Study on Mechanism of Formation and Quality Improvement of Petroleum-based Needle Coke

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Needle coke which has been the best filler of graphite electrodes need to be upgraded because the quality of graphite electrodes for electric arc furnace is improved with progress of steel making technique.

The role of respective feedstock based on mechanism of formation of needle coke is overviewed in terms of pretreatment of the feedstocks, such as modification of FCC decant oil (FCCDO), solvent deasphalten process, and heat treatment of low sulfur vacuum residue (LSVR), to improve the characteristics of the needle coke.

The mechanism of formation of needle coke is traced through the observation of the carbonization process using tube bomb which can provide nearly the same condition as delayed coker. Coefficient of thermal expansion (CTE), which is the most important property of needle coke, is strongly influenced by uniaxial orientation of flow texture in the coke. Gas evolution of solidification, therefore, is important for production of low CTE coke as well as formation of bulk mesophase. The carbonization condition, especially pressure and temperature, influences the above important factor. Furthermore, the co-carbonization of LSVR with FCCDO produced excellent needle coke of low CTE because formation of bulk mesophase and gas evolution at solidification were improved. As the amount of mosaic coke of high CTE affects the CTE of needle coke, in the present study, the modification of FCCDO and LSVR was studied to eliminate the formation of mosaic coke.

Addition of high aromatic pitch, dewaxing and heat treatment were highly effective for elimination of mosaic coke by modification of FCCDO. On the other hand, elimination of asphaltene by solvent extraction and heat treatment with hydrogen donor were highly effective as modification of LSVR.

1. Introduction

An enormous amount of iron and steel has been produced in the world to meet the demand of highly civilized society. Such has caused accumulation of iron and steel scraps of huge amount to be regenerated and recycled. Electric furnaces, principally operated for this purpose, require graphite electrode of superior performance to enable reduction of cost of steel making by stable long term operation. Needle coke, which is produced in delayed coker, is used as the best filler of high performance graphite electrodes. Stable quality of coke is required at low cost.

Delayed coking is one of the most popular thermal cracking processes, being commercially operated all over the world. The coke produced from the delayed coker, however, was frequently regarded as undesirable by-product and disposed as solid fuel. On the other hand, a careful selection of feedstock and cracking conditions made it possible to prepare needle coke meeting the requirements of the best filler of graphite electrode for the electric arc furnace.

Commercial needle coke is commonly produced from FCC decant oil (FCCDO) and vacuum residues of low sulfur crude oil (LSVR) as feedstocks. There are, however, problems including formation of mosaic coke of high CTE, sometimes, in case of using these feedstocks.

In the present review, the role of respective feedstock based on formation mechanism of needle coke is overviewed in terms of pretreatment of the feedstock to improve the characteristics of the needle coke. The scheme of this study is shown in Fig. 11). Such a block-diagram is available for coke production at low cost from any feedstocks.

2. Laboratory Preparation of Needle Coke Lump

A sample of feedstock (about 40 g) was placed in an aluminum foil tube and heat treated in a stainless steel cylindrical bomb (tube bomb), 22 mm in diameter and 150 mm in length. The...
bomb was heated in a sand bath and quenched in cold water. A whole lump of coke was recovered from the foil. Coke lumps, thus prepared, were then cut in sections parallel to the longitudinal axis of the bomb and polished to evaluate the anisotropic development of the exposed area under a polarized microscope. The coke lumps were then calcined at 1,000°C for 1 h to measure the coefficient of thermal expansion (CTE). The values were measured in a temperature range of ambient to 500°C. There was an intimate relationship between the CTE and optical anisotropy.

3. Feedstocks for the Laboratory Preparation of Needle Coke

Premium needle cokes have been produced from petroleum and coal tar residues2)-5). For the present study, LSVR, FCC-DO and their pretreated oils were used as the feedstocks. Their characteristics differed as shown in Table 1. Details on experimental pretreatment were described in previous papers6)-12).

4. Structure of Needle Coke

A lump of needle coke was reported to have shown excellent orientation along the vertical axis13),14). The present study, based on the microscopic examination of a whole coke lump, suggests that the pores were the centers of concentric symmetry, around which planar disk15,16) were oriented in a columnar arrangement. Hence, such a structure of the coke was compared to a bunch of cigars, each of them had its own symmetry center as shown in Fig. 217). It has been widely recognized, in the sectional surfaces of a calcined needle coke, that cracks run parallel to the axis of the flow texture18),19). The above structural model suggests that the cracks will run at the border of cigars, since shrinkage at the calcination stage should take place in order to decrease the diameter of each cigar. Thus, pores which are tracks of bubbles produced in the viscous mesophase during the carbonization are intimately related to the formation of the needle coke structure.

