Pitch Needle Coke for Graphite Electrodes in Steelmaking

1. Introduction

Pitch coke is a black carbonaceous material having visible pores and cracks and the maximum diameter of one coke piece is approximately 20 mm. The raw material of pitch coke is soft pitch, which is extracted from the bottom of distillation columns during coal tar distillation. Soft pitch is carbonized at approximately 450°C or higher to manufacture pitch coke. Pitch coke contains little ash and at this point, it greatly differs from metallurgical coke for ironmaking, which is manufactured though the dry distillation of coal, although both are the same carbonaceous materials.

From the end of the 19th century to the beginning of the 20th century, aluminum electrolytic refining and sodium chloride electrolysis, etc., were industrialized, which increased the demand for high-purity carbon electrodes. Consequently, in place of the metallurgical coke manufactured from coal, pitch coke containing very little ash started to be manufactured from coal tar-derived pitch using chamber ovens. After that, Nittetsu Chemical Industry Co., Ltd. (current Nippon Steel Chemical & Material Co., Ltd.) introduced a technology of Lummus Technology in the U.S. in 1968 to establish a manufacturing method involving delayed coking.

Meanwhile, the development of modern industry in the early 20th century rapidly increased the demand for special steel. To meet the demand, electric steelmaking technologies were advanced; the use of higher capacity furnaces began and high-power operations were promoted. After World War II, the production of ordinary steel from iron scraps began.

As the aggregate of graphite electrodes (see **Fig. 1**) used in electric steelmaking, only petroleum-derived needle coke was used because its purity was higher and the crystal structure was more developed compared with pitch coke. Under such circumstances, in 1980, both Nittetsu Chemical Industry (current Nippon Steel Chemical & Material) and Mitsubishi Kasei Kogyo Kabushiki Kaisha (current Mitsubishi Chemical Corporation) succeeded in industrially removing and purifying components that would hinder the development of carbon crystal structure in coal tar-derived soft pitch. This led to the start of the world-first industrial-scale production of coal tar-derived pitch needle coke.

2. Processes to Manufacture Pitch Needle Coke

Figure 2 illustrates the pitch needle coke manufacturing flow.

2.1 Tar distillation

Coal tar, which is a raw material for pitch needle coke, is obtained when coal is dry-distilled and it is produced as a by-product when metallurgical coke, which is mainly used to produce steel, is manufactured.

The generated coal tar is distilled to produce naphthalenes, tar acids, tar bases, creosote oil, and soft pitch (boiling point: 300°C or higher) through fractional distillation. The approximate production ratios of the afore-mentioned products are as follows: Naphthalenes:

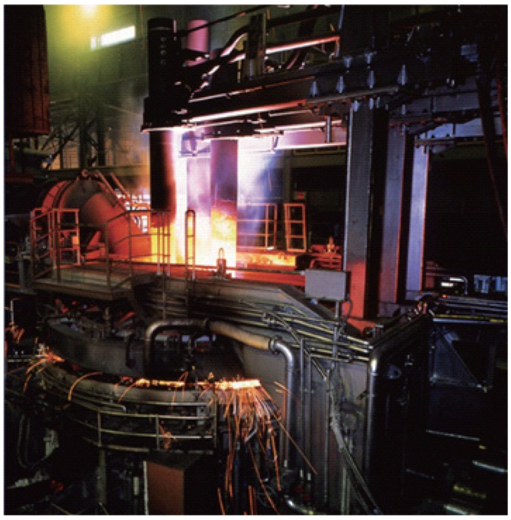

Fig. 1 Electric furnace for steelmaking and graphite electrode

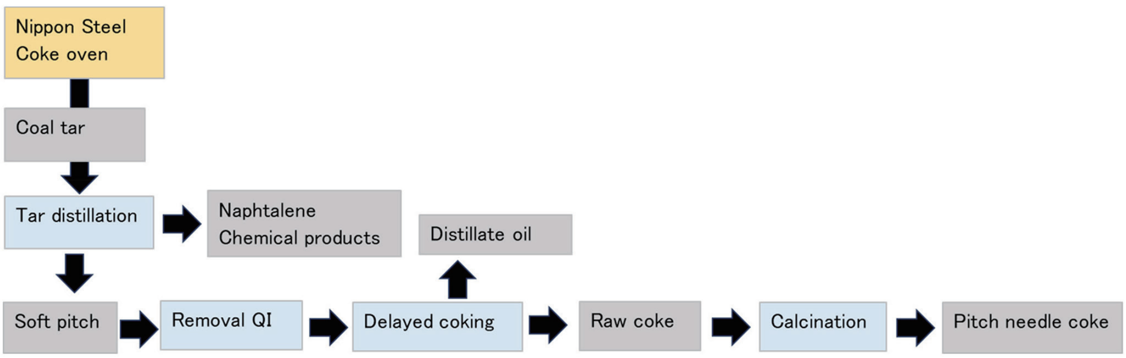

Fig. 2 Pitch needle coke manufacturing flow

10%, tar acids: 5%, tar bases: 5%, creosote oil: 10%, and soft pitch: 70%.

