

TENSILE STRENGTH AND MORPHOLOGICAL INVESTIGATION OF SiC-COATED CARBON FIBERS

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Abstract—SiC-coated film onto carbon fibers as a barrier of oxidation resistance and reaction between carbon fibers and metals was investigated. The chemical vapor deposition of silicon carbide onto carbon fibers was performed at various temperatures ranging from 700 to 1000°C using triisopropylsilane vapor carried by hydrogen gas. The strength of the SiC-coated carbon fibers was decreased due to deterioration of fibers and chemical attack of hydrogen on the surface of carbon fibers during the coating process. The oxidation and the thermal resistance of the SiC-coated carbon fibers compared to the uncoated carbon fibers were improved at temperature range of 600-800°C and 1000-1200°C, respectively. Morphological change by air oxidation at temperature range of 500-800°C was also investigated for the SiC-coated and the uncoated carbon fibers, respectively. The SiC-coated film between carbon fiber and aluminum was sufficient as a barrier of reaction on carbon fiber reinforced aluminum at temperature of above 1000°C.

Key words: Carbon Fibers, Tensile Strength, SiC-Coated Film, Chemical Vapor Deposition, Morphological Change of Carbon Fibers

INTRODUCTION

The enormous importance of advanced composites as most promising candidates for future lightweight materials is mainly based on high stiffness combined with high strength and low density of the fiber backbone. In this respect, carbon fibers surpass glass fibers as well as organic polyamid fibers although the latter exhibit higher toughness. Nevertheless, combinations of carbon fibers with one or both of these alternative reinforcement materials are well known to modern advanced composites and are given the name as hybrids [Bunsell, 1988].

However, they have low oxidative resistance, weak compatibility, and poor wettability. Furthermore they perform chemical reaction at high temperatures with several metals. In the fabrication of carbon fiber-aluminum composites, poor wettability of aluminum on carbon fibers was attributed to produce an unfavorable carbide at high temperatures [Baker and Bonfield, 1978]. Although carbon composites possess uniquely superior mechanical properties, an application of reinforced carbon fibers at high temperatures was also limited by the phenomenon of carbon oxidation. Under oxidizing condition at temperature of 500°C or higher, carbon readily chemisorbs oxygen and subsequently desorbs oxides of carbon [Yamamoto et al., 1994; Jones, 1991]. This oxidation process results in erosion of the structure and eventually in degradation of the material. To overcome these difficulties, a coating technique which was considered to be an effective method to modify the fiber-matrix interface was widely used in metal or ceramic matrix composites [Canmer, 1989]. Much works have been done in the coating onto carbon fibers using Ti, TiC, TiB₂, TiN, SiC, BN, and Ni as coating materials in metal matrix composites [Kohara and Nuto, 1980; Kohara et al., 1979; Masato, 1978; Leonhardt et al., 1991; Warren et al., 1978; Aggour et al., 1977;

Stumm et al., 1992; Pitkethly et al., 1993], but the study on oxidation resistance and reaction between the coated carbon fibers and metal at high temperatures was less. In this study, the characterization of the coated carbon fibers as a barrier of oxidation resistance and reaction between carbon fibers and metal was carried out by tensile strength and morphological investigation. Since silicon carbide (SiC) gives high performance in mechanical strength, wear resistance and chemical stability at high temperature [Scholz et al., 1993], SiC-coating onto the carbon fibers by chemical vapor deposition (CVD) was performed.

EXPERIMENTAL

1. Coating Method

Bundles of fibers were coated with silicon carbide by the chemical vapor deposition method. Generally SiC-coated film has been prepared by using SiCl₄ or CH₃SiCl₃ with hydrogen gas at temperatures of 1200°C or higher [Muench and Pfaffeneder, 1976; Chin et al., 1977; Noone and Roberts, 1966; Guiden, 1968]. In this study, triisopropylsilane [(CH₃)₂CH]₃SiH, Aldrich Chemical Co.} was also used as a precursor for SiC deposition. The PAN-based carbon fiber (HM-45, Toho Rayon Co. Japan) used as a base material had a tensile strength of 2.0 GPa and a diameter of 6-7 μm.

