UDC 661 . 666 - 487

Pitch-Based Carbon Fiber with Low Modulus and High Heat Conduction

Yutaka ARAI*1

Abstract

Quite a wide variety of properties can be given to pitch-based carbon fiber by controlling its graphite crystal. Herein introduced are characteristics and applications of the low modulus carbon fiber and the high modulus, high heat conduction carbon fiber, both of which could not be produced from the PAN carbon fiber. These new fiber products manufactured and marketed by Nippon Graphite Fiber have unique characteristics hitherto unseen in other materials.

1. Introduction

Carbon fiber is defined as a fiber substantially composed of the element carbon only. Application of carbon fiber has grown remarkably over the last 10 years. Its application covers widely varied industrial products in which light weight and high strength of the material form significant advantages, for example: daily utensils such as sporting goods (golf club shafts, fishing rods), mobile computers; high speed moving bodies such as aircraft, rockets, racing cars; and space satellite components. Its use has been recently expanded further to things such as: high speed industrial rolls; repairing materials for civil construction; large structures such as light weight truss members for buildings, bridge cables, etc.; and functional materials for lithium ion rechargeable batteries; and so forth.

The carbon fiber is classified in terms of raw material, product shape, material properties and other criteria. By the raw material, it is classified into the PAN-based carbon fiber made from polyacrylonitrile (PAN) and the pitch-based carbon fiber made from pitch of petroleum or coal tar and, by the shape of the fiber, it is classified into the continuous fiber shipped from a producers in the form of continuous filaments wound on spools and the short fiber shipped as cut after being treated in the form of tows or mats.

Whereas most of the PAN-based carbon fiber has a modulus of 230 GPa or so and its highest modulus available in the market is about 600 GPa, the commercially marketed pitch-based carbon fibers have modulus of 50 to 950 GPa. Thus, properties of the carbon fiber are widely varied depending on the raw material. The classification by the shape of the fiber, on the other hand, comes from the difference in manufacturing processes. A good part of the pitch-based carbon fiber is produced in the form of the short fiber, because it is more difficult to spin into threads than the PAN-based carbon fiber, and application of the pitch-based short carbon fiber is limited owing to the shape. The short carbon fiber is, however, suitable for mass production at low costs and has a firmly established market of its own as industrial materials.

The Nippon Steel group began researches into the pitch-based carbon fiber made from coal tar in the early 1980s and established Nippon Graphite Fiber Co. (hereinafter NGF), a specialist producer of the pitch-based continuous carbon fiber, in 1995 jointly with then Nippon Oil Company (now Nippon Mitsubishi Oil Corporation).

This paper introduces characteristics, advantages and development of applications of the pitch-based carbon fiber mainly focusing on NGF's pitch-based carbon fiber products.

2. Structure of Pitch-based Carbon Fiber

Fig. 1[1] shows the relation between modulus and tensile strength of the PAN-based carbon fiber and NGF's pitch-based carbon fiber. Whereas the PAN-based carbon fiber is available in the market in a range of strengthes up to 7,000 MPa and the range of modulus up to 600 GPa, mainly in the modulus grade of 230 GPa, the pitch-based carbon fiber has a wider modulus range from 50 to 950 GPa, as explained above.

When observed using a polarized light microscope, the raw material pitch for producing the pitch-based carbon fiber is classified into isotropic pitch, which does not exhibit liquid crystal properties (looking as shown in **Fig. 2** (a)), and mesophase pitch, which does exhibit the liquid crystal properties (as shown in Figs. 2 (c) and (d)).

