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Structure and Properties of Pitch-Based Carbon Fibers

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Abstract:

High-performance pitch-based carbon fibers produced from mesophase pitch are characterized by high strength and high modulus of elasticity. They also feature excellent thermal conductivity as a functional property. These properties are derived from the composition of the pitch-based carbon fibers from well-grown graphite crystals. During these ten years, extensive research and development have been conducted on the pitch-based carbon fibers, and a substantial progress has been achieved. This paper generally describes the production process, structure, properties, and reinforcement means and mechanism of pitch-based carbon fibers, centering around the Nippon Steel-developed Eskainos carbon fiber.

1.Introduction

Carbon fibers are composed mainly of carbon atoms. Thomas Edison's incandescent lamp filaments are said to represent the first application of carbon fibers[1]. Later in 1959, Union Carbide Corporation (UCC) of the United States started the commercial production of carbon fibers from a rayon precursor, which initiated the history of modern carbon fiber industry. Then in 1962, Japan's Nippon Carbon started the world's first commercial production of polyacrylonitrile (PAN)-based carbon fibers on the basis of Shindo's basic patent[2]. This was followed by an active development and commercialization of high-strength PAN-based carbon fibers chiefly in Britain, the United States and Japan, which has brought about today's state of the industry.

On the basis of Ohtani's research[3], Kureha Chemical Industry of Japan initiated in 1969 the commercial production of carbon fibers using the isotropic pitch precursor as raw material. The new process gives the benefit of extensive by-product utilization in addition to low product price offering. The basic structure of high-performance pitch-based carbon fibers also originates in the study of Ohtani[4]. In 1975, UCC (which later sold its carbon fiber operation to Amoco Performance Products, Inc.) commercially produced carbon fibers from the mesophase pitch precursor[5,6]. The carbon fibers UCC placed on the market, however, had a tensile strength of only about 2 GPa and were limited in usage by today's standards.

Today, lightweight, high-strength, and high-elasticity modulus carbon fibers are used mainly as base materials for advanced composites. High-performance carbon fibers having an elasticity modulus of 200 GPa or more and strength of 2 to 6 GPa are produced from PAN and mesophase pitch precursors. In particular, mesophase pitch-based carbon fibers are characteristic of more easily producing high elasticity modulus grades than PAN-based carbon fibers. For example, a 1000 GPa theoretical elasticity modulus of graphite crystals can be obtained in the laboratory. Because of their light weight and superior thermal conductivity, high-elasticity modulus mesophase pitch-based carbon fibers are attracting public attention as materials of components for such high-temperature service as in space and aircraft applications.

In the United States that led the commercialization of mesophase pitch-based carbon fibers, much energy has been expended in research and development, but American mesophase pitch-based carbon fibers still leave much room for improvement in cost and quality. In Japan where pitch-based carbon fibers were invented, the commercialization of mesophase pitch-based carbon fibers lagged behind for some time. Since about 10 years ago, however, active research and development have been car-

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ried out, focusing on cost reduction and strength increase. Recently, mesophase pitch-based carbon fibers with a tensile strength in excess of 4 GPa have appeared on the Japanese market.

This report outlines the production process and structure of high-performance pitch-based carbon fibers prepared from mesophase pitch, and describes the development of carbon fiber technology, centered on improving tensile strength.

2. Production and Structure of Carbon Fibers

2.1 Production process

In the typical production process of carbon fibers, the precursor fibers are prepared, converted to thermosetting fibers by infusibilization, and then carbonized and graphitized at a high temperature in an inert atmosphere. The difference in the precursor fibers, therefore, governs the difference in the basic structure of the finished carbon fibers. There are two pitches for precursor fiber pitch materials for pitch-based carbon fibers, i.e., optically isotropic pitch and anisotropic (liquid crystalline or mesophase) pitch. In each case, coal tar or heavy oil from petroleum refining or petrochemical production is reformed to a pitch with good spinnability, and prepared. General-purpose carbon fibers with a tensile strength of 0.6 to 1 GPa and tensile elasticity modulus of about 40 GPa are obtained from the optically isotropic pitch, while high-performance carbon fibers with a tensile strength of 2 to 4 GPa and a tensile elastic modulus of 150 to 900 GPa are prepared from the optically anisoropic, i.e., mesophase pitch.

