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High-Modulus Pitch-Based Graphite Fibers for Civil Engineering and Architectural Applications

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Abstract:

Carbon fibers have been traditionally used as functional and structural materials, mainly in the aerospace and recreational sports fields. In more recent years, many new applications for carbon fibers have been introduced in the civil engineering and architectural areas. Carbon fibers are classified into the PAN and pitch types according to their raw materials. We describe here the general characteristics of high-modulus pitch-based graphite fibers developed by Nippon Steel and the application of these fibers in the civil engineering and architectural sectors.

1. Introduction

Today, lightweight, high-strength, and high-modulus carbon fibers are used as reinforcing materials for advanced composites carbon fibers with a minimum tensile modulus of 200 GPa and a minimum tensile strength of 2 to 6 GPa, the so-called high-performance carbon fibers, i.e., are produced from PAN (polyacrylonitrile) or mesophase pitch precursors.

Union Carbide Corporation (UCC) of the United States first began the commercial production of carbon fibers using rayon as a precursor in 1959. Just as today, PAN-based carbon fibers were then actively commercialized in Britain, the United States, Japan, and other countries. In 1969, Japan's Kureha Chemical Industry succeeded in the production of the first isotropic pitch-based carbon fibers. Based on the research of Otani[1], UCC commercially made high-performance pitch-based carbon fibers from the mesophase pitch precursor in 1975[2,3]. UCC's mesophase pitch-based carbon fibers had a tensile strength of only about 2 GPa and found limited uses. Subsequent developments have made it possible to produce carbon fibers with far higher tensile strengths and moduli. Carbon fibers have been traditionally used as functional and structural materials, mainly in the aerospace and recreational sports areas.

For the post decade, Nippon Steel has been researching and developing mesophase pitch-based carbon fibers and their application technologies. In April 1995, Nippon Steel founded Nippon Graphite Fibers Corp. jointly with Nippon Oil.

This article gives an overview of the mesophase pitch-based carbon fibers developed by Nippon Steel and describes the application of these fibers in the areas where their excellent properties can be utilized most effectively; namely, the building engineering and building construction industries.

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2. Production Process of High-Modulus Pitch-Based Carbon Fibers and Properties of Composite Materials Made from Them

2.1 Production process of high-modulus pitch-based carbon fibers[4)]

Pitch-based carbon fibers are produced by the process shown in **Fig. 1**. Pitch is reformed from coal tar or petroleum residue and melt spun into precursor fibers (pitch fibers) measuring from a few micrometers to about 10 μm in diameter. The precursor fibers are gas-phase oxidized to thermoset and stabilize them. Subsequent carbonization and graphitization drive elements other than carbon out of the fibers and accelerate the growth of graphite crystals. This imparts the high modulus required of carbon fibers. The product is finally given several surface treatments to improve compatibility with the matrix when used in composite materials. **Table 1** lists the physical properties of commercial high-modulus pitch-based carbon fibers.

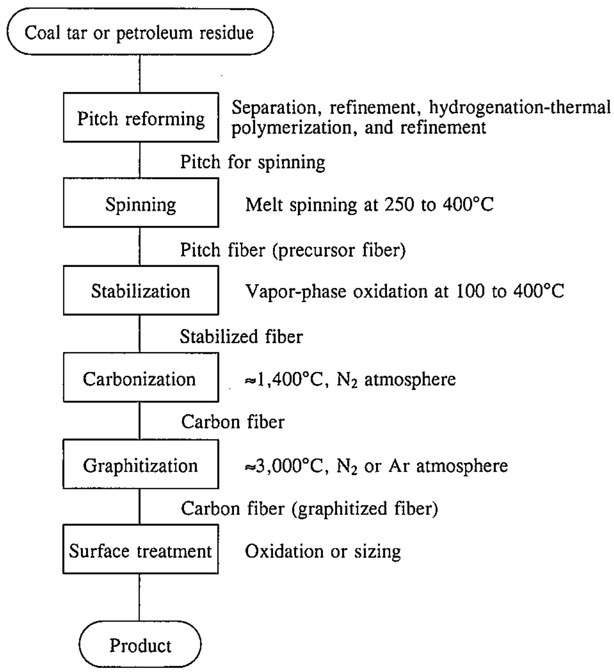


Fig. 1 Production process for pitch-based carbon fibers[4)]