*1 Nippon Graphite Fiber Corporation

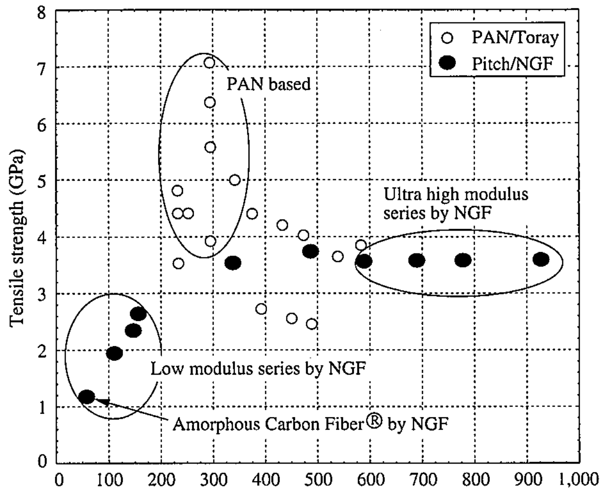


Fig. 1 Relation between modulus and tensile strength of carbon fibers

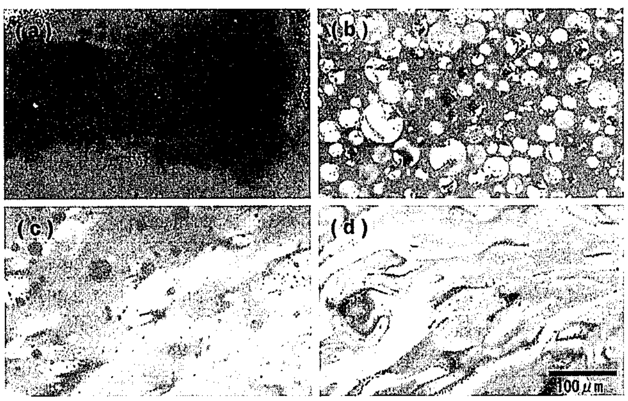


Fig. 2 Polarized light Micrographs of pitches
(a) Isotropic pitch, (b) Mesophase spheres in isotropic pitch
(c), (d) Mesophase (Anisotropic) pitch

When high polymer liquid crystal pitch, called the mesophase pitch, undergoes a melt spinning process, molecules of the high polymer liquid crystal are oriented when passing through a thin tube nozzle, forming tabular aromatic polymers aligned in the longitudinal direction[2]. A carbon fiber in which graphite layer planes are oriented in the longitudinal direction as shown in **Fig. 3**[3] is obtained through heat treatments for infusibilization, carbonization, etc. of the tabular aromatic polymers thus produced.

The graphite crystal has extremely high strength and rigidity in the direction of graphite layer plane (called "a" direction) as shown in **Fig. 4**[4] thanks to strong double bonds between carbon atoms. It is this structure that gives the strength and lightweight to the carbon fiber. The graphite crystal is characterized in that it has a negative thermal expansion coefficient near the room temperature and very high heat conductivity in the "a" direction. These characteristics are common to the high modulus pitch-based carbon fibers having well developed graphite crystals.

In contrast, when the isotropic pitch not showing the liquid crystal properties is used as the raw material, the fiber has neither the orientation of the graphite crystals in the longitudinal direction nor the developed graphite crystals described above. Consequently, the product fiber is quite different from ordinary carbon fibers: its modulus, strength and heat conductivity are low, and the thermal expansion coefficient is positive. The structure of the fiber made from the isotropic pitch is, as shown in **Fig. 5** (a) in a lattice image through an electron microscope, a random structure, unlike that of the fiber made from the mesophase pitch wherein the graphite crystals are regularly aligned longitudinally as shown in Fig. 5(b). As explained above, quite a wide variety of characteristics not seen with other materials can be given to the pitch-based carbon fiber by use of different kinds of raw material pitch or by controlling the graphite crystal growth during the fiber manufacturing process.

