RELATION BETWEEN SULFUR CONTENT AND X-RAY PROFILE OF COKE

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Introduction

It have been reported already that carbon materials containing sulfur and nitrogen form partially graphitized part at relative low temperatures below 2000°C. Recently, Fitzer et al(1) described that the catalytic effect of sulfur on graphitization of cokes with 0.4-0.7wt% sulfur causes the reduction of the activation energy for graphitization from 7-10eV to about 3-4eV between 1400°C and 2000°C.

This paper reports on the results of X-ray measurements and observation by high-electron microscope of high sulfur content petroleum cokes heat-treated between 1100°C and 1300°C in order to clarify the origin of partial graphitization within the sulfur containing cokes.

Experimental

Khafji and Gachsaran vacuum residues were heat-treated at 450°C for 15 hr. Meso-carbon microbeads were mesophase spherules formed in Khafji vacuum residue heat-treated at 420°C, and mesophase spherules were separated from the heated residue as quinoline-insolubles. These microbeads were heat-treated at 450°C for 15 hr. The sulfur contents in sample cokes are shown in Table 1.

Table 1. Sulfur content in the samples

Sample	Sulfur (wt%)
Khafji coke	6.7
Gachsaran coke	3.4
Microbeads	8.3

Those samples were heated at HTT above 1000°C, and were examined by X-ray measurement and high-resolution microscopy.

Results and Discussion

Khafji and Gachsaran cokes were heat-treated at 1000-1700°C for 0.5 hr. (002) X-ray diffraction profiles of the cokes consist of two components corresponding to ordinary soft carbon phase (26° component) and graphitized phase (26.5° component) for Khafji coke heat-treated above 1300°C and for Gachsaran coke heat-treated above 1400 °C. Representative (002) diffraction profiles are shown in Fig.1 for both the coke heat-treated at 1100, 1200 and 1300°C for various times in the range of 0.5 hr to 30 hr. At HTT 1200°C, the observed intensity of the 26.5° component for Khafji coke with the initial sulfur content of 6.7wt% increases with an increase of residence time, and the 26° component exists as a shoulder on the 26.5° component for Khafji coke heated for 30 hr. (Fig.1-a). In the case of Gachsaran coke, the two components of 26° and 26.5° components appear when the coke is heat-treated with times longer than the case of Khafji coke (Fig.1-c). The (002) diffraction profile of Khafji cokes heated at 1100°C for 30 hr is similar to that of the cokes heated at 1200 and 1300°C (Fig.1-b). Gachsaran coke heated at 1100°C for 30 hr exists the 26° component only (Fig.1-d).

For Khafji coke obtained at 1200°C for 30 hr, (112) diffraction apprats slightly, indicating a three dimentional order within the coke.

Fig.2 shows high-resolution micrograghs of Khafji cokes heat-treated at 1200°C for 0.5 hr and 30 hr. A lot of small layer plane segments can be seen in the coke heat-treated for 0.5 hr. There is no prefered orientation. The coke treated for 30 hr shows the existence of well-ordered layer planes. This well-ordered regions are present in quantity in the coke and are considered to correspond to the 26.5° component.

In Fig.3 are shown plots of sulfur content in the cokes as a function of HTT. Sulfur release in the cokes during heat-treatment occurs at a definite temperature for each coke, i.e., 1300°C for the Khafji coke and 1400°C for the Gachsaran coke. The temperatures at which sulfur release occurs suddenly, correspond to the temperatures at which the 26.5° component appears in the (002) diffraction profile. Therefore, the appearance of the 26.5° component may be related to the sudden release of sulfur in the cokes. A similar phenomenon was observed for the coke from a mixture of naphthalene and inorganic sulfur compound. In this case, the 26.5° component becomes predominant as the sulfur content decreases.

On the other hand, the meso-carbon microbeads were heat-treated at 1000-1500°C for 0.5 hr. The heated microbeads gave the (002) diffraction profiles of the 26° component only at all the temperature range of 1000°C to 1500°C. The sulfur contents in the heated microbeads, as shown in Fig.4

decrease gradually with the raising temperature from 450°C to 1300°C and decrease in fairly large quantities at the temperature between 1300°C and 1400°C. This sulfur release in the heated microbeads is different behavior from that in the Khafji and the Gachsaran cokes. (see Fig.3)

There is no appearance of the 26.5° component in the case of the heated microbeads. This indicates that the sulfur release which occurs gradually at the temperature below 1300°C reduces the catalytic effect of sulfur for the formation of the graphitized phase to be caused by the sulfur release, even if the sulfur content decreases in fairly large quantities at the temperature 1300°C and 1400°C.