Table 1 Physical properties of commercial high-modulus pitch-based carbon fibers

	Eskainos NU-80	Thornel P-120
Tensile modulus (GPa)	785	827
Tensile strength (GPa)	3.23	2.20
Density (kg/m³)	2,180	2,180
Graphite layer plane spacing d_{002} (nm)	0.3393	0.3374
Graphite layer lamination thickness L_c (nm)	21.8	28.6

2.2 Properties of composite materials made from pitch-based carbon fibers[5,6)]

Typical properties of composite materials (epoxy-based carbon-fiber-reinforced plastics, or CFRPs) made from carbon fiber reinforcement and epoxy resin matrix are given in **Table 2**. Nippon Steel's pitch-based carbon fibers are high not only in tensile modulus, but also in tensile strength, flexural strength, and interlaminar shear strength (ILSS).

3. Reinforcing Materials for Civil Engineering and Architectural Applications

One carbon-fiber-reinforced plastic (CFRP) application is carbon-fiber-reinforced concrete (CFRC) in the civil engineering and architectural areas. As shown in **Table 3**, CFRPs for CFRC are used in many forms. Nippon Steel has commercially produced one-dimensional CFRP strands and rods, and two-dimensional carbon fiber sheets and mesh-like fabrics. The CFRP strands, CFRP rods, and carbon fiber sheets are described below.

3.1 CFRP strands

3.1.1 Production process

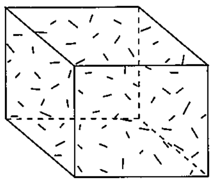
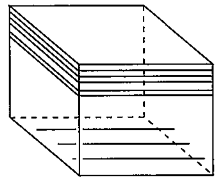
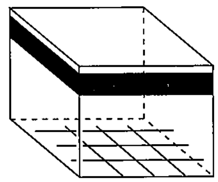
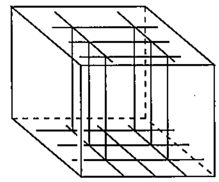
CFRP strands are produced by making filaments from carbon fibers and bundling the filaments together, as shown in **Fig. 2**. Filaments are formed by gathering about 6,000 to 12,000 high-modulus carbon fibers impregnated with an epoxy-based thermosetting resin and wrapped with a polymer braid as a skin. To form each strand, 7 to 37 filaments are bundled together while undergoing a heat treatment to set the resin. The strands are flexible enough to be wound on reels. Anchorages can be attached to

Table 2 Mechanical properties of carbon-fiber-reinforced epoxy composite materials[6)]

Fiber type		Manufacturer	0° tension		0° bending		0° compression		ILSS* (MPa)
			Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	
Pitch based	NT15	Nippon Steel	1,470	93.1	1,270	78.4	804	78.4	95.1
	NT20		1,960	118	1,670	108	696	108	100
	NT50		2,110	294	1,080	235	539	235	93.1
	NT60		2,060	353	931	284	490	294	93.1
	NT70		1,760	402	882	343	490	343	88.2
	NT80		1,670	451	784	392	441	392	78.4
PAN based	T300	Toray	1,760	132			1,570	127	108
	T800H		2,840	162			1,570	147	108
	T1000		3,530	157			1,570	147	98.0
	M50		1,180	265			784		
	M50J		1,960	260			882	245	78.4
	M60J		1,760	328			784	319	68.6
	LM16	Toho Rayon	1,550	90.2	1,380	87.2	1,260		

*ILSS: Interlaminar shear strength

Table 3 Application forms of carbon fibers as construction materials[6]

