Effect of Petroleum Cokes on Property Changes in Extruded Rods during Graphitization

M. Kakuta, N. Tsuchiya, H. Tanaka and K. Noguchi*

Koa Oil Company, Osaka Research Laboratory,
2-1 Takasago, Takaishi-Shi, Osaka 592, Japan
* Koa Oil Company, 2-6-2 Ohte-Machi, Chiyoda-Ku, Tokyo 100, Japan

(Received 11 June 1984)

Calcined cokes as well as baked rods using the same cokes as fillers were heat-treated at various temperatures, and their structural and property changes with heat treatment temperature were studied. Transitions in property changes with HTT in extruded rods were observed around 2,000°C, which were able to be related with the development of pores below 2,000°C and that of crystalline structure above 2,000°C in the coke particles. From this study, it was clearly recognized that the characteristics of the final graphite electrodes are strongly dependent on the properties of the raw material coke.

1. Introduction

In recent years, so-called needle-like coke has been used as fillers for graphite electrodes in the steel manufacturing industries in order to improve their thermal shock resistance. This type of coke has the properties of high density, low contents of ash and sulfur, low thermal expansion coefficient and the development of an optically anisotropic texture. We reported previously how the properties of the raw material coke affect the characteristics of the final products manufactured by extrusion and graphitization; thermal expansion coefficient and bending strength of the final products can be closely related with thermal expansion coefficient of the calcined coke.

In the present work, calcined cokes as well as baked rods using the same cokes as fillers were heat-treated at various temperatures, and their structural and property changes with heat treatment temperature were studied.

2. Experimental

Two calcined cokes were used; one is a regular-grade petroleum coke (the sample No. 4), which has been used in industries as a filler for graphite electrodes, and the other is a needle-grade one (the sample No. 7). In Table 1, the properties of the calcined cokes used are summarized. The sample No. 7 has a higher apparent density and lower thermal expansion coefficient than the sample No. 4. Microscopic observation reveals that the optical texture of the sample No. 4 is a mixture of mosaic and fibrous ones, while that of the sample No. 7 is mainly fibrous, as shown in Fig. 1. Both cokes were pulverized under 3 mesh (673μm) and were heat-treated at 1,400°C to 2,800°C in vacuum up to 2,000°C and thereafter in argon. The heating rate was 20°C/min. and holding time at a top temperature was 30 minutes. The coke samples heat-treated were subjected to chemical analyses of sulfur and nitrogen according to Japanese Industrial Standards (JIS) M8813 after pulverizing to a size of less than 60 mesh (280μm), and also to the measurement of interlayer spacing.

Table 1. Properties of calcined cokes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample description</th>
<th>Density (g/cm³)</th>
<th>Coefficient of Thermal Expansion (10°C-300°C) (10⁻⁵/°C)</th>
<th>Sulfur (wt. %)</th>
<th>Ash (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>E.P.C.</td>
<td>1.30</td>
<td>1.7</td>
<td>0.49</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>N.P.C.</td>
<td>1.39</td>
<td>1.2</td>
<td>0.52</td>
<td>0.05</td>
</tr>
</tbody>
</table>

E.P.C.: Electrode-Petroleum Coke  
N.P.C.: Needle-petroleum Coke  
Extruded Pieces, 1000°C HT (Baked)  
5mm dia. x 50 mm length,  
Longitudinal Direction
3. Results and Discussion

In Figure 2, the changes of properties with heat treatment temperature (HTT) are summarized on the coke particles themselves ($d_{002}$, La_{110}, and contents of sulfur and nitrogen) and on the extruded rods (bending strength, Young's modulus, electrical resistivity, bulk density and thermal expansion coefficient).