5. Mechanism of Formation of Needle Coke

The scheme of carbonization for anisotropic development to needle coke has been proposed by using a series of microscopic observations that compare coke with intermediates and products17),20),21). The model of carbonization into needle coke is illustrated in Fig. 317). Development of carbonization occurs in consecutive steps that include the formation of mesophase spheres and their growth and coalescence into a bulk mesophase of flow texture21)-25). This scheme clearly shows the route for the formation of large

### Table 1 Properties of Feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>S (wt%)</th>
<th>O (wt%)</th>
<th>C/H</th>
<th>( f^0 )</th>
<th>( \delta^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSVR</td>
<td>86.2</td>
<td>12.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.7</td>
<td>0.6</td>
<td>0.18</td>
<td>0.32</td>
</tr>
<tr>
<td>FCC-DO</td>
<td>88.9</td>
<td>9.5</td>
<td>0.1</td>
<td>0.4</td>
<td>1.1</td>
<td>0.8</td>
<td>0.54</td>
<td>0.32</td>
</tr>
</tbody>
</table>

a) Difference.  b) Carbon aromaticity according to Brown-Ladner method.  c) Degree of substitution of aromatic nucleus according to Brown-Ladner method.
isochromatic units of optical anisotropy, which was observed in needle coke. The extent of anisotropic development is strongly dependent on the conditions of carbonization, as well as on the feedstock.

The bulk mesophase is rearranged, into a flow texture parallel to the axis of test tube bomb, by gas evolution just at the point of solidification of the mesophase into a solid lump of needle coke. The period and amount of gas evolution at solidification of the mesophase essentially determine the extent of the orientation in the resultant coke. The period is strongly influenced by the temperature and pressure, as well as the structure and reactivity, of the feedstock. Three major factors (anisotropic development, viscosity of the bulk mesophase and gas evolution) essentially influence the quality of the needle coke. Optimum characteristic of each feedstock, in relation to reactivity and structure, therefore, may be required.

6. Optimum Condition of Carbonization to Improve the Quality of Needle Coke

The quality of needle coke depends on condition of carbonization, including both temperature and pressure, as well as properties of feedstock. These conditions and reactivity of feedstock influence the viscosity to increase, caused by condensation and the rate of gas evolution, further caused by the pyrolytic reaction, and thus affect the mesophase development and rearrangement of the resultant bulk mesophase. The influence of temperature and pressure on the carbonization profiles are summarized in Table 2. At the optimum temperature and pressure for a given feed, the viscosity increases moderately, allowing for sufficient growth and coalescence of the mesophase spheres to give a bulk mesophase of low viscosity.

At the same time, the amount of evolved gas at solidification is sufficient to rearrange the bulk mesophase into a needle-like orientation. At higher carbonization temperature, all of the changes take place very rapidly, which is too fast to allow growth of the isochromatic area. The development of the bulk mesophase and maximum evolution of turbulent gas tend to overlap. The texture, therefore, are arranged in a random fashion, forming flaky coke.

When the temperature is lower, the carbonization process is very slow. Carbonization of the components may not occur concurrently because of their respective different reactivities and lower mutual solubilities at the lower temperature. Gas evolved may not be sufficient to force the uni-axial arrangement of the bulk mesophase at solidification. As a result, needle coke is not so easily produced.

Higher pressure exceeding the optimum condition delays solidification because the lighter fractions in the feed do not vaporize and tend to dissolve the heavier fractions. This condition favors growth of the mesophase. The higher
pressure does not retard uni-axial arrangement because gas evolved at higher temperature tends to occur much earlier before solidification. No rearrangement of the bulk mesophase can be achieved, therefore, because of the early gas evolved at higher pressure.

7. Optimum Feedstock to Improve the Quality of Needle Coke

The reactivity of the feedstock is also important, having effect on the optimum carbonization conditions, because it influences not only the carbonization temperature and pressure, but also gas evolvement, which is also dependent upon the reactivity of the feedstock. Furthermore, the formation of bottom mosaic coke of higher CTE cannot be depressed only by the control of both carbonization temperature and pressure. Some kinds of modification of feedstocks and co-carbonization, therefore, were studied to improve the quality of needle coke, especially to eliminate the formation of bottom mosaic coke of higher CTE.

7.1. Co-carbonization of LSVR with a FCCDO

The co-carbonization of LSVR with FCCDO was studied at temperature range of 460 to 480°C.\(^{26,27}\) The co-carbonization certainly improved the orientation of flow texture and CTE of the coke. The nature of bulk mesophase and gas evolvement at the solidification stage for axial rearrangement of mesophase are strongly influenced by the carbonization reactivities of blended feedstocks. FCCDO moderates the carbonization progress of reactive LSVR, and LSVR supplies the sufficient gas evolvement during solidification, leading to excellent flow texture of axial arrangement. The formation of mosaic coke which may deteriorate the quality of the coke produced in a commercial delayed coker appeared to be caused by the phase separation between the paraffin and asphaltene fractions. Such a phase separation at an early stage found to be controlled within limits by the optimization of carbonization conditions. Montage photograph and microphotograph of the needle coke lump produced by tube bomb are shown in Fig. 4.