In the pitch treatment step of the pitch-based carbon fiber production process shown in **Fig. 1**, the starting heavy oil is separated, refined, hydrogenated or otherwise chemically treated, and then thermally polymerized into pitch for spinning. The pitch thus obtained is melt spun into precursor fibers (pitch fibers) measuring several to about ten micrometers in diameter. These thermoplastic pitch fibers are oxidized by gas-phase oxidation into infusible thermosetting fibers. Further, the subsequent steps of carbonization and graphitization remove almost all elements other than carbon from the fibers and grows graphite crystals. Carbon fibers are chemically stable by themselves, so that they are not readily assimilated with the matrix when used to make a composite material. They are further processed into the final product after a few more complex steps, such as fiber surface treatment to introduce functional groups into the fiber surface.

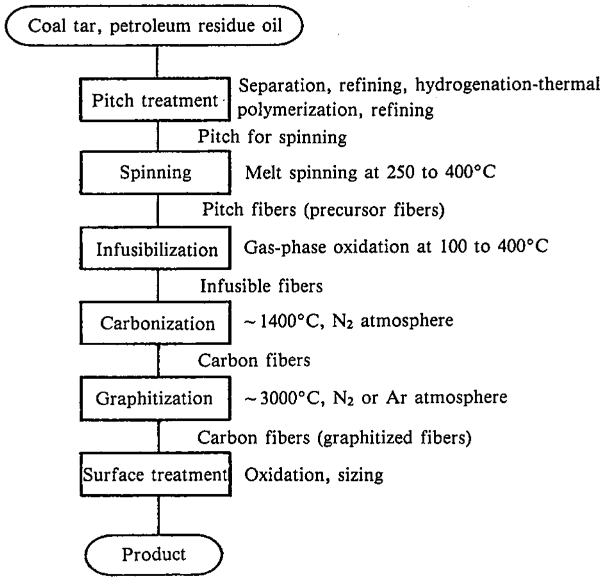

Fig. 1 Pitch-based carbon fiber production process

Pitch-based carbon fibers are produced by a combination of various techniques such as chemical reaction, melt spinning and high-temperature firing. It is only through a systematic combination of these techniques that carbon fibers of excellent quality can be obtained.

2.2 Structure of pitch-based carbon fibers

The mesophase pitch precursor for high-performance carbon fibers is a kind of nematic liquid crystal in which molecules predominantly composed of condensed polycyclic aromatic polymers with a planar structure are stacked. When molten mesophase pitch is deformed by shear, the planar molecules are arranged in the direction of shear deformation. As schematically illustrated in **Fig. 2**[7], a pitch fiber with the planar structure molecules of mesophase pitch highly oriented in the direction of the fiber axis is obtained in the melt spinning step. Since the component molecules of mesophase pitch tend to assumes a planar structure, the pitch fibers also have regularity in the cross-sectional direction normal to the fiber axis.

Photo 1 shows the polarized light micrographs of pitch fibers and the orientations of mesophase molecules as examined with

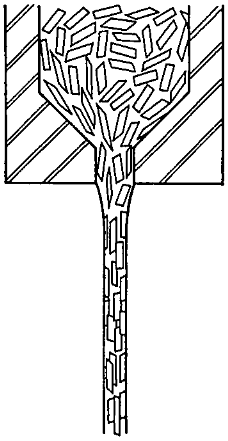

Fig. 2 Schematic illustration of orientation of mesophase pitch by spinning

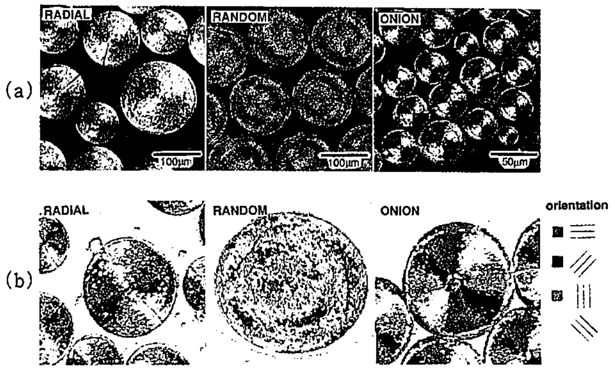

Photo 1 Polarized light micrographs of pitch fibers (a) and orientation of mesophase molecules (b)

a computer-aided microscopic texture analyzer for optically anisotropic substances[8,9]. The molecules comprising the mesophase pitch tend to assume varied orientations in the transverse direction of the fibers. This orientation pattern provides the mesophase pitch with transverse structures characteristic of mesophase pitch-based carbon fibers, such as radial, onion and random structures. These macrostructures observed by polarized light microscopy do not appreciably change in the subsequent steps of infusibilization, carbonization, and graphitization. As shown in the scanning electron micrographs of **Photo 2**, the carbon fibers still retain the macrostructures that are observed in the pitch fiber state.