Chemical vapor deposition of silicon carbide onto carbon fibers was carried out by changing temperature from 700 to 1000°C using triisopropylsilane vapor carried by hydrogen gas. Silicon carbide was deposited on the filament of carbon fiber in the apparatus shown schematically in Fig. 1. The reactor, made of mullite tube (60 mm in inside diameter and 1 m in length), was externally heated by electric furnaces. Triisopropylsilane fed through micro feeder was vaporized at the mouth of the reactor by the pre-furnace (150°C). To promote the mixing of triisopropylsilane vapor and carrier gas a honeycomb ceramic distributor was located at the

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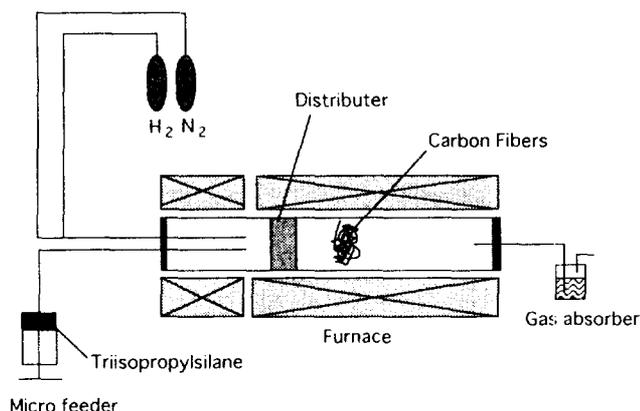


Fig. 1. Apparatus for SiC coating by CVD.

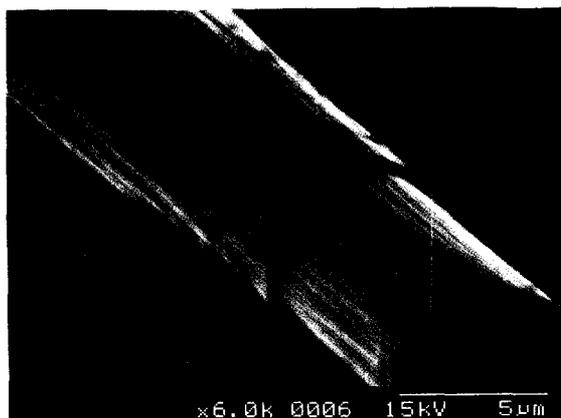


Fig. 2. Scanning electron micrograph of the SiC-coated carbon fiber.

distance of 20 cm from the reactor inlet. The concentration of triisopropylsilane in hydrogen gas (50-900 ml/min) was 0.04 to 20 vol%, and the reaction time was 10 to 30 min.

The carbon fiber reinforced aluminum (CFRAI) for investigating the reaction between carbon fiber and aluminum was prepared by Al-coating onto the SiC-coated or the uncoated carbon fibers in thickness of $0.5 \mu m$ using ion sputter apparatus (E-101, HITACHI).

2. Analytical Methods

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray (SEM-EDX, HITACHI S-2300) was used to examine the surface of the coated carbon fibers. The diffusion of aluminum into carbon fiber by reaction between fiber and aluminum interface was also investigated by a SEM-EDX line analyzer.

To examine the mechanical properties of the coated carbon fiber yarns, tensile strength test was carried out on a monofilament with a gage length of 5 mm and repeated 20 times for an average using Auto-Graph (AG-D, SHIMADZ).

The weight change of the uncoated and the SiC-coated carbon fibers during the heating up period to $900^\circ C$ was also investigated by thermal gravimetric analyzer (TGA-50, SHIMADZ). Sample of carbon fibers with 0.5 mm in size and 2 mg in weight was heated in an alumina crucible in air at a flow rate of 100 ml/min and a heating rate of $5^\circ C/min$.

The oxidation and thermal resistance was examined by measuring the tensile strength of the heat-treated SiC-coated carbon fibers for 1 h in air and inert gas (N_2), and compared with that of the original carbon fibers, respectively.

