An X-ray Diffraction Line Observed in Acid-treated Carbonized Coals and Paramagnetic Absorption

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During our extensive examinations of carbonization mechanism of various coals by means of X-ray diffraction[1], it has been experienced for several samples that a new diffraction line appears other than the usually observed carbon patterns which are indexed as (002) and (100). The characteristics of the line and its occurence are as follows:

(1) The lattice constant is 4.18 ±0.10Å, the line existing just inside (002) band. The line is fairly intense and sharp. (See Fig. 1).

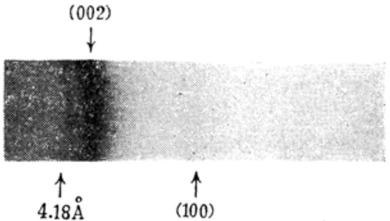

Fig. 1. The position of 4.18Å line

No other pattern than this and carbon patterns has been observed on the film, using Kodak No-screen X-ray film in 45 mm. radius powder camera covering 5–80° Bragg angle and Ni-filtered CuKα ray operated at 35 kV. and 20 mA. No low-angle band was recognized by a Geiger-counter goniometer recording up to 1° of Bragg angle.

(2) The line has been observed in the samples produced from the following bituminous coals (single or blended) and carbonized up to the following maximum temperatures: American coking coal, 520 and 620°C; Yatake coking coal, 500°C; blended coal slack of 25 parts American coking coal and 75 parts Yubari weakly coking coal, 600°C; blended coal slack of 6 kinds of bituminous coals in order to obtain a coherent coke, 200, 300 and 400°C. The volatile matter content (dry ash-free basis) of the single or blended coals prior to carbonization was approximately 34 to 43%. The carbonization was carried out in an experimental electric furnace at a rate of elevation of temperature of 3.3°C/min. in nitrogen atmosphere. At other carbonization temperatures, the similar coals did not show the line by similar treatments.

(3) The line appears only after the carbonized samples are boiled with 20% HCl for approximately forty hours or more, with reflux and frequent renewing, followed by alternative wetting and gentle evaporating with 40% HF in Pt crucible over fifteen times.

(4) The line is stable at room temperature for over one year, but disappears by heating the sample at 600°C for ten minutes in nitrogen atmosphere.

The probable mistakes in X-ray techniques, e.g., diffraction by CuKβ ray or WLα_2 ray, diffraction caused by camera body or sample amount, etc. have all been denied by careful experiments. The cause of the line is unlikely in the inorganic impurities, because the treatments with acids result naturally in gradual diminishing of inorganic components and, in particular, because no accompanying lines exist and the line disappears by heating the sample at 600°C. The lattice parameter is not consistent with any carbon halide patterns so far reported.

This phenomenon may be at fault but is interesting if it is remembered that the distinct paramagnetic resonance absorption has been reported recently for coals carbonized especially up to 500–600°C[2], and the absorption has been ascribed to the existence of some broken carbon bonds. The paramagnetic resonance absorption of one of the series which showed the line (cf. Table I) was measured by Mr. I Miyashita using a microwave of 3.2 cm. wave-length[3].

These results may imply that a correlation is expected to be found between the appearance of the 4.18Å line and the structural disturbance during a certain stage of carbonization before the carbon cluster commences to grow up to more rigid hexagonal lamellae in coke. To show a rather sharp diffraction pattern, the formation of a crystallographic lattice by means of acid treatments is expected, for example in the peripheries of cluster. The pre-existence of some broken bonds may be advantageous for further lattice development. According to Miyashita[4], the decrease of the absorption from 10×10^{-8} to 8.5×10^{-8} in accordance with the appearance of the line after acid treatments coincides with the general rule that the value of absorption decreases with the development of crystalline state, though he holds the view that the absorption may be due to a state of triplet and not necessarily to the broken bonds.

TABLE I

PARAMAGNETIC RESONANCE ABSORPTION OF CARBONIZED COALS

Coal slack carbonized: 25 American coking coal and 75 Yubari weakly coking coal.

Sample No.	Carbonization Temperature °C	4.18Å Line	x_g
1	400	−	2.6×10^{-8}
2	600	−	$10.\ \times10^{-8}$
3*	600	+	8.5×10^{-8}
4	800	−	No absorption

* Sample 3, which shows the 4.18Å line, was prepared by treating Sample 2 with acids as described above.

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