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Effect of Iron and Chromium on the Graphitization Behavior of Sulphur-containing Carbon

V. A. Tyumentsev*, E. A. Belenkov*, S. I. Saunina*, S. A. Podkopaev, and G. P. Shveikin*****

* *Chelyabinsk State University, ul. Br. Kashirinykh 129, Chelyabinsk, 454136 Russia*

** *Chelyabinsk Electrode Works, Chelyabinsk, Russia*

*** *Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences, ul. Pervomaiskaya 91, Yekaterinburg, 620219 Russia*

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Abstract—The graphitization behavior of sulphur-containing carbon materials and the effects of iron and chromium were studied. After heat treatments at 1300–1600°C, the carbon materials containing >1.5 wt % S or 0.3 wt % S + 1.5 wt % Cr_2O_3 consist of rather perfect ($\Delta d/d \simeq 0.002$), large (>100 nm) graphite particles and ultrafine carbon matrix. The addition of fine iron particles decreases the amount of graphite particles formed at these temperatures by a factor of two.

INTRODUCTION

Carbon materials prepared from petroleum cokes are typical ultrafine-grained systems. However, unlike oxide powders, they contain substantial amounts of dissolved impurities, including sulphur [1]. On heating, grain growth in these materials is accompanied by removal of dissolved impurities. These concurrent processes activate mass transfer in microvolumes of the carbon material, leading to the formation of fairly large, up to 1 μm in size, graphite particles [2, 3]. The resulting nonuniformity in grain size and phase composition deteriorates properties of the material. According to [4], iron additions improve the performance of graphitized carbon. However, the effects of metallic additives on the properties of graphitized carbon produced from high-sulphur cokes have not yet been investigated in sufficient detail. In this work, we studied the effect of Fe, Fe_2O_3, and Cr_2O_3 additives on the graphitization behavior of high-sulphur carbon materials.

EXPERIMENTAL

We studied samples prepared from cokes using pitch as a binder and containing 0.3, 1.5, or 2.5 wt % S and various amounts of fine-particle additives. The samples were heated in a Tammann furnace at 300 K/h to the preset temperature and held there for 3 h. X-ray diffraction (XRD) measurements were performed on a DRON-3 diffractometer (filtered CuK_α and CoK_α radiations). The uniformity of the material was assessed by transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

The effect of sulphur impurity on the formation of polycrystalline graphite from carbon manifests itself at

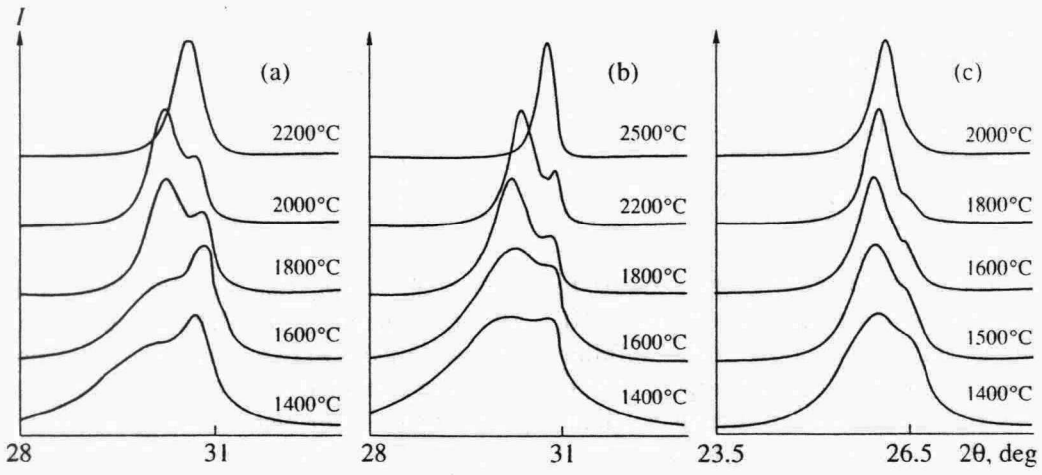

Fig. 1. 002 XRD profiles of heat-treated carbon materials containing (a) 2.5 wt % S, (b) 2.5 wt % S + 10 wt % Fe, and (c) 0.3 wt % S + 1.5 wt % Cr_2O_3.