	Shape of carbon fiber			
	Short fiber	One-dimensional	Two-dimensional	Three-dimensional
Application form (image)	 • Usually, chopped fibers about 3 to 30 mm long	 • Long fibers (winding) • CFRP rods	 • Carbon fiber sheets • Mesh-like fabrics	 • Three-dimensional fabrics
Directionality of strength	• Equal strength in all directions in principle (isotropy)	• Reinforcement in one direction	• Reinforcement in two directions (anisotropy)	• Interlaminar reinforcement to improve delamination resistance
Flexural strength (mortar specimens)	• 45MPa (Vf5.3%)[7]		• 120MPa (Vf3.8%)[8]	• 160MPa (Vf3.8%)[8]
Application problem	• Properties of carbon fiber are put to use at low rate. • CFRC is difficult to mix and place.	• It takes time to arrange reinforcements. • It is necessary to improve bond strength.	• Interlaminar strength is low.	• Productivity is low.
Application example	• Large monument in Baghdad (Kajima Corp.) • Akasaka Ark Mori Building in Tokyo (Kajima Corp.)	• Aseismic reinforcement of chimney (Obayashi Corp./Mitsubishi Kasei Co.) • Pedestrian bridge in Funabashi, Chiba Prefecture (Kumagai Gumi Co./Nippon Concrete Ind.) • Shingu Bridge in Ishikawa Prefecture	• Thin out part of rebar of bridge piers (Taisei Corp./Tonen Corp.) • Shimizu Jisho Yokohama Building (Shimizu Corp.) • Free access floor panels (Kanebo Ltd./Nippon Steel Corp.)	• Tokyo Gas district cooling center building "Shinagawa Bay City Tower" (Kajima Corp./Arisawa Mfg. Co.)

Note: This table has been prepared using reference information from "World of Carbon Fibers" published by Japan Carbon Fiber Association and Table 5 in Kogyo Zairyo ("Industrial Materials" in Japanese), No. 13, 89 (1990).

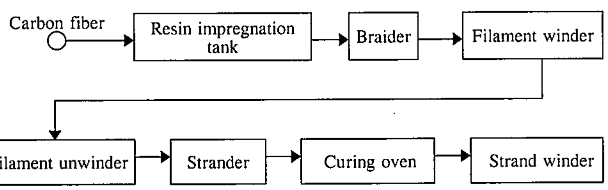


Fig. 2 Strand production process

the ends of the strands so that they can be joined with other structures.

3.1.2 Mechanical properties

General views of CFRP strands are shown in **Photo 1**, and their mechanical properties are summarized in **Table 4**.

The high-modulus CFRP strands have the following features:

(1) Their modulus is 150 to 210 GPa, equivalent to that of steel strands for prestressed concrete (PC).

(2) Their specific gravity is 1.7, about one-fifth of that of steel.

(3) They excel in acid and alkali resistance and have high corrosion resistance.

(4) They are nonmagnetic.

(5) They can be wound on reels.

(6) They can be easily cut for application in shield tunneling, as will be described later.

3.2 CFRP rods

3.2.1 Production process

CFRP rods are shown in **Photo 2**. They are produced by spiraling resin-impregnated carbon fibers around the surface of a core

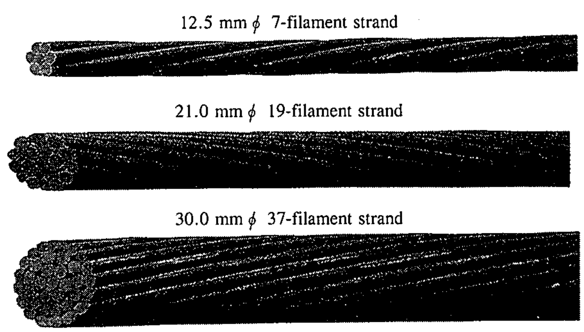


Photo 1 CFRP strands

Table 4 Mechanical properties of CFRP strands

Construction	Nominal diameter (mm)	Nominal cross-sectional area (mm²)	Guaranteed proof stress (kN)	Modulus (GPa)	Unit weight (g/m)
7 filaments	12.5	97.0	107.8	206	182
19 filaments	21.0	263.2	225.4	167	495
37 filaments	30.0	538.3	426.3	147	1,010

Values of mechanical properties other than proof stress are for reference only.

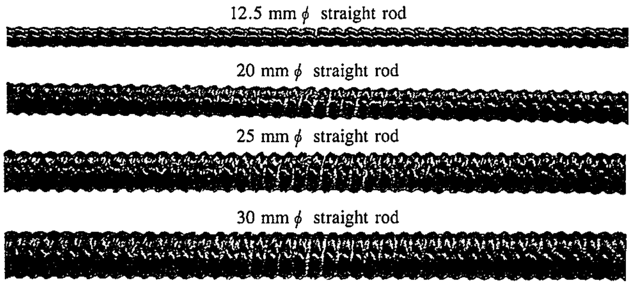


Photo 2 CFRP rods

Table 5. Specifications of CFRP rods

Size (mm φ)	Nominal diameter (mm)	Nominal cross-sectional area (mm²)	Guaranteed tensile strength (kN)	Tensile modulus (GPa)	Unit weight (g/m)
12.5	12.5	122.7	117.6	196	260
17.0	17.0	227.0	205.8	196	431
20.0	20.0	314.2	274.4	186	575
25.0	25.0	490.9	401.8	186	865
30.0	30.0	706.9	548.8	186	1,219

Values other than proof stress are for reference only.