2.2 Delayed coking

Coal tar is a mixture classified as a condensed polycyclic aromatic compound. Carbonizing coal tar produces high-crystalline carbon. However, coal tar contains quinoline insoluble matter (QI) (amorphous carbon) and that hinders the development of crystals. Only after an industrial method to remove such QI had been developed, the production of pitch needle coke that would be able to be used as the aggregate of graphite electrodes for electric steelmaking become possible.

Nittetsu Chemical Industry developed a process to industrially remove QI from soft pitch on its own. After the preliminary treatment process involving this technology, the soft pitch is heated in a heating tube furnace to approximately 450 to 500°C or so and then charged into a delayed coker. The charged heavy components are carbonized in the delayed coker through a pyrolysis polycondensation reaction and turned into raw coke. The generated gas is distilled from the upper section of the delayed coker, along with uncarbonized oil contents, and sent to a fractional distillation column. The fractional distillation column separates the distillate oil, as needed, to collect such matter. Usually, there are two delayed cokers; when one is filled with raw coke, then a raw material is charged into the other coker. For the delayed coker filled with raw coke, steam is used to put out unreacted oil contents and then water is put into the coker for cooling. Once cooled, the top and bottom plates are removed from the coker and a high-pressure water jet is used to cut the raw coke so as to take out the cut pieces.

2.3 Calcination

The raw coke pieces cut and taken out of the coker contain 5 to 10% of volatile matter. To remove such volatile matter, the raw coke is heat-treated at approximately 1 400°C (calcination).

In the calcination process, the raw coke is heated at temperatures up to 150°C to dry water content (7 to 12%) contained in it. Then through heating up to approximately 800°C, volatile matter in the raw coke vaporizes, and the resolution of hydrocarbon (generating methane and hydrogen gas) and combustion occur. In addition, the coke greatly shrinks in this stage. After that, in the heating-up process from 800 to 1 400°C, the coke is dehydrogenated and oxidized. By when the temperature reaches approximately 1 400°C, the concentration of hydrogen in the coke decreases to 0.05%.

3. Quality Characteristics of Pitch Needle Coke

Table 1 lists the general standard quality of pitch needle coke.

Figure 3 shows the appearance of pitch needle coke manufactured from a raw material from which QI was removed, along with its crystal structure observed with a polarizing microscope. The figure also shows the appearance of pitch coke manufactured from a raw material containing QI and its crystal structure as a comparison.

The black pitch needle coke shining in silver gray has several-millimeter pores and cracks. In addition, the results of the observation with a polarizing microscope show that the pitch coke has a mosaic structure because QI hindered the growth of the crystals while the crystals of the pitch needle coke were oriented.

Table 1 Standard quality of pitch needle coke

Real density (g/cm^3)	2.14
Moisture (%)	0.1
Ash (%)	0.05
Volatile matter (%)	0.1
Fixed carbon (%)	99.8
C. T. E Thermal expansion coefficient (10^{-6}/°C)	1.0

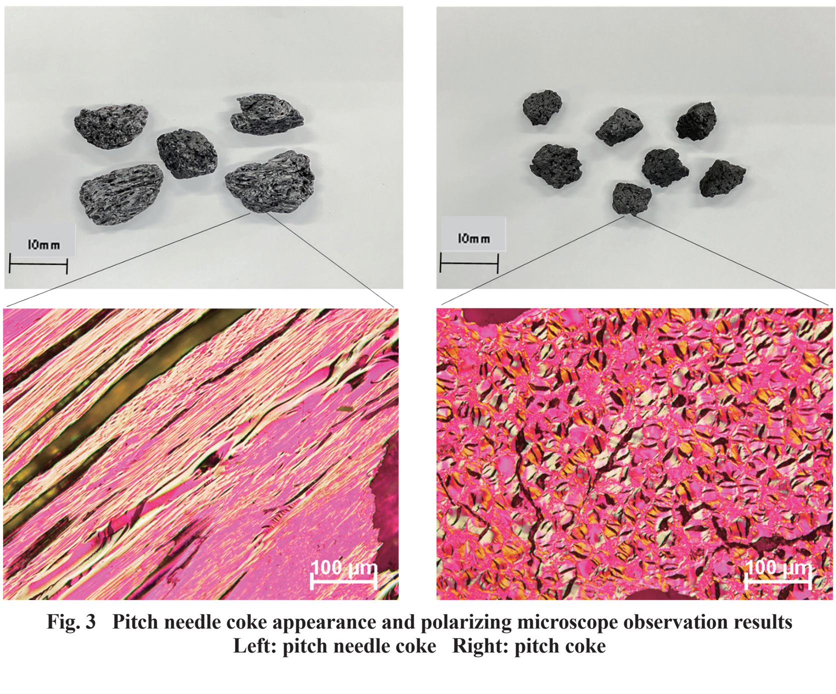

Fig. 3 Pitch needle coke appearance and polarizing microscope observation results
Left: pitch needle coke Right: pitch coke