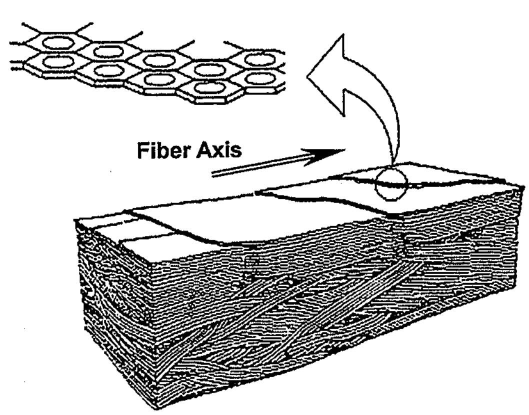


Fig. 3 Structure model of carbon fiber

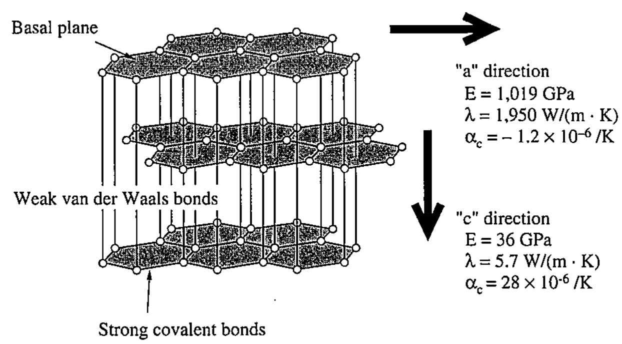
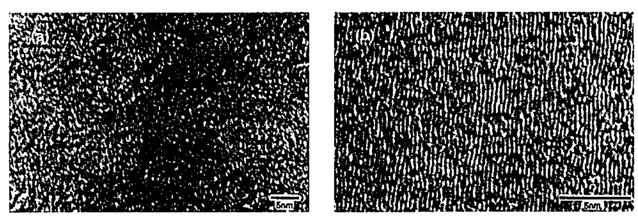


Fig. 4 Graphite crystal structure



(a) XN-05 (Amorphous Carbon Fiber®) **(b) XN-40 (high modulus pitch-based carbon fiber)**

Fig. 5 Lattice-fringe image of longitudinal section of GRANOC fibers

3. Low Modulus Carbon Fiber

In this section the characteristics and applications of low modulus carbon fiber with controlled graphite crystal growth are described.

Material properties of the low modulus carbon fiber products of NGF are listed in **Table 1**[5]. What is characteristic of the low modu-

Table 1 Properties of low modulus carbon fiber and other reinforcing fibers

Fiber designation				GRANOC XN-05	GRANOC XN-10	GRANOC XN-15	PAN-CF (230GPa)	Fiberglass (T-glass)	Kevlar 49
Fiber properties		Tensile strength	(MPa)	1,180	1,750	2,500	4,900	4,600	3,400
		Tensile modulus	(GPa)	55	106	155	230	83	130
		Elongation	(%)	2.0	1.7	1.6	2.1	5.5	-
		Density	(g/cm³)	1.65	1.70	1.85	1.8	2.49	-
		Electrical resistivity	(10^{-6}Ωm)	28	110	20	16	-	-
		Thermal conductivity	(W/(m·K))	5	-	6	9	-	-
		CTE	(10^{-6}/K)	+ 3.4	− 0.1	− 0.8	− 0.4	+ 2.7	-
Composites properties	Tensile	Strength	(MPa)	640	980	1,460	2,800	1,900	1,380
		Modulus	(GPa)	34	64	92	137	49	76
		Strain to failure	(%)	1.8	1.5	1.4	1.8	3.9	-
	Compression	Strength	(MPa)	870	1,070	1,150	1,400	970	276
		Modulus	(GPa)	32	64	85	129	55	-
		Strain to failure	(%)	2.9	2.1	1.8	1.4	1.8	-
	Comp. strength/tensile strength raito			1.36	1.09	0.79	0.50	0.51	0.20
	Matrix resin			130°C epoxy					unknown

lus carbon fiber is that the tensile strength and the compressive strength are better balanced than other reinforcing fiber materials. Some useful applications have been developed taking advantage especially of the large fracture strain under compression.