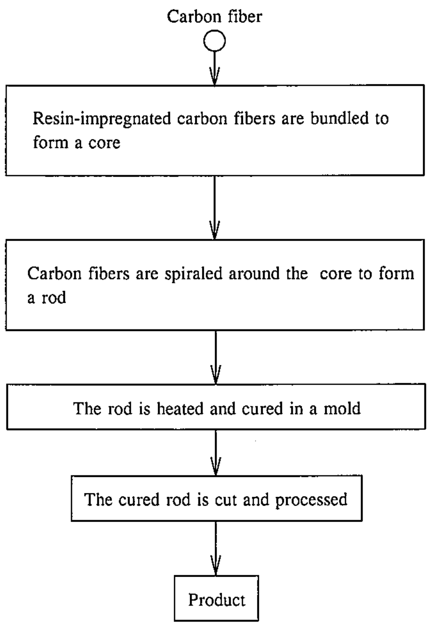


Fig. 3 Production process for CFRP rods

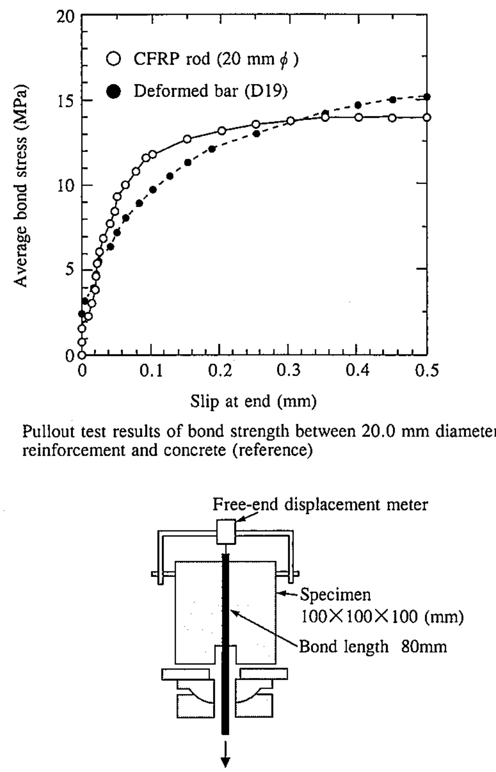


Fig. 4 Pullout test of bond strength between reinforcement and concrete

made from a composite of high-modulus pitch-based carbon fibers and epoxy-based thermosetting resin, and then curing and forming the assembly (see **Fig. 3**).

3.2.2 Mechanical properties

The specifications of CFRP rods are given in **Table 5**. High-modulus CFRP rods share the first four properties of CFRP strands noted in 3.1.2. Since CFRP rods have more carbon fibers arranged in the longitudinal direction than CFRP strands, their strength is higher for the same cross-sectional area (outside diameter). The bond strength between CFRP rods and concrete is also high.

The results of pullout bond strength tests on CFRP rods and deformed steel reinforcing bars of almost the same diameter are shown in **Fig. 4**. The CFRP rods have a bond strength equal or superior to that of the deformed steel bars. Metal anchorages can be attached to the ends of the CFRP rods using an expanding agent, as shown in **Photo 3**. The metal anchorages can be threaded or otherwise fabricated to mechanically join the CFRP rods to other structures. The CFRP rods can be formed into various shapes, as shown in **Photo 4**. They can also be easily cut.