RESULTS AND DISCUSSION

1. Tensile Strength of the SiC-coated Carbon Fiber

In general, the coating morphology depends on various reaction parameters including coating temperature, precursor concentration, flow rate of carrier gas, reaction time, etc. In order to obtain an uniform coating thickness on all filaments, various deposition techniques were tried by changing the vapor phase concentration of triisopropylsilane (0.04-20 vol%), the flow rate of carrier gas (50-900 ml/min), reaction temperature ($700-1000^\circ C$) and reaction time (10-30 min).

Fig. 2 shows a scanning electron micrograph of the surface of the SiC-coated carbon fiber under the following conditions: reaction time, 10 min, temperature, $800^\circ C$, 0.047 vol% of triisopropylsilane in hydrogen (700 ml/min). This SEM investigation

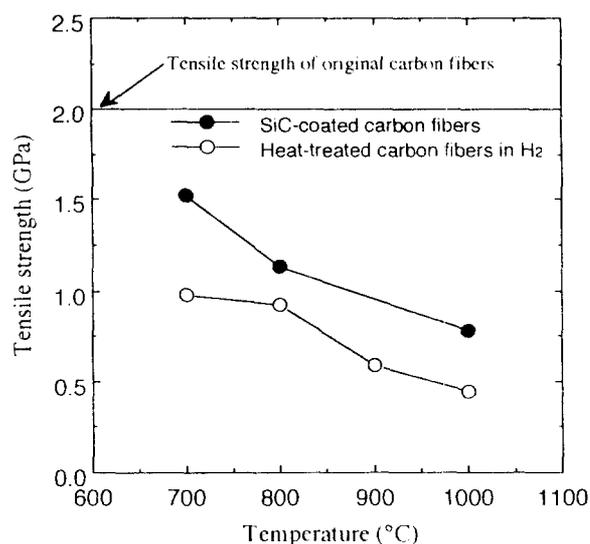


Fig. 3. Effect of SiC-coating on the tensile strength of carbon fibers.

revealed that the fiber bundles were coated homogeneously in $0.3-0.5 \mu m$ of thickness under the given conditions.

The tensile strength of the coated carbon fibers were examined by a monofilament tensile test. The strength of the SiC-coated carbon fiber is plotted as a function of the coating temperature in the range of $700-1000^\circ C$ and compared with those of only heat-treated fibers in hydrogen atmosphere for 30 min in Fig. 3. The tensile strengths of both the coated and the heat-treated fibers were decreased with increasing temperature. The tensile strength for the SiC-coated fiber decreased to 60% of the original value at $800^\circ C$. The SiC-coated carbon fibers at other temperatures except $800^\circ C$ showed poor morphological properties. The decrease of weight of the heat-treated carbon fibers in hydrogen was also found in the range of 10% of the value of the uncoated fibers.

The effect of carrier gases (hydrogen and nitrogen) on the strength of fibers was studied to investigate the strength degradation of the heat-treated carbon fibers. Fig. 4 showed the strength of the heat-treated fibers without coating at high temperatures in response to carrier gases, hydrogen and nitrogen. For both carrier gases, the strength of the uncoated heat-treated fibers was decreased. However, the heat-treated fibers in nitrogen showed no weight change and higher strength than that of the heat-treat-