On all of the properties examined, bending strength, Young's modulus, electrical resistivity, bulk density and thermal expansion coefficients in two directions, marked differences are observed between the rods derived from two kinds of cokes having different optical texture even at the stage of baking (around 1,000°C). These differences are kept at a whole range of HTT, except electrical resistivity on which no difference is detected above 2,000°C. As shown in Fig. 2-a and 2-b, on the other hand, the structural parameters, interlayer

Table 2. Mixing ratio of coke particles with different sizes and binder pitch.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Sizes</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From</td>
<td>To</td>
</tr>
<tr>
<td>Coke Particles</td>
<td>8 mesh (2380 μm)</td>
<td>20 mesh (840 μm)</td>
</tr>
<tr>
<td></td>
<td>20 mesh (840 μm)</td>
<td>35 mesh (420 μm)</td>
</tr>
<tr>
<td></td>
<td>100 mesh (149 μm) under</td>
<td>-</td>
</tr>
<tr>
<td>Coal Tar + Binder Pitch</td>
<td>28 mesh (590 μm) under</td>
<td>-</td>
</tr>
</tbody>
</table>
* Softening Point: 98°C
Effect of Petroleum Cokes on Property Changes in Extruded Rods during Graphitization

Fig. 2. Changes of properties on the coke and the rods prepared from the same coke with heat treatment temperature.

- Interlayer spacing, $d_{002}$
- Apparent crystallite size, $La_{110}$
- Sulfur content
- Nitrogen content
- Bending strength
- Young’s modulus
- Electrical resistivity
- Bulk density
- Thermal expansion coefficient.

- ○-○: the sample No. 4,
- △-△: the sample No. 7.

spacing $d_{002}$ and crystallite size $La_{110}$, of coke particles show no particular differences between two cokes.

On most of the properties, transitions of their HTT dependence are observed at about 2,000°C; on electrical resistivity, a transition from gradual to sharp decrease (Fig. 2-g), and on Young’s modulus and bending strength from sharp decrease to slight increase (Fig. 2-e and 2-f). A similar transition in HTT dependence is also detected on bulk density of the rod made from the coke No. 4 (Fig. 2-h). Thermal expansion coefficients of the longitudinal and the transverse (along and across grains) directions, however, do not show any transition in their HTT dependence, showing gradual decrease in whole range of HTT.

The properties on coke particles are also found to show similar transitions around 2,000°C; interlayer spacing $d_{002}$ starts to decrease suddenly (Fig. 2-a), and crystallite size $La_{110}$ shows a significant increase (Fig. 2-b) above 2,000°C. Sulfur and nitrogen contents of the coke particles are drastically reduced below 2,000°C, particularly almost all nitrogen in coke driven out up to 2,000°C (Fig. 2-c and 2-d). It is well-known that driving-out of cracked hydrocarbons and other impurity atoms, such as sulfur and nitrogen, develops pores in coke particles\(^3\). Some types of cokes show abnormal expansion called “puffing” around 2,000°C, which is attributed mainly to the quick driving-out of sulfur contained in the cokes\(^4\text{--7}\). Other ingredients such as nitrogen are also considered to cause similar effects\(^8\text{--9}\). Such a non-reversible expansion in coke particles brings about the development of pores in the formed bodies derived from the coke.

Therefore developments of crystalline structure and that of pores with HTT in coke particles are presumed to cause the changes in various properties with HTT and their transitional changes at about 2,000°C in the rods prepared from the cokes. A sharp decrease in electrical resistivity above 2,000°C is considered to be due to the development of crystalline structure in the coke particles. Its small change below 2,000°C and a small difference between two kinds of rods suggest little effect of pore development in the coke particles. On the other hand, sharp decreases in bulk density, Young’s modulus and bending strength with HTT
upto 2,000°C seem to depend mainly on the development of pores in the coke particles. Marked differences in these properties between two kinds of rods are clearly due to the difference in pore structure of the coke particles as shown in Fig. 1. It is reasonable to observe a large difference in these properties on the rods prepared from two kinds of cokes already at baking stage. Slight increases in these properties above 2,000°C may be attributed to the crystallite growth and the development of graphite structure.

Conclusively, transitions of property changes with HTT in extruded rods made from cokes were observed around 2,000°C, which were able to be related with the development of pores below 2,000°C and that of crystalline structure above 2,000°C in the coke particles. From this study, it was clearly recognized that the characteristics of the final graphite electrodes are strongly dependent on the properties of the raw material coke.

Acknowledgement — The authors express thanks to Mr. J. Suzuki, Managing Director of Koa Oil Company, for his help in the presentation of this paper.

References