Microstructures, on the other hand, significantly change through the steps of carbonization and graphitization. As schematically illustrated in **Fig. 3**[10], the planar molecules of mesophase pitch develop a six-membered ring structure at about 1300°C, stretch the folded portions with the expansion of the planar structure, and exhibit a graphite crystal structure with a wide layer structure during heat treatment at 2000°C or above.

It is known that the expansion direction of graphite layer planes and the inclination of the fiber axis (expressed as the orientation degree or angle) govern the modulus of carbon fibers and that graphitization parameters, such as interlayer spacing, thickness and expansion, are related to the tensile strength[11]. To obtain high elasticity modulus and high strength, carbon fibers should preferably have graphite crystals oriented well in the direction of the fiber axis and have the growth of graphite crystals retarded to some degree or be low in graphitizability.

Fig. 4 shows the relationship between the graphite crystal stacking thickness L_c, one of the graphitization parameters, and the tensile strength of mesophase pitch-based carbon fibers graphitized at 2500°C and provided with approximately the same elasticity modulus. A carbon fiber of small L_c, i.e., low graphitizability is known from the figure to possess a high tensile strength. Improvement in elasticity modulus, i. e., orientation of graphite crystals is contradictory to the retardation of graphitizability. Technology is being developed for lowering graphitizability while maintaining the orientation of graphite crystals by appropriate mesophase pitch arrangement and spinning method[12].

Nippon Steel's coal pitch-based carbon fiber Eskainos NU-80 is compared with Amoco's Thornel P-120 as shown in **Table 1.** As shown, Eskainos NU-80 is roughly equal to Thornel P-120 in elasticity modulus, but is much higher than the latter in tensile strength. **Fig. 5** shows the appearance of the 112 diffraction line, as an indicator of the development of graphite crystals, and the separation of the 100 and 101 diffraction lines. Although Eskainos NU-80 has a higher tensile elasticity modulus, it does not reveal the appearance of the 112 diffraction line that indi-

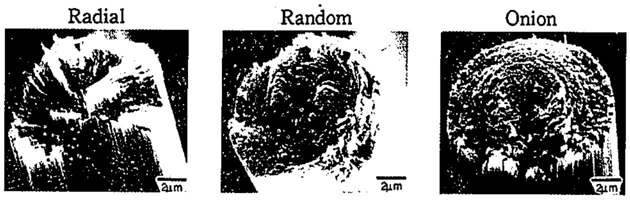

Photo 2 Cross-sectional micrographs of pitch-based carbon fibers with different structures

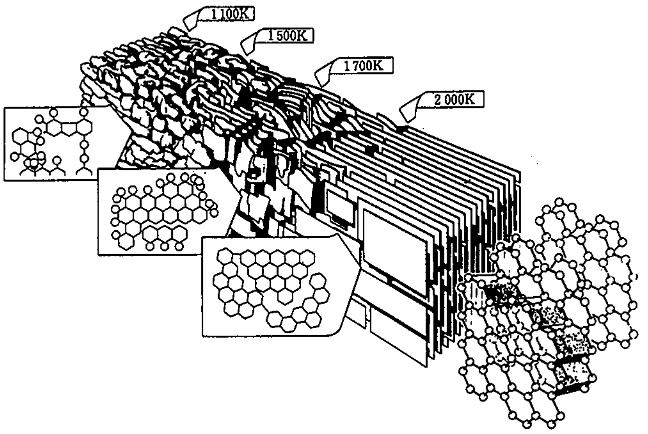

Fig. 3 Change from mesophase to graphite in carbonization and graphitization steps

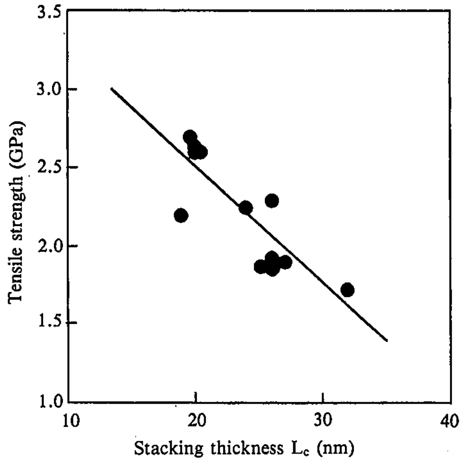

Fig. 4 Stacking thickness L_c versus tensile strength of graphite crystals

Table 1 Properties of commercially available high elasticity-modulus pitch-based carbon fibers