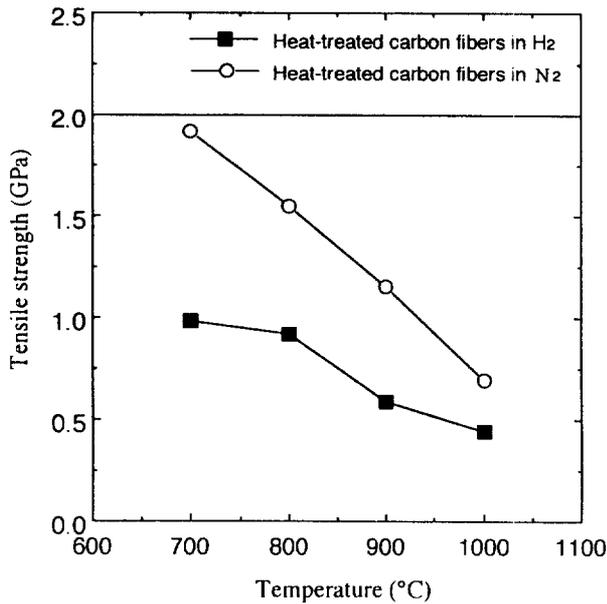


Fig. 4. The tensile strength of heat-treated carbon fibers in H₂ and N₂.

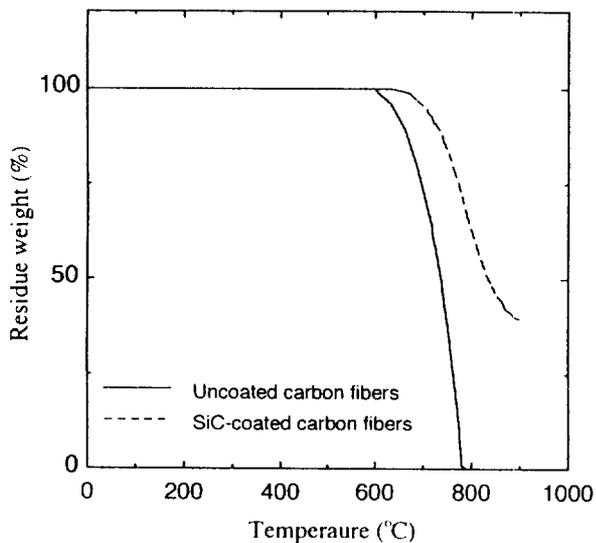


Fig. 5. TGA curves of the uncoated and the SiC-coated carbon fibers in flowing air.

ed fibers in hydrogen. From the results described above, we derived the conclusion that the strength degradation of carbon fibers was resulted from deterioration of fibers and/or chemical attack of hydrogen on the surface of carbon fibers during the curing process in high temperatures.

2. Oxidation and Thermal Resistance of SiC-coated Carbon Fibers

As mentioned above, for application of carbon fiber reinforced composites at elevated temperatures, oxidation resistance of carbon fibers is a most critical factor. We examined oxidation and thermal resistance of the SiC-coated carbon fibers in air at high temperatures.

Fig. 5 shows the TGA curves of the coated and the uncoated carbon fibers (PAN) in flowing air, respectively. In the case of

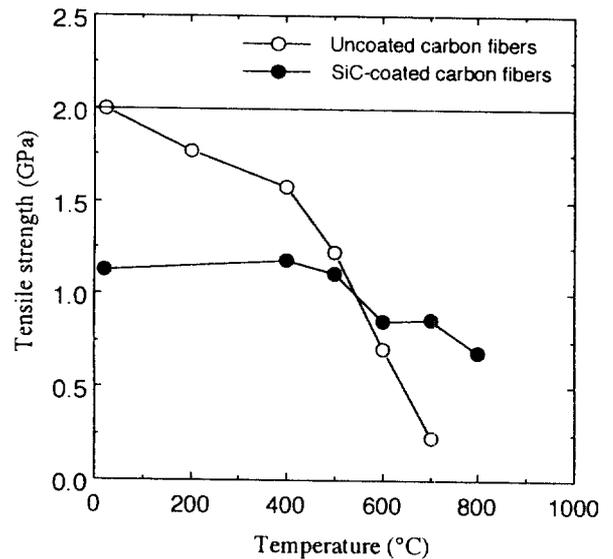


Fig. 6. Comparison of the tensile strength between the uncoated and the SiC-coated carbon fibers after air oxidation.

the uncoated carbon fibers, the weight loss started at a temperature of about 600°C and thereafter, the weight loss was quite sharp, consequently, 100% weight loss of the fibers occurred at 800°C. In other studies, Kobayashi et al. [1992] and Dhami et al. [1991] have reported that the weight loss of mesophase pitch based carbon fibers started at a temperature of about 400-500°C. On the other hand, the SiC-coated carbon fibers showed higher oxidation resistance; i.e., the weight loss started at 700°C but is gradually up to 800°C. Thereafter, the weight loss was also proceeded stiffly. However, the residual weight accounted for 40% of the original one.