7.2. Modification of FCCDO to Improve the Quality of Needle Coke Produced in Co-carbonization with LSVR

7.2.1. Addition of High Aromatic Pitch

Co-carbonization of LSVR and FCCDO with the aid of Ashland A-240 pitch was studied to eliminate the bottom mosaic coke of higher CTE.\(^8\) The mechanism of formation of bottom mosaic coke is presumed to be as follows: the heaviest asphaltene of high reactivity in the LSVR is carbonized into quinoline insoluble (QI) sphere of low solubility in the paraffinic matrix because of insufficient aromaticity of FCCDO, at the early stage of the carbonization, precipitating spheres formed under such circumstances to the bottom, without any growth or coalescence, to form the mosaic coke. On the other hand, higher aromaticity of the matrix mediates such QI spheres and forms homogeneous texture in the whole area of coke. Higher aromatic FCCDO, therefore, may be expected to solve the problem of bottom mosaic coke, providing favorable CTE.

7.2.2. Dewaxing of FCCDO

As previously described, addition of high aromatic pitch was effective to eliminate the formation of bottom mosaic coke. Dewaxing of FCCDO was studied, using three kinds of FCCDO to increase the aromaticity of FCCDO\(^7\). As a result of this study, one of dewaxed FCCDO produced an excellent quality coke, free of any bottom mosaic coke. The analyses of light aromatic fractions in dewaxed FCCDO indicated that extent of alkyl substitution and its length are different from each other, and that higher the aromaticity of the fraction, the more favorable it is to eliminate the bottom mosaic coke.

7.2.3. Heat Treatment of FCCDO

Heat treatment of a FCCDO, of comparable higher paraffin content in the co-carbonization with LSVR, was studied to eliminate the unfavorable bottom mosaic coke.\(^8\) The heat treat-
ment of FCCDO removed paraffins and alkyl groups of longer chains on aromatic ring. Highly aromatized FCCDO increased mutual solubilities of components, which relates homogeneous reaction in the matrix at early stage co-carbonization, dissolving viscous mesophase derived from the most reactive portion in LSVR, which causes bottom mosaic structure.

The conception of favorable FCCDO, modified to produce the needle coke of better quality in the co-carbonization with LSVR, is summarized in Fig. 5. Modification of reactivity of the feedstock gives excellent coke. The general approaches for modification can be classified into two categories: first, the modification of the composition, second, the modification of the chemical structure. For the first approach, less paraffinic fraction in composition of FCCDO is better to prevent the phase separation of asphaltene fractions. For second approach, highly aromatized FCCDO, which has short alkyl side chain on aromatic ring, moderates carbonization.

7.3. Modification of LSVR to Improve the Quality of Needle Coke Produced in Co-carbonization with FCCDO

7.3.1. Solvent Deasphaltene Treatment of LSVR

Solvent deasphaltene treatment was applied to a LSVR to reduce or eliminate bottom mosaic coke which is formed in its co-carbonization with a paraffinic FCCDO. The amounts of C_5, C_6 and C_7 straight paraffins removed were 9, 3 and 1% of the asphaltene fractions from its heavier portions, respectively, according to their solubilities, giving C_5, C_6 and C_7 deasphalted oil (DAO).

The more asphaltene fractions are removed, the more mosaic coke, which forms their separate carbonization, are prevented. The complete removal, however, was achieved only by the co-carbonization of C_5 and C_6 DAO with FCCDO.

C_7 DAO still formed mosaic coke in its co-carbonization. From the analyses of DAO, it is suggested that the heavy portion of the asphaltene causes the formation of bottom mosaic coke.

7.3.2. Heat Treatment of LSVR

Pyrolytic modification of asphaltene fraction in a LSVR was studied to eliminate the bottom mosaic coke formation in its co-carbonization with FCCDO.

Highly restrictive conditions for pyrolytic modification of LSVR were found to be effective to eliminate bottom mosaic coke formation in its co-carbonization. Pyrolytic modification at higher or lower temperature than that of optimum conditions caused formation of the bottom mosaic coke. The analyses of heat-treated LSVR suggested that the heat-treated modification depolymerized the asphaltene and improved aromaticity, while producing closely limited amounts of heavy fraction or mesophase. Such a modified LSVR may obtain thermal stability and solubility in blending with FCCDO, to control co-carbonization, preventing phase separation at early stage. Schematic illustration of pyrolytic reaction of LSVR is shown in Fig. 6.

