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**ECOKOTE-S Adopted in Fuel Tanks**

Nippon Steel has accepted orders for its specially-developed “ECOKOTE-S™” for fuel tanks for Chevrolet Volt electric vehicle. It is a tin-zinc-coated corrosion-resistant steel sheet that contains no lead or other environment-loading substances.

**Investment in Cold Rolling Mill in Nigeria**

Nippon Steel and Marubeni-Itochu Steel Inc. have reached an agreement with Midland Rolling Mills Limited in Nigeria in regard to equity investment in MRM. Each of Japanese companies is to respectively invest US$ 3 million in MRM which manufactures cold-rolled steel in Nigeria.

**NSSC FW2: Highly Corrosion-resistant Ferritic Stainless Steel**

Nippon Steel & Sumikin Stainless Steel Corporation has newly developed NSSC® FW2 (Forward Two), a “highly corrosion resistant, low-interstitial ferritic stainless steel”, having corrosion resistance equal or superior to SUS304. It features 40% reduction in rare metals through use of tin (Sn).

**Resumption of Delivery of Galvanized Steel Pipes**

Nippon Steel confirms that the delivery of galvanized steel pipes, which had been suspended as previously announced, has resumed since late September of 2010. The company has since taken measures to ensure stable manufacturing conditions and revised its inspection system.
The Genesis of Product Making

Pitch-based Carbon Fiber
—Raising the Added Value of Carbon Materials Derived from Coal Tar—

Nippon Graphite Fiber Corporation, a Nippon Steel Group company, produces pitch-based carbon fiber with considerably higher added value. This type of fiber is produced using carbon materials (impregnated pitch) derived from coal tar, which is a byproduct of blast-furnace ironmaking. Due to its high performance with regard to strength and modulus, pitch-based carbon fiber is increasingly being applied in a wide range of fields—industry, construction, space and aircraft, and sports and leisure.

The current issue highlights the production technology used to make pitch-based carbon fiber and the strengths of Nippon Graphite Fiber Corporation, together with suggestions regarding the future direction of related application development.
Two kinds of carbon fiber are produced: PAN-based fiber employing acrylic fibers used for cloths; and pitch-based carbon fiber employing byproduct materials derived from the coal carbonization process in ironmaking and from the oil refining process. Nippon Graphite Fiber (NGF) produces carbon fiber employing the impregnated pitch contained in coal tar, a byproduct generated during coal carbonization. Impregnated pitch is a hard (heavy) pitch that is produced by heat-treating the high-purity pitch used for needle coke and, further, by volatilizing lightweight components. NGF procures all the necessary impregnated pitch used as raw material for carbon fiber from the Hirohata Works of C-Chem Co., Ltd. (a joint company between Nippon Steel Chemical and Sumikin Chemical).

In 1981, Nippon Steel started the technological development of pitch-based carbon fiber for use in the construction and machinery industries, with the aim of promoting advanced applications of byproducts derived from coal carbonization in ironmaking. In 1985, the company built a pilot plant at its Hirohata Works to accumulate production technology knowhow related to carbon fibers. In 1995, Nippon Steel and Nippon Oil Co. (currently JX Nippon Oil & Energy), the latter of which is strong in the development of carbon fiber materials for space, sports and leisure fields, integrated their carbon fiber-related businesses to establish NGF (currently a group company of Nippon Steel Materials Co., Ltd.). Since then, NGF has supplied high-quality pitch-based carbon fiber for diversifying and emerging markets.

PAN-based carbon fibers are the mainstay of the entire carbon fiber market. However, PAN-based carbon fiber has a standard value of 240 GPa (300 GPa for aircraft) for its modulus, which indicate anti-deformability, and is difficult to produce with a high modulus of 500 GPa or more. Consequently, the production of fiber having such a high modulus inevitably requires higher cost.

On the other hand, with pitch-based carbon fiber, it is comparatively easy to properly produce fibers having moduli ranging from 50 GPa to 900 GPa. In order to distinguish these from 300 GPa-class products, a strong field for PAN-based fiber, NGF is directing its efforts towards the development of carbon fiber in the low and high modulus ranges. (Refer to Fig. 1)
Modification into Spinning Material Appropriate for Carbon Fiber Employing Hydrogen

In order to modify the impregnated pitch procured from C-Chem into spinning material suitable for the production of carbon fiber, after hydrogenation, the pitch is first subjected to thermal polymerization*1, in which lightweight substances are blown off by means of high-precision distillation, and are then removed of minute impurities by means of filtration (Fig. 2). The hydrogen plays two roles: to remove the sulfur and nitrogen contained in coal tar, and to change the molecular structure of the impregnated pitch so as to convert it into 6-membered ring carbon*2 in which graphite crystals can easily grow. The 6-membered ring carbon is converted to graphite crystals by means of heating, and as the crystals grow, their strength and modulus increase. Impregnated pitch in its original form cannot be sufficiently converted to graphite crystals, and even when subjected to heat treatment, a fully developed graphite structure does not result (isotropic pitch). However, a regularly-aligned molecular (liquid crystal) structure can be produced, even in a liquid state, by adding hydrogen to adjust the molecular structure of the impregnated pitch (mesophase pitch). Mesophase pitch that is liquid-crystallized in a well balanced manner has a softening point (the temperature at which the substance starts to melt) below the thermal decomposition temperature and, therefore, can be used as a material for producing high-quality carbon fiber (Photo 1). (Isotropic pitch can be used for producing general-purpose low modulus carbon fiber.)