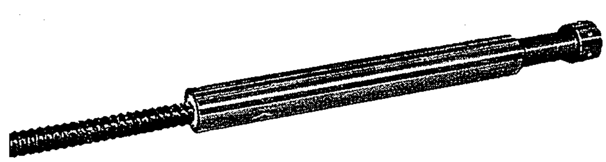


Photo 3 Metal anchorage

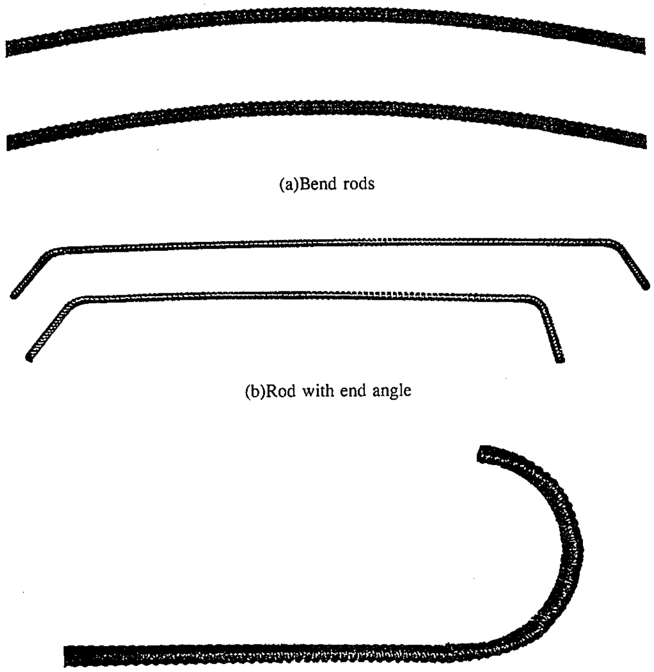


Photo 4 Various shapes of CFRP rods

4. Application of CFRPs to CFRC

4.1 Design concept

When utilized as concrete reinforcements, CFRP strands and rods can be handled in the same way as conventional steel wires and reinforcing bars. When they are used in concrete beams subject to bending, cross-sectional-flatness holding assumption (Euler-Bernoulli hypothesis) in the beam deformation was confirmed by loading tests[9] (see **Photo 5**).

4.2 Advantage of high-modulus reinforcing material

Consider a reinforcing material in a concrete member subject to bending. As the reinforcing material increases in modulus (or the modular ratio n), the neutral axis of the member moves closer to the position of the reinforcing material (or moves away from the compression edge of the concrete), and the compressive stress developed in the concrete is reduced (see **Fig. 5**). It follows then that the higher the modulus, the smaller the bending deformation (strain) of the reinforcing material becomes. When the depth of the member is limited to a low value, a high member strength can be achieved with a high-modulus reinforcing material. Herein lies the advantage of using high-modulus CFRP strands and rods.

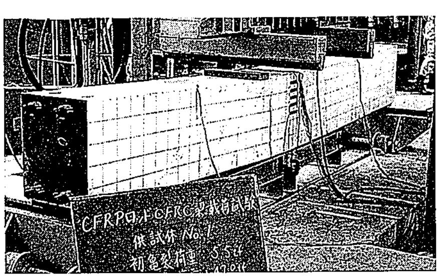


Photo 5 Loading test of concrete member

Specific values are given here for concrete beams subject to bending when the effective depth of the members is predetermined. The cross section is assumed to be rectangular, and the reinforcement and concrete are assumed to carry tensile and compressive forces, respectively. The design conditions are shown in **Table 6**. The physical properties of high-modulus and intermediate-modulus CFRP rods used as reinforcing materials are shown in **Table 7**. The physical properties of the intermediate-modulus CFRP rods are inferred from those of PAN-based carbon fibers. The results of calculation by the allowable stress design method are given in **Table 8**.

A primary design criterion is that the stress produced in a member should not exceed the allowable stress of the member. **Table 8** clearly shows that high-modulus CFRP rods are favored in this case.

Examples in which CFRPs can be effectively utilized by making the most of this high modulus are described below.