Property	Eskainos NU-80	Thornel P-120
Tensile elasticity modulus (GPa)	785	827
Tensile strength (GPa)	3.23	2.20
Density (kg/m^3)	2180	2180
Graphite layer plane spacing d_{002} (nm)	0.3393	0.3374
Graphite layer stacking thickness L_c (nm)	21.8	28.6

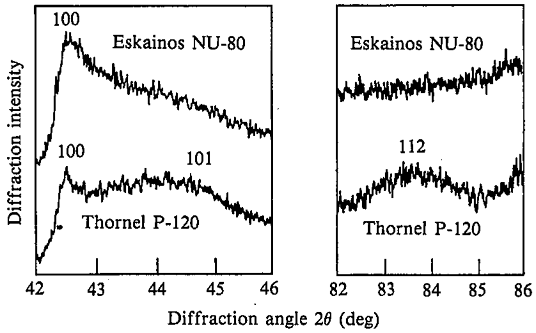

Fig. 5 X-ray diffraction spectra of commercially available pitch-based carbon fibers

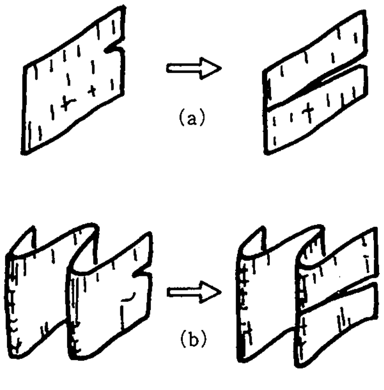

Fig. 6 Crack propagation models of flat-plate graphite structure (a) and folded graphite structure (b)

cates a three-dimensionally ordered graphite structure and the separation of the 100 and 101 diffraction lines. This means that NU-80 is prepared to a fiber structure with graphitizability lower than P-120.

Analysis by transmission electron microscopy (TEM)[13,14] indicates that Thornel's graphite layer plane structure is shaped as shown in **Fig. 6(a)**, while Eskainos's graphite layers are folded in the transverse direction of the fibers, as shown in **Fig. 6(b)**[15]. Eskainos is not different from Thornel in the orientation of graphite crystals in the direction of the fiber axis, but it folds in the transverse direction, which retards the growth of graphite crystals and impedes the propagation of cracks to ensure a high strength.

2.3 Features of pitch-based carbon fibers

Pitch-based carbon fibers produced from mesophase pitch are of such a structure that graphite crystals developed to some degree are extremely highly oriented in the direction of the fiber axis. Besides their high tensile elasticity modulus, they retain the properties of graphite. Some of their characteristic properties are given in **Table 2**. Among them, chemical stability and thermal conductivity deserve particular note.

From a chemical stability point of view, the formation of carbide at the fiber-matrix interface when the carbon fiber is used in a metal matrix composite is fewer than in PAN-based carbon fibers, which is claimed to enhance tensile strength. When used as reinforcement fibers in a ceramic matrix, pitch-based carbon fibers are more suited than PAN-based carbon fibers because they are higher in oxidation resistance.

Pitch-based carbon fibers have an extremely high thermal conductivity of 2400 W/mK in the a-axis direction of graphite crystals[16]. High-elasticity modulus pitch-based carbon fibers possess a thermal conductivity much higher than other materials, especially per unit weight. P-130X shown in the **Fig. 7** is the pitch-based carbon fiber which was developed by Amoco with the aim of improving thermal conductivity. Its thermal conductivity is approximately 50% of that of the ideal graphite. This high thermal productivity is already utilized in such applications as brakes, rocket nozzles, and engine cones. Such other applications as electronic device packages and satellite heat radiators are now under development[16]. Besides, pitch-based carbon fibers have some properties that are not obtainable from other materials for extremely severe applications.