Photo 1 Change of Carbon Fiber Structures due to Difference of Material Pitch

*1 Polymerization: Forming of compounds larger in size than the original substance through the chemical bonding of two or more molecules composed of one or more kinds of substances

*2 6-membered ring: Chemical material having 6 atoms bonded in a ring state
Pitch modified as the spinning material becomes carbon fiber via the production process shown in Fig. 3. In the spinning process by which pitch is converted to fibers having a diameter of about 10 µm (one-tenth of a hair), the pitch crystals are aligned longitudinally by means of die (nozzle) configuration and the stirring method; at the same time, physical properties such as modulus and strength are optimized by controlling the method used to align and laminate the layers in which the crystals are arranged or by controlling the sectional structure (Fig. 4). Only three companies in the world can produce high-strength and high-modulus carbon fiber employing mesophase pitch as the spinning material. Among them, only NGF can produce pitch-based carbon fiber having a crystal orientation controlled so as not to allow cross-sectional cracking of the fiber, a quality defect (Photo 2).

Yarn produced by the spinning of as many as 12,000 ultrafine, non-processed pitch-based carbon fibers has a low softening point (300°C), which causes melting when the fibers are sub-

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**Figure 3 Production Process for Pitch-based Carbon Fiber**

- Raw material pitch modification (Fig. 2)
- Spinning material pitch
- Spinning
- Pitch fiber
- Infusibilization treatment
- Infusibilized fiber
- Carbonization
- ~1,400°C nitrogen gas
- Graphitization
- ~3,000°C nitrogen gas or argon gas
- Surface treatment
- Oxidation and sizing treatment
- Product

**Figure 4 Crystal Orientation of Mesophase Pitch in Spinning Process**

The pitch crystals are aligned longitudinally by means of die (nozzle) configuration and the stirring method and physical properties are optimized by controlling the method used to align and laminate the crystal layers.

**Photo 2 Carbon Fiber with Cross-sectional Cracking**

Fiber cross section cracking leads to the quality defect.
jected to high-temperature heat treatment. To solve this problem, oxygen and other elements are added in advance to eliminate hydrogen and other elemental impurities, while at the same time the molecular bonding capability is improved by precisely controlling the chemical reaction used to raise the softening point (infusibilization treatment by means of gaseous phase oxidation). The resulting infusibilized fiber is heated and baked in an oxygen-free state to remove impurities and elements other than carbon in order to raise the carbon density (carbonization). Following this, the carbon crystals are regularly rearranged by further raising the heat-treatment temperature to improve the modulus and strength (graphitization; the same crystal structure found in pencil lead).

Because the carbon fiber thus manufactured is most commonly applied in concert with resin, the fiber is subjected to surface treatment to improve its bonding capacity with resin and its workability during secondary processing.

Commonly, pitch-based carbon fiber material is produced by bundling 6,000~12,000 carbon fibers with a diameter of 10 µm (Photo 3). To meet the need for lighter weight, NGF has initiated the industrial production of carbon fiber material manufactured by bundling 400 fibers with the world's finest diameter of 7 µm and modulus similar to that of 10 µm-diameter carbon fibers.
In order to meet various applications, NGF supplies a variety of pitch-based carbon fibers of different moduli, such as yarn, fabric, and prepreg manufactured by impregnating thermosetting resins (Photo 4). Extensive application development of carbon fiber, such as the CFRP composite material developed by Nippon Steel Composites Company (established in 1988 and integrated into Nippon Steel Materials in 2010), is one of the strengths of the new market development program being promoted by NGF.

Currently, carbon fiber with a low modulus (50~150 GPa class) is increasingly being applied in golf club shafts and fishing rods. On the other hand, high-modulus carbon fiber (600 GPa or more), which is difficult to produce for PAN-based carbon fiber, is used in various rolls for printing and film production, in the arms of liquid crystal and semiconductor transfer robots and in construction reinforcing members by fully capitalizing on such performances as zero thermal deformation, lightness of weight and high strength. (Refer to Photo 5) More recently, high modulus material is applied in racing bicycle frames requiring both lightness of weight and high rigidity.

The fields with high expectations for expanded application growth include the shafts of machine
tool motors, and robot arms and beams. In particular, the long beams of large-capacity machine tools are heavy and suffer reduced fabrication accuracy due to vibration. Thus, fabrication accuracy improves with the adoption of lightweight carbon fiber-reinforced plastic with high vibration damping capacity (Photo 6).

High modulus carbon fiber has high thermal conductivity (ease of thermal conduction), and its coefficient of thermal expansion can be minimized to zero by composite use with other materials (Figs. 5 and 6). Due to these characteristic performances, pitch-based carbon fiber has recently been adopted for the heat radiation members of electronic equipment, solar panel members, and the antenna members of artificial satellites operating in space under temperature fluctuations as great as 200°C or more, depending on the extent of exposure to sunlight (Photo 7).

Pitch-based carbon fiber offers characteristic performances such as high elasticity (900 GPa) and high thermal conductivity (900 W) not found in other materials.
in any other materials in practical use. NGF is promoting the market development of these fibers in two directions.

One is to replace metallic materials with carbon fiber in industrial applications. With energy savings being called for in diverse industrial fields, lightweight pitch-based carbon fiber with high rigidity can contribute to the reduction of weight in production equipment and devices.

Another direction of market development is application development in the consumer product field, which capitalizes on such performances of pitch-based carbon fiber as high thermal conductivity and zero C.T.E. (coefficient of thermal expansion). For example, with the growing need for higher functionality and higher density in electronic equipment devices, carbon fiber is seen to have a high heat-radiation capacity, which is required of high thermal-conducting electronic materials capable of improving device reliability.

On the strength of reinforced supply capacity realized by the startup of new production lines in the fall of 2010, NGF is further promoting new market development for high-performance pitch-based carbon fiber.

Because of the complicated inner configuration required to send waves with pinpoint accuracy to a specified area, zero thermal deformation is inevitably necessary as a member performance value.