A series of tests were carried out on composite specimens made of a low modulus carbon fiber (XN-05 of NGF) and a PAN-based high strength carbon fiber (T700S of Toray), using an instrumented Charpy impact machine shown in **Fig. 6**. The result is that, as seen in **Table 2** and **Fig. 7**, the specimens in which the low modulus carbon fiber was used on the compression side demonstrated fracture initiation energy more than twice that of the blank specimen[6, 7]. When applied, for example, to a golf club shaft structured as shown in **Fig. 8**, the low modulus carbon fiber remarkably enhances the flexural strength, fracture initiation energy and fracture displacement of a pipe[7] as shown in **Fig. 9**. Application of these effects to the head end

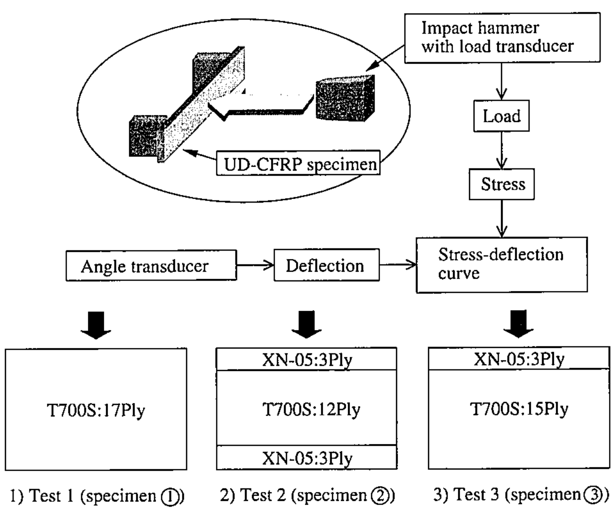


Fig. 6 Charpy impact machine and specimens

Table 2 Results of Charpy impact tests

		T700S (Specimen①)	T700S/ XN-05 (Specimen②)	T700S/ XN-05 (Specimen③)
		Test-1	Test-2	Test-3
Flexural strength	(MPa)	1,697	1,663	2,303
Relative Flexural strength	(–)	1.00	0.98	1.36
Flexural modulus	(GPa)	111	63	91
Fractures deflection	(mm)	5.3	10.1	9.8
U1	(kJ/m²)	107	217	250
Relative U1	(–)	1.00	2.02	2.34
U2	(kJ/m²)	50	433	19
U3	(kJ/m²)	157	650	269

Note 1) Flexural properties were measured in Charpy impact tests
Note 2) U1: Fracture initiation energy, U2: Fracture propagation energy, U3: Absorbed impact energy
Note 3) Fiber volume of CFRP was normalized to 60%