7.3.3. Modification of LSVR by Heat Treatment Aided with Hydrogen Donor

A powerful hydrogen donor has been extensively studied in coal liquefaction. During the pyrolytic reactions of petroleum residue as well as of coal, the donor providing hydrogens was such as tetrahydrofluoranthene (4HFL). The donor is useful, being expected to control the pyrolytic reactions for radical stabilization (capping), which is bond fission through hydrogenation at the aromatic sites and hydrocracking. Thus, pyrolytic depolymerization of asphaltene fraction in LSVR was achieved at 480–500°C with the aid of 4HFL as a hydrogen donor. Such depolymerization was effective for decrease of the bottom mosaic coke in co-carbonization with FCCDO. The role
of the hydrogen donor in such pyrolysis was discussed to clarify the scheme for reducing the molecular weight of the heaviest portion in the asphaltene without the formation of coke precursor. The dealkylation accelerated with the donor may fission the methylene bonds with the aromatic nuclei in the asphaltene. Therefore, the aromaticity and thermal stability of the heat-treated LSVR may be increased.

7.3.4. Catalytic Hydrotreatment of LSVR

Catalytic hydrotreatment of a LSVR was studied to eliminate the formation of bottom mosaic coke of higher CTE. A Ni–Mo/Silica–Alumina catalyst designed for residual oils converted completely the asphaltene fraction in LSVR to be soluble in hexane at 400 ºC, under 15 MPa H₂. Excellent needle coke, free of bottom mosaic texture, was produced from the hydrotreated LSVR in the co-carbonization with FCCDO. Another catalyst for the heavy distillate left some amount of hexane insoluble asphaltene fraction, although it was certainly depolymerized. Such a hydrotreated LSVR still formed a little but distinct amount of mosaic texture. The pore distribution of support in the catalyst may be important factor in the hydrotreatment of LSVR.

The evaluation on modification of LSVR in this study is summarized in Table 3.

All method on modification of LSVR is effective to eliminate the formation of bottom mosaic coke of higher CTE.

8. Conclusions

Large amount of petroleum needle coke, very essential feed for electrode and other carbon artifacts, has been long produced in delayed cokers. Gradually, its quality is improved at reduced cost, being based principally on empirical or trial-and-error approaches. More logical approaches to develop ideal coke and its production have become necessary in recent years, because recycling of a huge amount of scraps have started, economically and efficiently. In the present paper, authors described some basic aspects to produce the needle coke of excellent quality. Carbonization in the tube bomb has well simulated the coking in the commercial coker, allowing the study of mechanism of reaction in the laboratories. The precise recognition of differences between tube bomb and delayed coker may provide keys to further precise understanding of coking in the delayed coker drum where complex physical, chemical and transport phenomena take place simultaneously. More extensive trial and study of co-carbonization using blends of wider range of feeds is expected to improve the quality of needle coke.

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要 旨
石油系ニードルコークスの生成機構と品質向上に関する研究
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電気炉製鋼用人造黒鉄電極は製鋼技術の進歩とともに著しく品質改善され、これに伴い電極用フィラーであるニードルコークスに対する品質改善が強く要望されている。本研究では、石油系ニードルコークスの生成機構を明らかにするとともに、その生成過程において原料油の果たす役割を芳香族性の観点から総合的にとらえ、流動接触分解残油（FCCDO）の一連の改質、あるいは低塩基減圧残油（LSVR）中のアスファルテンの除去、さらには分解を行って不均質なコークスの発生原因を論理的に明確化するとともに、その品質改善を試みた。

実装向けの新炭化条件が再現できるチューブ式を用いて原料油を各種条件で熱処理し、ニードルコークスの生成機構を提案した。ニードルコークスの性状の中で最も重要な熱膨張係数（CTE）は、炭素結晶層面の磁配対性に強く影響され、バルクメソフーズの形態変成ならびにバルクメソフーズが固着しニードルコークスに移行する際のガス発生量が適切であることが重要であることが明らかになった。また、FCCDO と LSVR を共重油すると、良好なバルクメソフーズが形成され、かつ炭化固定時のガス発生量が適量であるため、低 CTE のニードルコークスが得られることが明らかにされた。一方、ニードルコークスの CTE は、CTE が低いモザイク組織のコースの多層に強く影響される。本研究では、モザイク組織のコース生成の抑制を目的として FCCDO ならびに LSVR の種々の改質を試みた。FCCDO の改質によってモザイクコースの生成を抑制する方法としては、A-240 ビッチのような芳香族性の高いビッチの添加、脱ろう、熱処理が効果的であることが、コース生成機構をベースに明らかにされた。一方、LSVR の改質についてもモザイクコースの生成を抑制する方法としては溶剤脱少し、熱分解、水素供与剤存在下の熱分解が、効果的であることが明らかになった。

Keywords
Carbonization, Needle coke, Vacuum residue, FCC decant oil, Bottom mosaic coke