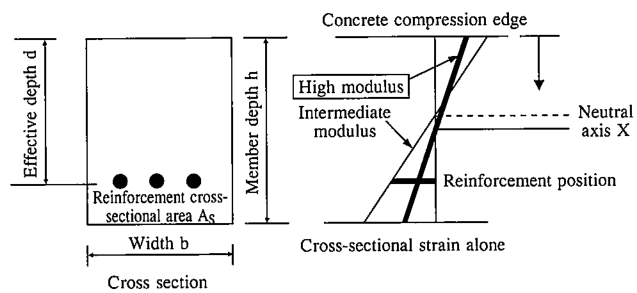


Fig. 5 Strain in rectangular beam subject to bending

Table 6 Design conditions

Bending moment	1176kN · m/m
Groove width	80cm
Member width	55cm
Member depth	70cm
Effective depth	65cm

Table 7 Physical properties of reinforcing materials and concrete

Type of reinforcing material	Nominal diameter (mm)	Total cross-sectional area of reinforcement (cm^2)	Allowable stress (MPa)	Elastic modulus (GPa)	Modular ratio n
High-modulus CFRP rod	30	3534.5 (5 rods)	582.1	186	9
Intermediate-modulus CFRP rod	30	3534.5 (5 rods)	815.0	124	6
Concrete	–	–	34.3	–	–

Table 8 Stress produced in reinforcement and concrete

Type of reinforcing material	Stress (MPa)		Position of neutral axis from concrete compression edge (cm)	Judgment
	Reinforcement	Concrete		
High-modulus CFRP rod	577.8	33.39	22.23	OK
Intermediate-modulus CFRP rod	566.7	38.61	18.86	NG

4.3 Examples of application

4.3.1 The NOMOST™ method for direct-start, direct-arrival shield tunneling machine using shafts constructed of advanced concrete

In the civil engineering field, CFRP is applied in a tunneling method which employs a shield machine to open shafts. In a novel material-shield-cuttable tunnel-wall system (NOMST), a shield machine enters or reaches a shaft retaining wall constructed of concrete reinforced with CFRP strands or rods. While the cutter-head of the shield tunneling machine cannot cut the steel-reinforced concrete it can directly cut the CFRP-reinforced concrete due to the cuttability of the CFRP material. With the NOMST method, there is no need to improve the ground in the affected area, and workers do not have to break the retaining wall and face the attendant risk of ground collapse. The cutter bits of the shield machine directly cut an opening into the retaining wall (see **Fig. 6**)[10]. The NOMST method was developed by Nippon Steel jointly with Japan's eight general contractors. The main persons engaged in this development were awarded a 1994 technology development prize by the Japan Society of Civil Engineers[*1].

When the NOMST method is applied to a caisson, for example, CFRP rods are first placed and assembled like steel reinforcement in the portion to be directly cut and opened by the shield, and the concrete is then poured in (see **Photo 6**). Since its first application in September 1992, the NOMST method had been used in more than 40 construction projects as of December 1996.

4.3.2 High-modulus carbon fiber (CF) sheets

High-modulus carbon fiber (CF) sheets consist of carbon fibers oriented unidirectionally. They are applied as reinforcement to the surface of concrete or steel plate using a cold-setting resin (see **Photo 7**). The specifications of high-modulus CF sheets are given in **Table 9**. The effect of a high-modulus CF sheet in reinforcing a concrete beam as determined by flexural test is shown in **Fig. 7**. The flexural strength of the concrete beam can be significantly increased by the high-modulus CF sheet reinforcement. CF sheets are light in weight and do not require heavy machinery for their installation. By reducing the total number of sheets required to restrict overall deformation, the utilization of high-modulus CF sheets is believed to help reduce construction costs.

Now that deterioration of structures built during the high-growth period is highlighted as a social problem in Japan, repair and reinforcement with CF sheets is expected as a cost-effective solution.