Fig. 6 shows the strength of the uncoated and the SiC-coated carbon fibers which were oxidized at temperature of 400-800°C for 1 h in air circumstance. In the case of the uncoated carbon fibers, the rapid degradation of strength started from 400°C and at 700°C, the strength of fibers was decreased to 10% of the original value. In the case of the SiC-coated carbon fibers whose strength was reduced at the coating process, the degradation of strength started at 500°C and up to 800°C, the strength of fibers was decreased gradually to 60% of the original value. The improvement of oxidation resistance of the coated carbon fibers at temperatures of 500-800°C was observed, however, at temperature of 1000°C or higher, the coated carbon fibers also exhibited poor oxidation resistance. It could be mentioned that the oxidation resistance of the SiC-coated carbon fibers was more specific at the temperature range of 600-800°C.

To verify an oxidation behavior of the carbon fibers, the morphological change by air oxidation at high temperatures was investigated using SEM. Fig. 7 and 8 showed SEM micrographs of the oxidized carbon fibers for 1 h. In the case of the uncoated carbon fibers (Fig. 7), after oxidation, striations appeared on the fiber surface at 400°C and pits appeared above 500°C. The number and size of pits increased as the temperature increased, and then 30-40% of carbon fibers burned off subsequently. In the case of the SiC-coated carbon fibers (Fig. 8), the cracked coating surface appeared at 500°C, and oxidation at the cracked point was progressed at higher temperatures of 700°C. After the oxidation, only the coated part was remained at 800°C. These SEMs clearly show-

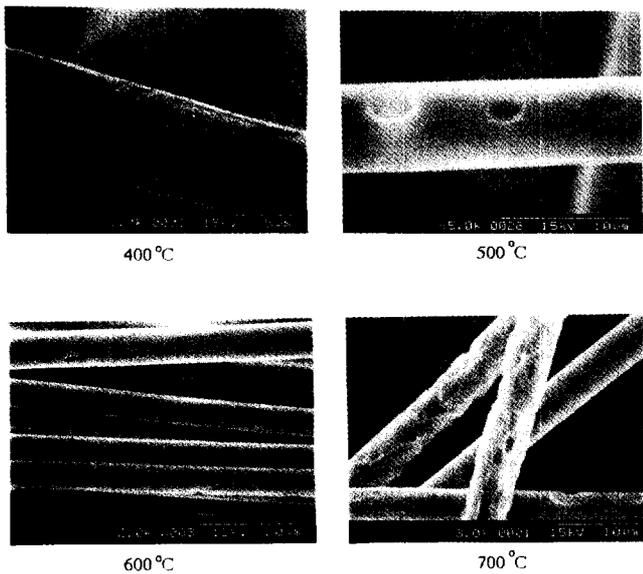


Fig. 7. Changes in oxidation morphology of carbon fibers in response to oxidation temperatures.

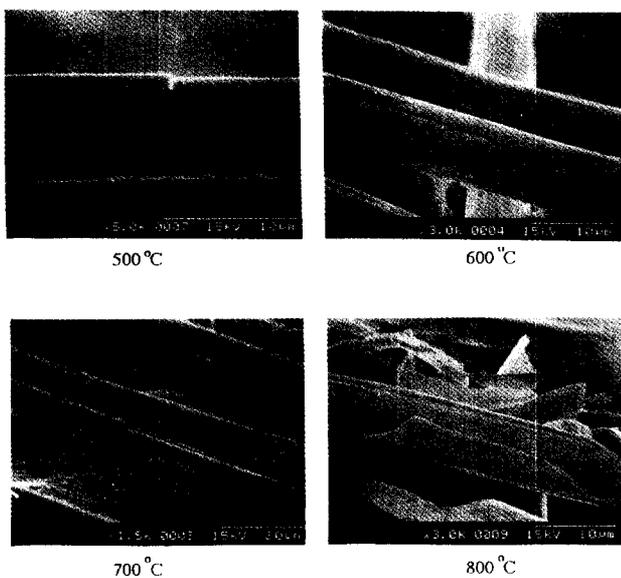


Fig. 8. Changes in oxidation morphology of the SiC-coated carbon fibers in response to oxidation temperatures.

ed that the oxidation proceeded from outer to inward surface.

