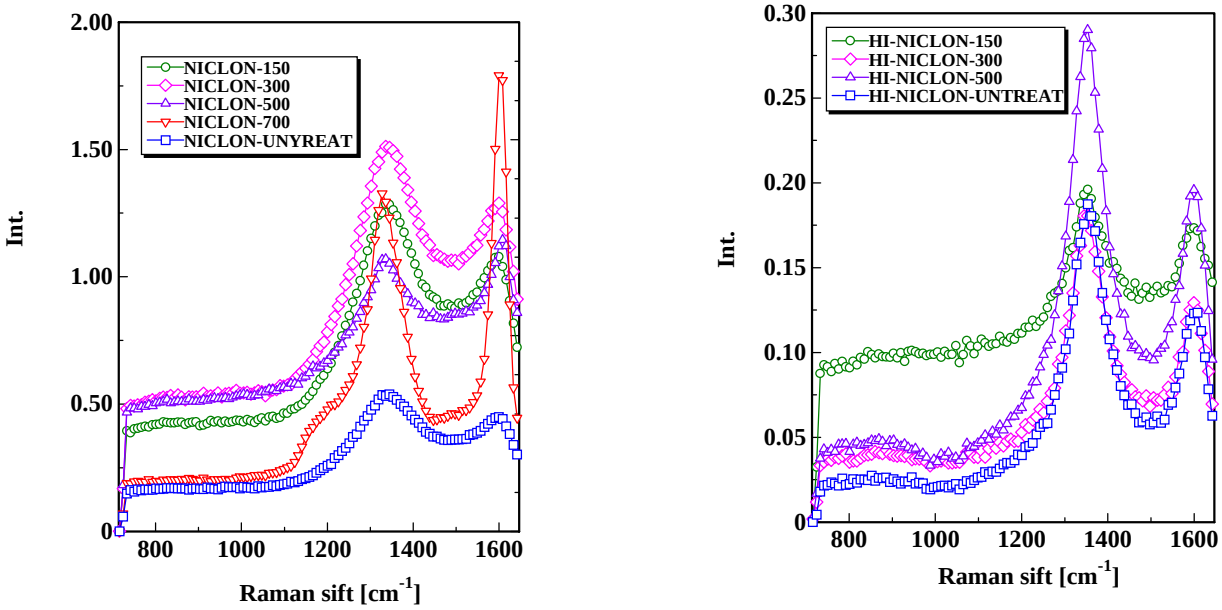


Figure 4 shows the results of Raman spectroscopy of both fibers before and after treatment. Raman bands of carbon are 1580cm^{-1} of sp^2 for graphite and 1322 cm^{-1} of sp^2 for diamond. Both of them are very sharp. When disorder of the atomic array of graphite or diamond becomes higher, another Raman band(G-band) of 1335 cm^{-1} appears besides 1580cm^{-1} of D-band. In the case of amorphous carbon, the peak of profile of Raman spectroscopy becomes weak and broad. The distance between two peaks increases with increasing the disorder.

In this experiment, wavelength of 514.5nm of Ar laser was used. Observation was carried out to detect the surface of less than 10nm in depth of the fiber. Results are shown in Figure 4. As is shown, the peak for treated samples were higher than as-received fiber. It shows the carbon film was formed on the fiber by the treatment. Though the film is too thin to be observed by SEM, both results of EDX and Raman spectroscopy agree well with each other, and show the existence of carbon film.

The strength of NICALON was higher than HI-NICALON before the treatment. On the contrary, modulus of HI-NICALON was higher than of NICALON. Degradation of SiC fiber in hydro-thermal process was investigated by tensile test. Figure 5 show the results of treatment temperature dependence of tensile strength of the fibers. Average tensile strength was 1.54GPa for as-received of NICALON fiber and 2.12GPa for HI-NICALON. The strength of HI-NICALON is approximately 30% higher than the others.

The strength of NICALON was 1.60GPa after treated at 300• , which was the same level as the as-received fiber. When the temperature increased to 500• the strength decreased to 1.05GPa after treatment, which was 35% less than the fiber treated at 300• .

In the case of HI-NICALON, the strength decreased to 1.82GPa after treated at 300• , which is slightly lower than the as-received fiber. The strength was 1.91GPa after treated at 500• , which is the same level as the fiber after treated at 300• .

After all, the carbon film was formed by hydro-thermal treatment at 300• , and both fibers maintain the strength after the treatment at that temperature.

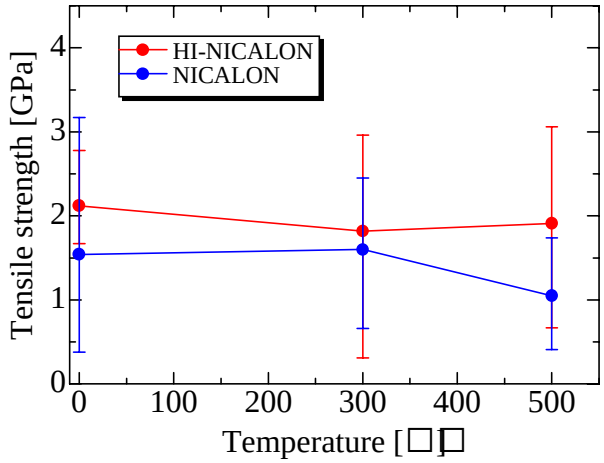


Figure 5 Tensile strength of NICALON and HI-NICALON fibers before and after hydro-thermal treatment at various temperatures for 4h.

It was deduced by observation of the fiber surface that the carbon film was formed by selective corrosion and dissolving of Si from SiC fiber at the high temperature under high pressure. From described results and literatures[3], the process of forming the carbon film on the fiber is presumed as follows:

$$SiC + 2H_2O \bullet SiO_2 + C + 2H_2 \quad \bullet \bullet \quad (a)$$

$$SiCxOy + (n-y)H_2O \bullet SiO_2 + xC + n H_2 \quad \bullet \bullet \quad (b)$$

$$SiO_2 + nH_2O \bullet SiO_2 \bullet nH_2O \quad \bullet \bullet \quad (c)$$

CONCLUDING REMARKS

Original strength of HI-NICALON is higher than one of NICALON. No damage was observed at the surface, and the strength of both fibers was maintained after hydro-thermal treatment up to 300• . From these results, hydro-thermal treatment at 300• for 4 hours is suitable to form a thin carbon film without deterioration of the fiber.

REFERENCES

1) A. OKURA, H. HUKUDA, Y. KAGAWA, and T. NISHI, “Material Technology 17 Composite”, Tokyo University, (1984), 1-9
2) A.J.PERRY, B.INEICHEN, B.ELIASSON, “JOUNAL OF MATERIALS SCIENCE vol.9”, (1974), 1376-1378
3) Yu.G.GOGOTSI, M. YOSHIMURA, “NATURE VOL 367”, (1994), 628-630