Table 2 Functional properties of pitch-based carbon fibers

Chemical properties	Higher acid and alkali resistance than PAN-based carbon fibers Higher elevated-temperature air resistance than PAN-based carbon fibers
Thermal properties	Low coefficient of thermal expansion High thermal conductivity
Electromagnetic properties	High electrical conductivity (magnetic shielding effect) Large X-ray transmission

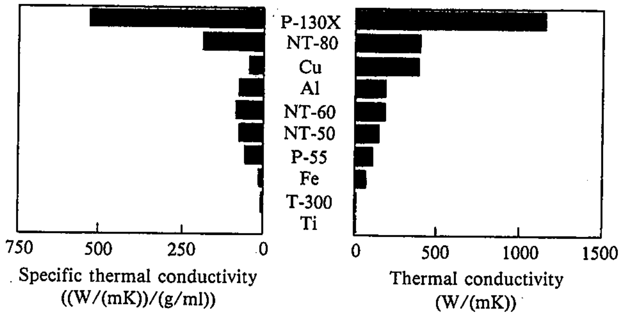

Fig. 7 Thermal conductivity and specific thermal conductivity of various carbon fibers

3. Approach to Higher Strength

Pitch-based carbon fibers easily provide a high modulus of elasticity, but on the other hand are brittle because of their highly developed graphitizability. As aforementioned, the effort at increasing the strength started with changing the average fiber structure into a folded graphite crystal structure through the development of a pitch and spun fiber structure controlling method. Today's approach to increasing strength involves improvements not only in the pitch precursor and spinning step, but also in the infusibilization and carbonization steps.

In the infusibilization step, the reaction gas (oxygen in most cases) diffuses through the solid-phase pitch fibers, reacts with the active components of the pitch, and is immobilized. The reaction involved is the polymerization of pitch fibers mainly through the dehydrogenation and the immobilized oxygen. As schematically illustrated in **Fig. 8**, the oxidizing gas shifting from the gas phase to the solid phase proceeds from the fiber surface toward the core while reacting with a B component of high activity in the pitch (for example, aliphatic carbon) and a C component of lower activity (for example, aromatic carbon)[17]. The reactivity of the surface and core of fibers measuring about 10 μm in diameter can be controlled by appropriately adjusting the oxidizing gas and the reaction conditions. Free adjustment of the reactivity of the fiber surface and core is an important factor in obtaining the desired strength as described later.

The oxidizing gas introduced in the infusibilization step is released for the most part as carbonic gas in the carbonization step. Fiber portions that have more excessively reacted with the oxidizing gas in the infusibilization step release larger amounts the carbonic gas in the carbonization step. When the fiber surface is selectively overoxidized by appropriately controlling the reaction, the amount of volatile elements to be released during carbonization increases to cause fine pores in the carbon fibers.

Fig. 9 shows the change in the specific surface area of fibers

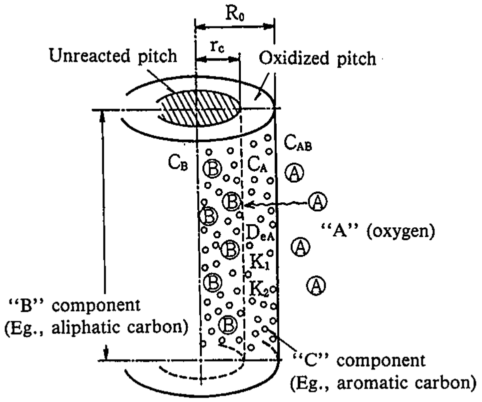

Fig. 8 Reaction model of infusibilization

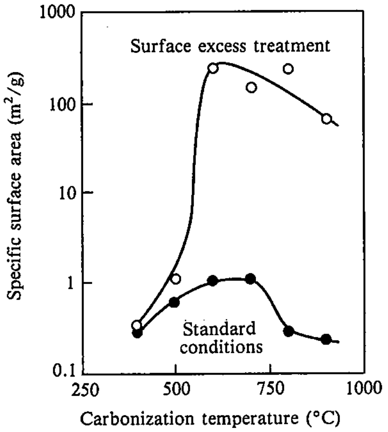

Fig. 9 Change in specific surface area in carbonization step with different infusibilization conditions

in the carbonization step. The formation of pores very significantly changes with the reaction conditions in the infusibilization step[18]. The porosity can be obtained through the combination of infusibilization and carbonization, or forcibly by an activation treatment of fibers carbonized at lower temperatures[19,20]. These fine pores gradually close in the graphitization stage, but leave microcracks in the fiber surface, which leads to strength enhancement.

The strength development mechanism is as schematically illustrated in **Fig. 10**. Microcracks formed in the fiber surface are considered to increase toughness by increasing the propagation length of main cracks that govern the fiber strength[21]. By this mechanism, the tensile strength of high-elasticity modulus pitch-based carbon fibers is improved by 40 to 80% from the level of conventional carbon fibers[22].