Reference

(1) E. Fitzer and S. Weisenburger, Carbon, 14, 195 (1976)

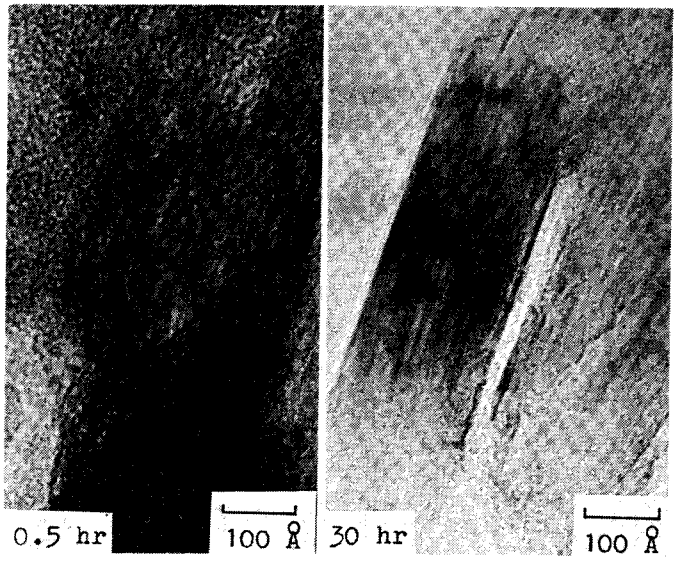

Fig. 2 High-resolution electron micrographs of Khafji cokes

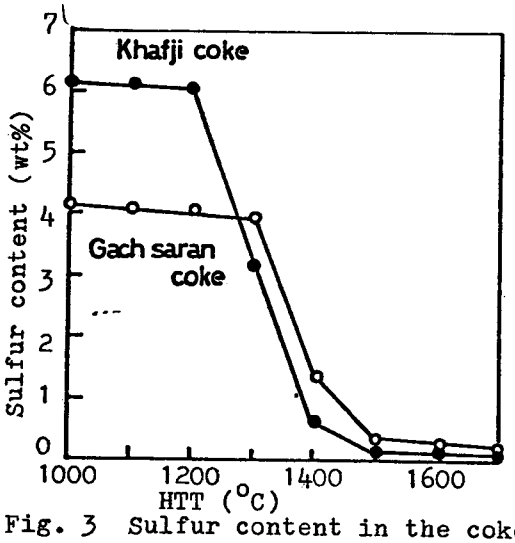

Fig. 3 Sulfur content in the cokes

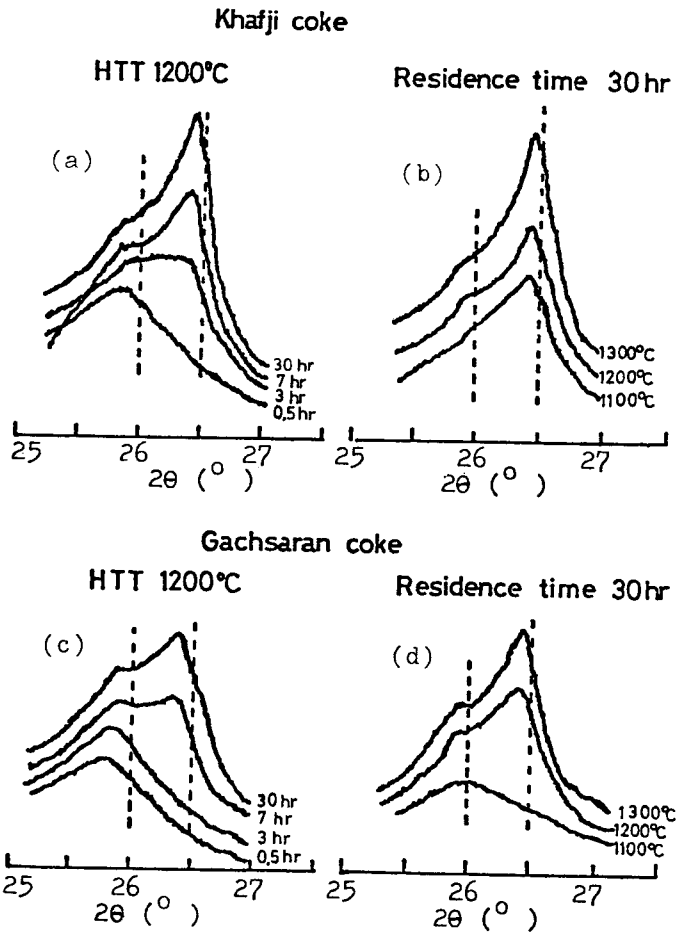

Fig. 1 (002) diffraction profiles

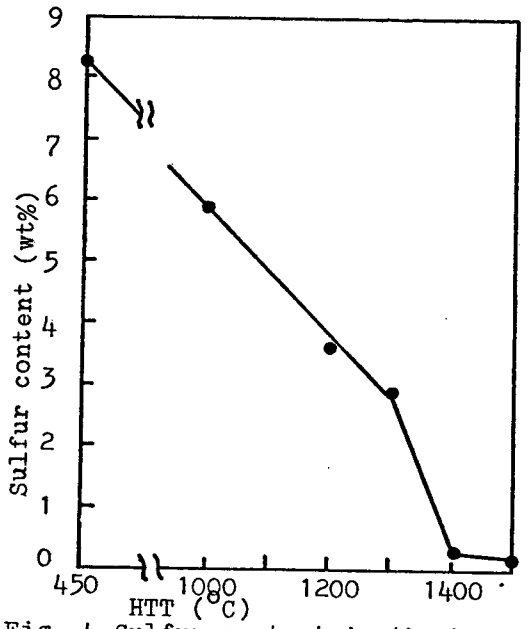

Fig. 4 Sulfur content in the heated microbeads