Chemistry

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1957

SovietRxiv

Abstract

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ON THE QUESTION OF THE GRAPHITIZATION OF CARBONACEOUS SUBSTANCES

(Presented by Academician G. V. Kurdyumov, 14 XI 1956)

In an X-ray study of the graphitization of cokes it was found that, on the radiographs of samples calcined at a temperature of 1700–1800°, narrow lines appear, located at angles of 22°35′ (intense line), 33° (weak), and 41°45′ (intense). The positions of these lines, as is seen from Fig. 1 and Table 1, coincide neither with the positions of the lines of the α-modification of graphite nor with the positions of the lines characteristic of β-graphite. The calculation of the angular positions of the graphite lines was carried out both for the spacing between the layers in the graphite crystal $d = 3.35$ Å and for $d = 3.42$ Å, characteristic of the network structure of carbon.

Table 1

Indices of graphites	Modification of graphite	θ for $d =$ 3.35 Å	θ for $d =$ 3.42 Å	θ of additional lines observed in images	Indices of Si solution in Fe	Lattice parameter	Silicon concentration, %
002	$\alpha + \beta$	13°20′	13°				
100	α	21°10′	21°10′				
$10^2/_3$	β	21°46′	21°39′				
101	α	22°20′	22°15′	22°36′	110	2.84	13
$10^3/_4$	β	23°14′	23°				
004	$\alpha + \beta$	27°18′	26°44′	∼ 33°	200		
110	$\alpha + \beta$	38°44′	38°44′				
112	α	41°48′	41°40′	41°43′	211	2.84	13
006	$\alpha + \beta$	43°42′	42°24′				

The fact that the positions of the above-mentioned lines are close to the positions of the graphite lines (the lines located at an angle of 22°35′ to the graphite line (101) and at an angle of 41°45′ to the graphite line (112)) apparently allowed some researchers to regard these lines as belonging to a special modification of graphite. Thus, in work (1) a β-graphite modification, artificially obtained

Fig. 1

Figure 1: Fig. 1

by calcining petroleum coke, is reported, with parameters *a* and *c* larger than those of natural β-graphite. In work (2) data are presented from which the conclusion was drawn that the temperature at which graphitization begins for the carbonaceous substances studied by the author is 1700°. Both of these conclusions do not agree with the experimental data known from the literature on the study of the graphitization of carbonaceous substances. In a number of works (3, 4) it has been shown that, with a relatively large change in the parameter *c* in various carbonaceous substances depending on the conditions of their formation (coals of different degrees of metamorphism, peat, carbon blacks, cokes, etc.), the parameter *a* remains constant and equal to 1.42 Å for the most diverse carbonaceous substances. Also convincing are the data (5), according to which the onset of true

graphitization occurs only at a temperature of 2000°. In these cases, broad maxima from the oblique planes of graphite (101) and (112) appear on the radiographs, while the maxima (002) and (004) shift toward larger angles (during graphitization the distance between the layers decreases from 3.42 Å to 3.36 Å).

Below are presented additional data obtained by us in the study of the graphitization of carbonaceous substances. It is of interest to clarify the nature of the non-carbon diffraction lines that are found on radiographs of cokes calcined at a temperature of 1700-1800°. Study of a large amount of spectral-analysis data showed that in carbonaceous substances (cokes), even after their very thorough deashing, traces of iron, silicon, and aluminum are found. It would therefore be natural in such a case to assume the presence in the cokes of small amounts of oxides of iron, silicon, and aluminum. According to physicochemical-analysis data (6), at temperatures of 1700-1800° there is an intensive process of reduction of silicon from its oxides by solid carbon. The presence in the carbonaceous substance of iron atoms accelerates the process of silicon reduction, accompanied by the formation of the compound FeSi. Taking these data into account, it could be supposed that the non-carbon lines found on radiographs of cokes calcined at a temperature of 1700-1800° belong to an α-solid solution of silicon in iron. To check this assumption, the lattice parameter was determined from the position of the lines on the radiographs (regarding them as reflections (110), (200), (211) of a body-centered lattice). From the values of the latter, the concentration of silicon in the solution Si in Fe was calculated; for a number of specimens it proved to be equal to 10-13%. This result agrees well with the Fe—Si phase diagram (6,7), according to which the maximum silicon content in the solid solution of Si in Fe at room temperature is 13%.

Fig. 1. Microphotograms of the 100 and 101 lines: *a* —coke calcined at 1700°; *b* —graphite. Along the abscissa axis here and in Fig. 2 are plotted distances from the center of the photograph.

Fig. 2

Figure 2: Fig. 2

The assumption that in cokes calcined at temperatures of 1700-1800° a solid solution of silicon in iron is formed is confirmed by experiments with reed charcoal. We subjected pure reed charcoal to calcination, and the same charcoal with small additions of iron and silicon oxides. On the radiograph of pure reed charcoal only the maxima (002), (100), (004), and (110), characteristic of a reticular structure (^{4}), are found; on the radiographs of reed charcoal with additions of iron and silicon oxides, however, lines located at angles of 22°36′, 33° and 41°44′ are also clearly manifested. At calcination temperatures of 1900-2000° the lines of the α-solid solution of silicon in iron are not found. This can be explained by the fact that at temperatures of 1900-2000° the vapor pressure, and consequently also the evaporation rate, of the solid solution increases sharply (^{6}). At the same time the evaporation rate increases with decreasing external pressure, as is evident from Fig. 2, which gives microphotograms of radiographs in the angular region from 20 to 23°.

All the data presented above unambiguously confirm the supposition that the lines appearing on radiographs of cokes and other carbonaceous substances calcined at temperatures of 1700-1800° belong—

belong to the α-solid solution of Si in Fe. The formation of a solid solution of silicon in iron at temperatures of 1700-1800° is observed not only when cokes are fired under laboratory conditions.

On radiographs of coke specimens taken from the hearth of a blast furnace, fairly intense lines are also found at the angles: 22°28′—22°40′; 32°40′—33°; 41°40′—41°46′.

Fig. 2. Microphotograms: **a**—of coke annealed at 1700° at $p = 400$ mm Hg; **b**—of the same coke annealed at 1700° at $p = 40$ mm Hg.

Conclusions

It has been shown that firing cokes at temperatures of 1700-1800° is accompanied by the formation of an α-solid solution of silicon in iron. On radiographs in these cases, narrow lines appear at the angles 22°35′, 33°, and 41°45′.

In studying the graphitization of carbonaceous substances at temperatures above 1600°, one should take into account the possibility of the formation in these substances of a solid solution of silicon in iron. The angular position of the diffraction lines of the solid solution is close to the position of the graphite lines, which may serve as a source of erroneous conclusions about the character of graphitization.

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of the Central Scientific-Research
Institute of Ferrous Metallurgy

Received
5 XI 1956

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Note: Figure translations are in progress. See original paper for figures.