The thermal resistance of the coated carbon fiber in an inert gas (N_2) was investigated by comparing the strength of the coated fibers with that of the uncoated fibers after heat treatment at high temperatures of 800-1200°C. As shown in Fig. 9, the strength of the uncoated carbon fiber was decreased sharply from 800°C and 75% of the original strength was lost at 1200°C. On the other hand, the SiC-coated carbon fibers maintained 40% of the original strength constantly at 800-1200°C and, particularly, showed much higher strength than that of the uncoated carbon fibers at 1000-1200°C.

Consequently, although the strength of carbon fibers was decreased after SiC-coating as shown in Fig. 3, the improvement

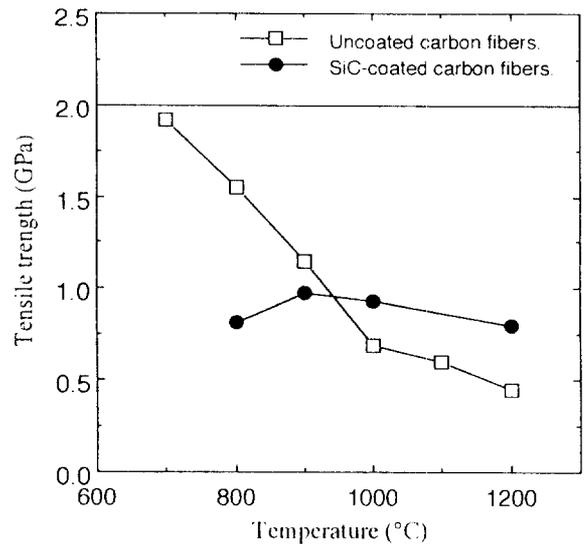


Fig. 9. Comparison of the tensile strength between the uncoated and the SiC-coated carbon fibers after heat treatment in N_2 .

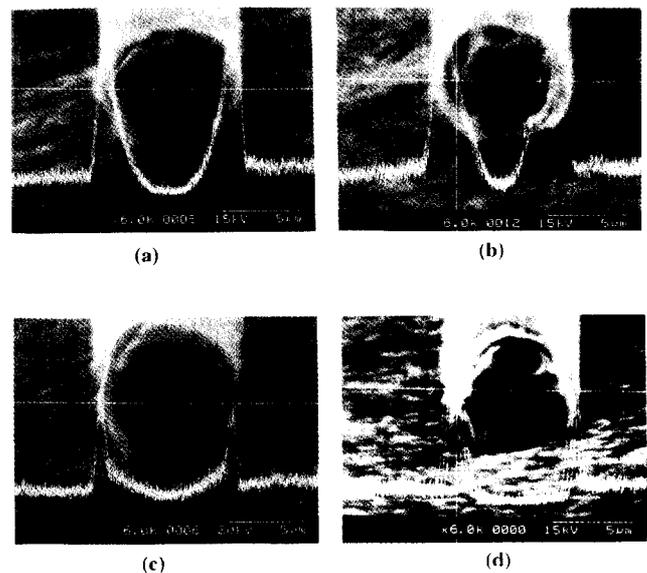


Fig. 10. SEM-EDX analysis of Al in heat-treated CFRAl composites.

- 20 hr heat-treated CFRAl without SiC interface.
- 40 hr heat-treated CFRAl without SiC interface.
- 20 hr heat-treated CFRAl with SiC interface.
- 40 hr heat-treated CFRAl with SiC interface.

of oxidation and thermal resistance of the SiC-coated carbon fibers in the range of high temperatures was observed.