Such control of the fiber surface structure is closely related to the surface treatment performed to improve adhesion to the matrix when the carbon fibers are used in composite materials. Anodic oxidation is a general method of surface treatment applied to FRP carbon fibers. An oxidation treatment conducted to improve adhesion to the resin is known to introduce defects onto the surface of high-elasticity modulus carbon fibers and to lower their tensile strength. Control of the fiber surface structure, however, can improve the interlayer shear strength (ILSS), an indicator of fiber adhesion to the resin, of modified carbon fibers with an elasticity modulus of 600 GPa without lowering the tensile strength, as shown in **Fig. 11**.

Nippon Steel has been improving the Eskainos carbon fibers according to the above-mentioned concept of strength improvement. **Fig. 12** shows the historical change in the tensile strength of Eskainos carbon fiber grades over a tensile modulus range of 400 to 500 GPa. The NU series recently launched on the market is 7 μm in fiber diameter against 10 μm for the conventional NT series as shown in **Photo 3**, and is substantially improved in handleability as well as the tensile strength in the high-elasticity modulus region.

4. Conclusions

The production process, structure, and properties of high-performance pitch-based carbon fibers made from mesophase pitch have been outlined. Measures taken to increase their tensile strength and the ideas involved have also been described. Japan started the full-scale development of pitch-based carbon fibers about 10 years ago, which will find widespread use from now on as truly basic materials in various application fields.

Although not mentioned here, pitch-based carbon fibers have some drawbacks in terms of compressive strength and other

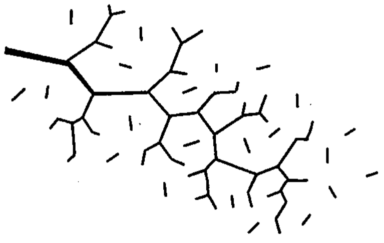

Fig. 10 Branching of main cracks due to microcracks

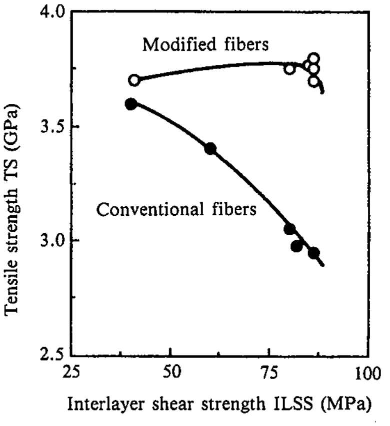

Fig. 11 Interlayer shear strength versus tensile strength

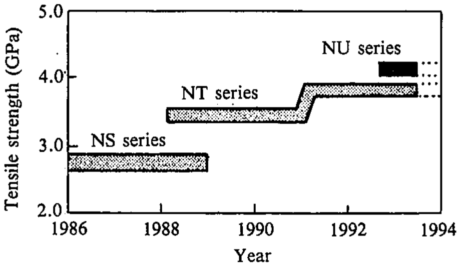

Fig. 12 Change in tensile strength of Eskainos carbon fibers

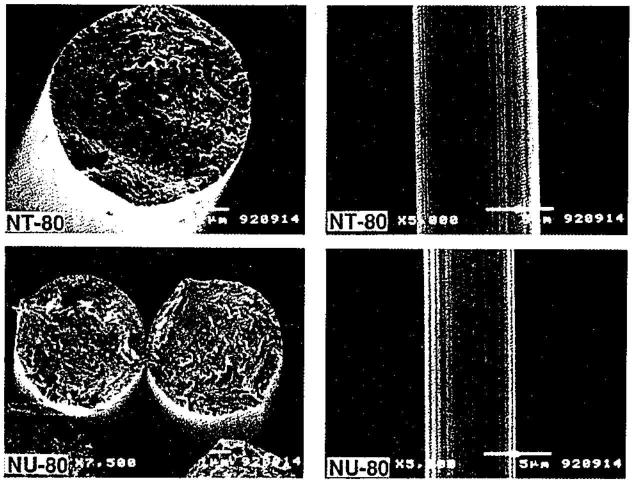

Photo 3 Scanning electron micrographs of Eskainos carbon fibers
Top: NT series (NT-80), Bottom: NU series (NU-80)

properties as compared with PAN-based carbon fibers and some inorganic fibers. The authors who have been engaged in the development of the Eskainos carbon fibers, however, strongly feel that the present weaknesses of these pitch-based carbon fibers can be eliminated through future research and development activities.

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