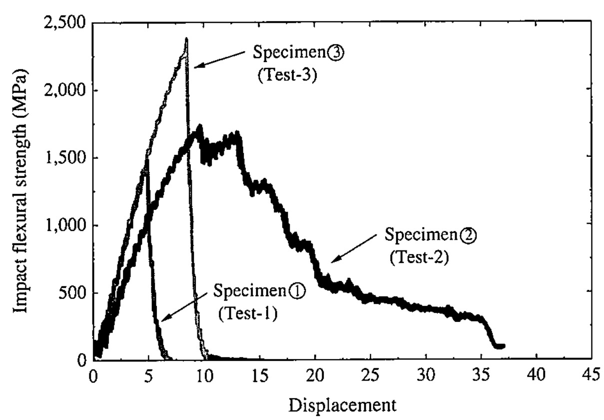


Fig. 7 Stress-displacement curves of CFRP in the Charpy tests

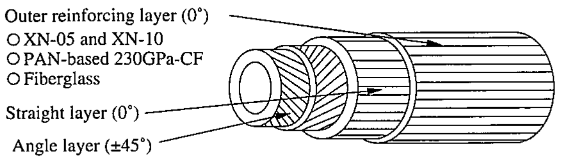


Fig. 8 Stacking sequence of hybrid pipe

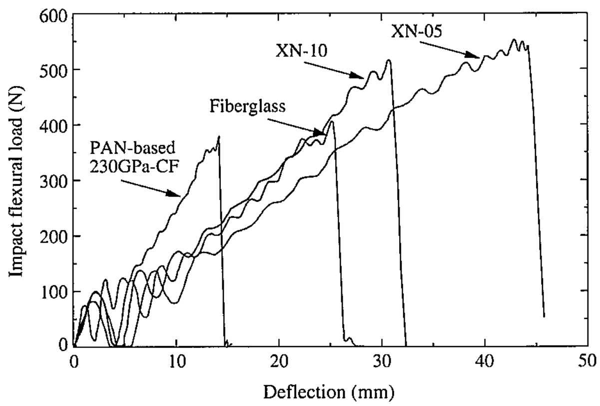


Fig. 9 Impact flexural load-deflection of hybrid pipes

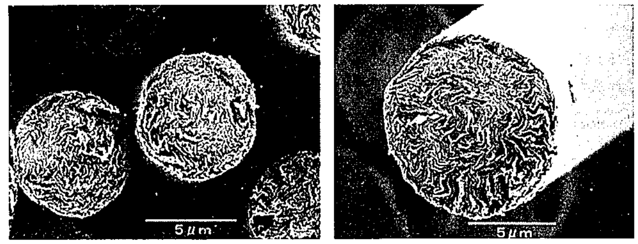
of a golf club shaft made it possible to design light weight and high strength shafts having a flexible head end portion, and many golf clubs having a good feeling of impact and are capable of hitting long distances have been sold. This reinforcing effect is expected to be applicable not limited merely to the golf club shafts but to other widely varied fields of industry such as aerospace industry where a high weight/strength ratio is especially important.

The XN-05 is unique among low modulus carbon fiber products in that it is the only carbon fiber product having a positive thermal expansion coefficient and that its modulus, thermal conductivity and other properties are little affected by a heat treatment at 3,000°C or so, even when a heat treatment is required at a subsequent process like in the case of C/C composites. For this reason, new applications of the product are expected to come out, such as a thermal expansion compensation material or a material for the C/C composites.

4. High Modulus, High Thermal Conductivity Carbon Fiber

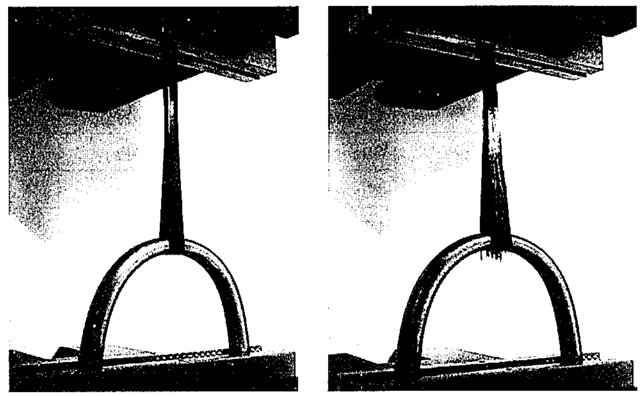
The pitch-based carbon fiber having graphite crystals developed along the fiber axis has high thermal conductivity and modulus in the longitudinal direction. A thermal conductivity of 1,000 (W/m·K) or so, far higher than that of metals, is achievable and a modulus in the longitudinal direction of 950 GPa or so, nearly equal to the theoretical value, has actually been obtained. No other materials offer such extremely high thermal conductivity and modulus. On the other hand, the higher the modulus of the carbon fiber the smaller its elongation and, consequently, the more difficult its handling. Thus the high modulus, high thermal conductivity carbon fiber is difficult to form and, therefore, its excellent performance may not be fully realized in actual applications.

As a measure to alleviate the problem, NGF makes the fiber diameter smaller. Whereas conventional pitch-based carbon fiber has a diameter of 10 μm, NGF's high modulus carbon fiber has a diameter of 7 μm as shown in **Fig. 10**. Excellent handling performance of NGF's products is clearly seen in **Fig. 11** where one of the NGF's