3. SiC-coated Film as Reaction Barrier

To investigate the role of SiC-coated film as a barrier of reaction between carbon fibers and aluminum, the prepared carbon fiber reinforced aluminum (CFRAI) was heat-treated at 1000°C for 20 and 40 hrs. Fig. 10 shows shifting of Al-peak in the heat-treated CFRAl by Al line analysis using SEM-EDX. In CFRAl without SiC-coated film [Fig. 10(a), (b)] the shift of Al-peak toward carbon fiber was increased with the heat-treating time and

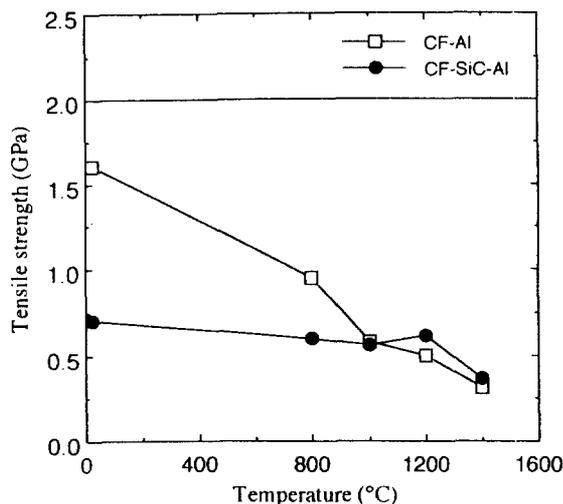


Fig. 11. Effect of SiC-coating on the tensile strength of heat treated CFRAl in N_2 . (CF-Al: CFRAl without SiC interface, CF-SiC-Al: CFRAl with SiC interface)

presumed that there would be an interfacial reaction between aluminum and carbon fibers. Diffusion rate of Al toward carbon fiber at 1000°C measured from SEM micrograph of Fig. 10 was found as 0.039 $\mu\text{m/hr}$. In CFRAl with SiC-coated film [Fig. 10(c), (d)] the shift of Al-peak was not appeared and presumed that the SiC-coated film acted as a reaction barrier in the interface of CFRAl.

Fig. 11 shows the strength of the heat-treated CFRAl at 800–1400°C in nitrogen atmosphere. After Al-coating, the strength of both CFRAl with and without SiC-coated film was decreased due to the low strength of Al (0.25 GPa) compared with that of carbon fibers (2.0 GPa) and was also decreased as increasing heating temperature. While the strength of the CFRAl without SiC-coated film was decreased sharply to 1200°C and 30% of the CFRAl in room temperature, the CFRAl with SiC-coated film maintained the strength in room temperature constantly at 1200°C. If it is possible to improve the strength of the SiC-coated carbon fibers, the CFRAl with SiC-coated film will be used at high temperatures effectively. Since the degradation of the CFRAl with SiC-coated film was slower than that of without SiC-coated film, the strength of SiC-coated carbon fibers should be improved to produce better properties of CFRAl at high temperatures.

CONCLUSION

The strength of the SiC-coated carbon fibers by CVD was decreased due to deterioration of fibers and chemical attack of hydrogen on the surface of carbon fibers during the curing process at given temperatures.

However, the improvement of oxidation and thermal resistance of the SiC-coated carbon fibers at high temperatures were observed by comparing the strength of the SiC-coated carbon fibers with those of the uncoated carbon fibers. From the morphological investigation of the oxidized carbon fibers, it was found that the oxidation of the SiC-coated carbon fibers started from the cracked point of the coated surface and after the oxidation of carbon fibers, the SiC-coated part remained. The SiC-coated film on carbon fiber reinforced aluminum was found sufficient as a barrier of reaction

between carbon fiber and aluminum at high temperatures.

The improvement of the strength of the SiC-coated carbon fibers is required to enhance the oxidation and thermal resistance at high temperatures.