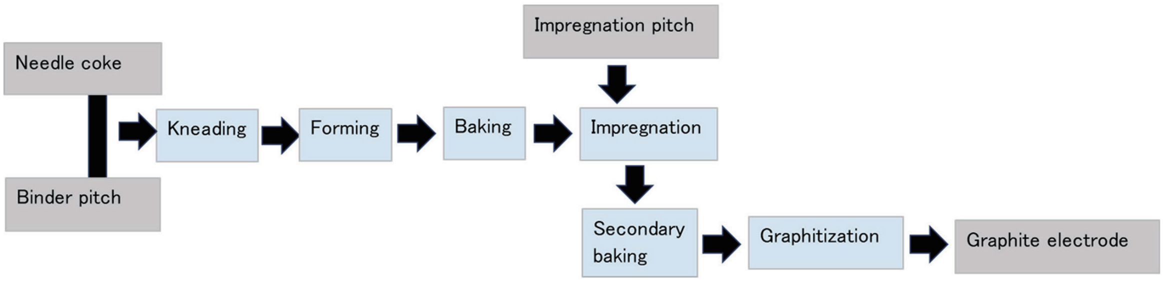

Fig. 4 Graphite electrode manufacturing flow

4. Graphite Electrodes for Electric Steelmaking

Graphite electrodes for steelmaking are used at high temperatures and thereby petroleum-derived coke and pitch needle coke are used as the aggregate coke of such electrodes because their crystal structure has been well developed.

Figure 4 illustrates the flow for manufacturing graphite electrodes for steelmaking. Needle coke is used as the aggregate of graphite electrodes for steelmaking and it is blended with binder pitch. Although the mixing ratios are adjusted according to the electrode size and other factors, the ratio of needle coke is around 75% and that of binder pitch is around 25%. The blended needle coke and binder pitch are kneaded at approximately 150°C and the material turns to a paste. This kneaded material as a paste is extrusion molded to produce cylindrical formed rods, which are prototypes of electrodes. In this stage, the binder pitch in the formed bodies contains many volatile components. Accordingly, the formed bodies are baked at approximately 900°C so as to carbonize the binder pitch. During baking, the binder pitch volatilizes and the density decreases. To recover the decreased density, secondary baking is performed to impregnate pitch into voids remaining after the baking and carbonize the impregnated pitch. The baked bodies (semi-manufactured goods) that underwent the secondary baking are graphitized at approximately 3 000°C to manufacture graphite electrodes for steelmaking.

Graphite electrodes for steelmaking are used to melt scraps through arc discharge in electric furnaces. Graphite electrodes are used under severe conditions and the ends of electrodes in use are exposed to high temperatures of 3 000°C or higher. Accordingly, importance is attached to the quality of needle coke (main raw material)—the thermal expansion coefficient, in particular. As characteristics of pitch needle coke, more crystal structure has been grown and the thermal expansion coefficient of products obtained after graphitization is lower compared with petroleum-derived needle coke thanks to the characteristics of coal tar, which is a raw material for needle pitch coke classified as a condensed polycyclic aromatic compound.

5. Improvement of the Quality of Pitch Needle Coke

In the graphitization process in which heat treatment at approximately 3 000°C is performed to manufacture graphite electrodes for steelmaking, indirect energizing type Acheson furnaces were formerly used. Acheson furnaces were developed in the 1900s and are still widely used as graphitization equipment. In the 1960s, the adoption of lengthwise graphitization (LWG) furnaces began; in LWG, baked semi-manufactured products are directly energized to complete graphitization in a short period of time. Nowadays, LWG furnaces are mainly used in the graphitization process to manufacture graphite electrodes.

With the introduction of LWG furnaces, irreversible thermal expansion called puffing started occurring as a result of rapid temperature increase and heating. Such puffing decreases the density of electrodes, posing a quality problem.

Pitch needle coke and petroleum-derived needle coke products for which puffing was reduced were developed and in the 2000s, Nippon Steel Chemical Co., Ltd. (current Nippon Steel Chemical & Material) developed pitch needle coke for which puffing was greatly reduced and now such coke is widely used.

6. Conclusion

Electric steelmaking involving graphite electrodes for steelmaking is expected to greatly contribute to CO_2 emissions reduction, in addition to the recycling of scraps. Pitch needle coke is also substantially contributing as a material that supports electric steelmaking. Starting from coal tar (a by-product of ironmaking), pitch needle coke is expected to support the steelmaking industry in the future as well.

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