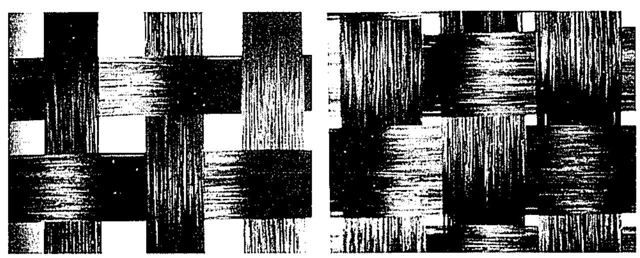
1) NGF's YS-tyeo fiber: 7-μm diameter **2) Conventional fiber: 10-μm diameter**

Fig. 10 Sectional views of NGF's YS-type fiber and conventional fiber



1) YS-90A (load: 98 N) **2) Conventional high modulus carbon fiber (load: 0.98 N)**

Fig. 11 Clip test (clip diameter: 4 mm)



1) Before spreading **2) After spreading**

Fig. 12 Spread fabric of high modulus carbon fiber

products is compared with a conventional material in a clip test[8]. The improvement in handling made it possible to weave the carbon fiber into various kinds of fabric. **Fig. 12** shows a lightweight fabric called spread fabric. Fabrics of a 900-GPa class modulus and 500 and 600 W/(m·K) of thermal conductivity have been developed[9]. NGF's high modulus grade carbon fiber products and their fabrics are listed in **Tables 3** and **4**.

Besides the conventional applications where the advantage of material rigidity is made use of, these high modulus fibers and fabrics have been applied to space satellite components such as antenna reflectors, solar panels and heat radiation structural surfaces for electronic equipment, etc. thanks to the high thermal conductivity and the fact that it is possible to realize zero thermal expansion. By use of the CFRP composite materials with the pitch-based carbon fiber replacing aluminum alloys, performance of the space satellite devices is improved and precision of communication and space/global observation is enhanced[10].

Table 3 Properties of NGF high modulus carbon fibers and composite laminates

				YS-95A	YS-90A	YS-80A	YSH-70A	YSH-60A	YSH-50A
Fiber properties		Tensile strength	(MPa)	3,530	3,530	3,630	3,630	3,830	3,830
		Tensile modulus	(GPa)	920	880	785	720	630	520
		Elongation	(%)	0.3	0.3	0.5	0.5	0.6	0.7
		Density	(g/cm^3)	2.20	2.19	2.17	2.14	2.12	2.10
		Filaments per yarn		1.5K/3K/6K	1.5K/3K/6K	1K/3K/6K	1K/3K/6K	1K/3K/6K	1K/3K/6K
		Yield	(g/km)	125/250/520	125/250/520	75/250/520	75/250/520	75/250/520	75/250/520
		Electrical resistivity	($10^{-6}\Omega m$)	2.3	2.7	5	5	6	7
		Thermal conductivity	(W/(m·K))	600	500	320	250	180	120
		CTE	(10^{-6}/K)	– 1.5	– 1.5	– 1.5	– 1.5	– 1.4	– 1.4
Composite laminate properties	0 deg tensile	Strength	(MPa)	1,900	1,900	1,960	1,960	2,150	2,150
		Modulus	(GPa)	540	520	470	430	380	310
		Ultimate elongation	(%)	0.3	0.3	0.3	0.4	0.5	0.6
	90 deg tensile	Strength	(MPa)	25	25	25	37	37	43
		Modulus	(GPa)	5.5	5.6	5.9	6.2	6.5	3.8
		Ultimate elongation	(%)	0.5	0.5	0.5	0.6	0.6	0.6
	0 deg flexural	Strength	(MPa)	640	640	640	720	770	920
		Modulus	(GPa)	460	440	390	360	320	245
	0 deg compression	Strength	(MPa)	340	360	380	460	490	530
		Modulus	(GPa)	540	520	460	410	350	260
	In-plane shear modulus		(GPa)	5.1	5.1	5.0	5.0	4.9	4.8
	ILSS		(MPa)	60	60	64	68	70	85