REFERENCES

- Aggour, L., Fitzer, E., Heym, M. and Ignatowicz, E., "Thin Coatings on Carbon Fibers as Diffusion Barriers and Wetting Agents in Al Composites", *Thin Solid Films*, **40**, 97 (1977).
- Baker, S. J. and Bonfield, W., "Fracture of Aluminum-Coated Carbon Fibers", *J. Mater. Sci.*, **13**(6), 1329 (1978).
- Bunsell, A. R., "Fiber Reinforcements for Composite Materials", Composite Materials Series Vol. 2, Elsevier Science Publishers in Netherlands (1988).
- Canmer, D. C., "Fiber Coating and Characterization", *Am. Ceram. Soc. Bull.*, **68**(2), 415 (1989).
- Chin, J., Gantzel, P. K. and Hudson, R. G., "The Structure of Chemical Vapour Deposited Silicon Carbide", *Thin Solid Films*, **40**, 57 (1977).
- Dhami, T. L., Manocha, L. M. and Bahl, O. P., "Oxidation Behaviour of Pitch Based Carbon Fibers", *Carbon*, **29**(1), 51 (1991).
- Guiden, T. D., "Deposition and Microstructure of Vapor-Deposited Silicon Carbide", *J. Am. Ceram. Soc.*, **51**(8), 424 (1968).
- Jones, L. E. and Thrower, P. A., "Influence of Boron on Carbon Fiber Microstructure, Physical Properties, and Oxidation Behavior", *Carbon*, **29**(2), 251 (1991).
- Kobayashi, K., Funabashi, H. and Uchiyama, Y., "Morphological Change of Mesophase Pitch-Based Carbon Fiber by Air Oxidation at High Temperature", *TANSO*, **151**, 27 (1992).
- Kohara, S. and Nuto, N., "Compatibility of SiC-Coated Carbon Fiber with Aluminum", *J. Japan Inst. Metals*, **44**(4), 271 (1980).
- Kohara, S., Nuto, N. and Imanishi, Y., "TiC Coating on Carbon Fiber and the Compatibility of TiC Coated Carbon Fiber with Aluminum", *J. Japan Inst. Metals*, **43**(7), 589 (1979).
- Leonhardt, G., Kieselstein, E., Podlesak, H., Than, E. and Hofmann, A., "Interface Problem in Aluminum Matrix Composites Reinforced with Coated Carbon Fibers", *Mater. Sci. Eng.*, **A135**, 157 (1991).
- Masato, K., "Silicon Carbide Coatings on Carbon Fibers", *J. Japan Inst. Metals*, **42**(2), 131 (1978).
- Muench, W. V. and Pfaffeneder, I., "Epitaxial Deposition of Silicon Carbide from Silicon Tetrachloride and Hexane", *Thin Solid Films*, **31**, 39 (1976).
- Noone, N. J. and Roberts, J. P., "Pyrolytic Deposites of Silicon Carbide", *Nature*, **212**, 71 (1966).
- Pitkethly, M. J., Doble, J. B. and Jacques, P., "Interfacial Shear Strength Evaluation of Ceramic-Coated Carbon Fiber", *J. Mater. Sci. Lett.*, **12**(18), 1439 (1993).
- Scholz, M., Fub, W. and Kompa, K. L., "Chemical Vapour Deposition of Silicon Carbide Powders Using Pulsed CO_2 Lasers", *Adv. Mater.*, **5**(1), 38 (1993).
- Stumm, T., Fitzer, E. and Wahi, G., "Chemical Vapour Deposition of Very Thin Coatings on Carbon Fiber Bundles", *J. Phys. III France*, **2**(8), 1413 (1992).
- Warren, R., Anderson, C. H. and Carlsson, M., "High-Temperature Compatibility of Carbon Fibers with Nickels", *J. Mater. Sci.*, **13**(1), 178 (1978).
- Yamamoto, O., Sasamoto, T. and Inagaki, N., "Coating of SiC-Gradient Carbon Material with Mullite Film and its Oxidation Resistance", *J. Ceram. Soc. Japan*, **102**(2), 165 (1994).