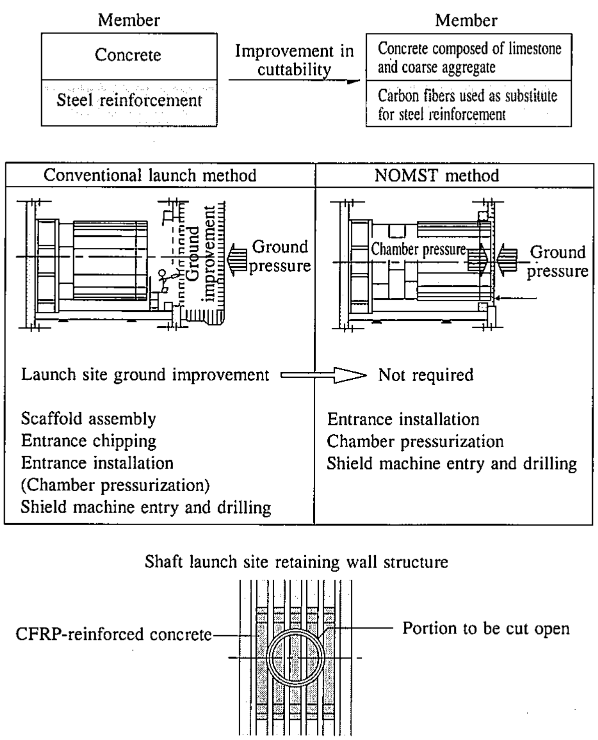


Fig. 6 NOMST method

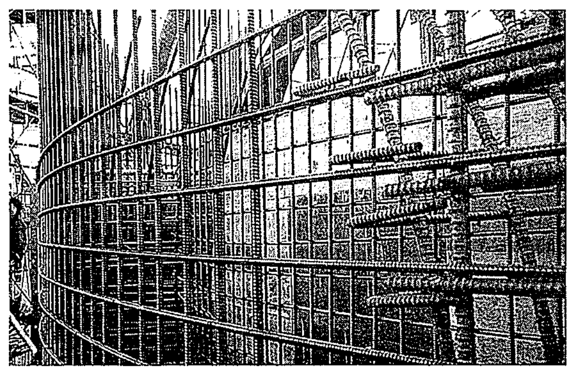


Photo 6 Placement and assembly of CFRP rods as concrete reinforcement for NOMST method

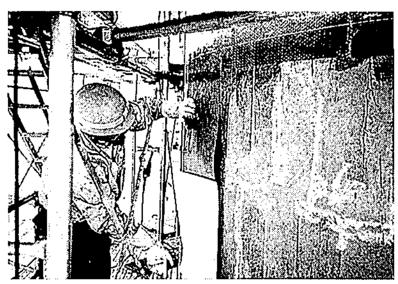
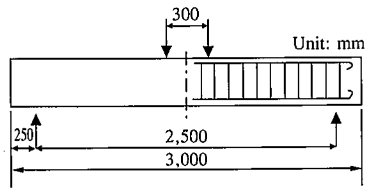


Photo 7 Installation of high-modulus carbon fiber sheet

Table 9 Specifications of carbon fiber sheets

Type	Areal weight (g/m²)	Design thickness (mm)	Tensile strength (N/cm of width)	Design strength (MPa)	Tensile modulus (kN/cm of width)	Design modulus (GPa)
FTS-C1-20	300	0.167	5,780	3480	384	230
FTS-C5-30 (high modulus)	300	0.165	4,900	2,940	614	372
FTS-C6-30 (high modulus)	300	0.144	3,530	2,450	706	490



Schematic of bending test specimen
Specimen dimensions : 300-mm deep, 200-mm wide, and 3,000-mm long

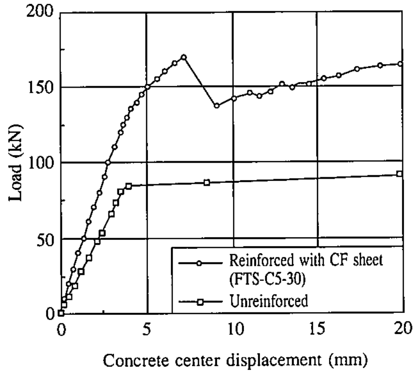


Fig. 7 Bending test of concrete beams

5. Conclusions

Carbon fiber applications have expanded from the aerospace field to the recreational sports field. On the eve of the twenty-first century, pitch-based carbon fibers are expected to be widely applied together with PAN-based carbon fibers in the civil engineering and architectural areas, making optimal use of their properties. To this end, it will be crucial not only to develop more efficient production processes and more effective applications for pitch-based carbon fibers, but also to reduce the total costs for the production and utilization of pitch-based carbon fibers. When we consider the application of carbon fibers to structures with long service lives, we must also study the long-term properties (durability) of CFRP materials. We will devote much time and effort in the future to solve these problems.

The CFRP strands introduced here were jointly developed by Nippon Steel, Nippon Steel Chemical, and Suzuki Metal Industry. The CFRP rods were jointly developed by Nippon Steel and Nippon Steel Chemical. The high-modulus CF sheets were jointly developed by Nippon Steel, Nippon Steel Chemical, and Tonen Corp.

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