Table 4 NGF's high modulus carbon fiber fabrics

Grade	Product	FAW (g/m^2)	Count (Yarn/1-inch)	Yarn	Remark
520GPa	SF-YSH50A-75	75	12.5/12.5	YSH-50A-10S(1K)	Plain fabric with spreading
	5HS-YSH50A-110	110	18.5/18.5	YSH-50A-30S(3K)	5-harness stain weave
	5HS-YSH50A-140	140	23.5/23.5	YSH-50A-10S(1K)	5-harness stain weave
	PF(S)-YSH50A-200	200	10/10	YSH-50A-30S(3K)	Plain fabric with mild spreading
700GPa	SF-YSH70A-75	75	12.5/12.5	YSH-70A-10S(1K)	Plain fabric with spreading
	PF(S)-YSH70A-75	75	12.5/12.5	YSH-70A-10S(1K)	Plain fabric with mild spreading
	PF-YSH70A-100	100	16.5/16.5	YSH-70A-10S(1K)	Plain fabric
	5HS-YSH70A-140	140	23.5/23.5	YSH-70A-10S(1K)	5-harness stain weave
	5HS-YSH70A-300	300	15/15	YSH-70A-30S(3K)	5-harness stain weave
800GPa	SF-YS80A-75	75	12.5/12.5	YS-80A-10S(1K)	Plain fabric with spreading
500W/(m·K) (900GPa)	SF-YS90A-100	100	10/10	YS-90A-15S(1.5K)	Plain fabric with spreading
	SF-YS90A-125	125	6.25/6.25	YS-90A-30S(3K)	Plain fabric with spreading
	SF(4HS)-YS-90A-200	200	10/10	YS-90A-30S(3K)	4-harness stain weave with spreading
600W/(m·K)	SF-YS95-100	100	10/10	YS-95A-15S(1.5K)	Plain fabric with spreading

Application of the pitch-based carbon fiber will expand in the fields where thermal conductivity is significant, such as heat radiators and diffusers for electronic devices, heat spreaders for superconductor magnets, furnace wall material for nuclear reactors, etc. thanks to its higher thermal conductivity and smaller specific gravity than metals.

5. Closing

It has been nearly 20 years since development of the high performance pitch-based carbon fiber was initiated. Still new carbon fiber products are being developed and introduced to the market from time to time, which fact shows that the pitch-based carbon fiber is a very attracting and unfathomable material. Its application has been dramatically expanded over the last few years. In view of its material properties surpassing the performance extremes of many other materials as described herein, Nippon Graphite Fiber is sure of further expansion of its application and willing to continue supplying materials satisfying users' requirements.

References

1) Carbon Fiber Society of Japan: Carbon Fiber–Characteristics and Handling. revised edition. Tokyo, Carbon Fiber Society of Japan, 2000, p.7
2) Singer, L. S.: Carbon. 16 (6), 409 (1978)
3) Morita, K.: Carbon Fiber Industry. 1st Edition. Tokyo, Kindai Henshusha, 1984, p.6
4) Bertram, A., Beasley, K., Torre, W.: Naval Engineers J. 104 (3), 276 (1992)
5) Kiuch, N., Sohda,Y., Arai,Y., Ohno, H., Shima, M.: 45th International SAMPE Symposium, 2000-5, p.782-793
6) Kiuch, N., Sohda, Y., Takemura, S., Arai, Y., Ohno, H., Shima, M.: Proc. 6th Japan Int. SAMPE Symposium, 1999-10, p.133-136
7) Ohno, H., Shima, M., Takemura, S., Sohda, Y.: 44th International SAMPE Symposium, 1999, p.782-793
8) Kiuch, N., Ozawa, K., Komami, T., Katoh, O., Arai, Y., Watanabe, T., Iwai, S.: 30th SAMPE Technical Conference, 1998, p.68-77
9) Kihara, T., Kiuch, N., Komami, T., Katoh, O., Arai, Y., Nakamura, T., Watanabe, T., Ishikawa, G.: Proc. 6th Japan Int. SAMPE Symposium, 1999-10, p.1131-1134
10) Ozaki, T., Kabashima, S.: Mitsubishi Electric Technical Report. 73 (2), 151 (1999)