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d, L_c, $\Delta d/d$, and G values for partially graphitized carbon materials

Weight percent of sulphur and additives	t, °C	d_{002}, nm	L_c, nm	d'_{002}, nm	$(\Delta d/d) \times 100$	L_c, nm	G, %	d''_{002}, nm	$(\Delta d/d) \times 100$	L_c, nm
		observed profile		first component				second component		
2.5% S	1200	0.3474	5.8	0.3374	<0.1	>100	28	0.3513	1.23	12
	1400	0.3436	6.4	0.3373	<0.1	>100	18	0.3448	0.71	26
	1600	0.3432	8.6	0.3374	<0.1	>100	56	0.3463	0.64	22
	1800	0.3428	13	0.3374	<0.1	>100	18	0.3437	0.57	38
	2000	0.3420	18	0.3373	<0.1	>100	14	0.3425	0.46	43
	2200	0.3397	26	–	–	–	–	–	–	–
2.5% S	1200	0.3466	7	0.3370	0.27	>100	2.5	0.3469	4.2	11
10% Fe	1400	0.3465	8	0.3370	1.1	>100	14	0.3480	3.07	7
	1600	0.3442	12	0.3367	1.05	>100	20	0.3456	2.04	24
	1800	0.3430	20	0.3362	0.23	95	6	0.3434	1.28	45
	2200	0.3416	28	0.3368	0.32	>100	14	0.3423	0.86	52
	2500	0.3376	54	0.3365	0.27	>100	62	0.3383	0.51	75
1.5% S	1400	0.3461	30	–	–	–	–	–	–	–
	1500	0.3430	15	0.3360	0.42	>100	14	0.3440	2.59	15
	1600	0.3429	35	0.3365	0.77	>100	16	0.3440	1.69	26
	1700	0.3425	35	0.3360	0.69	>100	9	0.3431	1.47	35
	1800	0.3415	44	0.3354	<0.1	>100	0.7	0.3416	0.84	42
	2000	0.3397	44	–	–	–	–	–	–	–
1.5% S	1400	0.3448	26	0.3360	0.68	>100	5	0.3452	3.17	25
1% Fe_2O_3	1500	0.3444	23	0.3365	0.67	>100	8	0.3450	2.46	21
	1600	0.3430	25	0.3360	0.33	>100	4	0.3433	1.74	22
	1700	0.3430	35	–	–	–	–	–	–	–
0.3% S	1400	0.3447	7.4	–	–	–	–	–	–	–
	1600	0.3434	6.7	–	–	–	–	–	–	–
	1700	0.3427	16	–	–	–	–	–	–	–
	1800	0.3428	16	–	–	–	–	–	–	–
	2000	0.3409	21	–	–	–	–	–	–	–
0.3% S	1400	0.3422	6.5	0.3353	<0.2	75	5.4	0.3425	2.43	20
1.5% Cr_2O_3	1500	0.3421	10	0.3353	<0.1	>100	4.8	0.3425	1.60	32
	1600	0.3421	13	0.3359	<0.2	75	7.7	0.3426	1.38	34
	1700	0.3422	15	0.3359	<0.2	90	2.4	0.3426	0.73	35
	1800	0.3414	20	0.3359	<0.1	>100	1.2	0.3415	0.59	41
	1900	0.3386	24	–	–	–	–	–	–	–
	2100	0.3387	25	–	–	–	–	–	–	–
0.3% S	1400	0.3449	7.3	–	–	–	–	–	–	–
1.5% Fe_2O_3	1600	0.3440	11	–	–	–	–	–	–	–
	1700	0.3428	19	–	–	–	–	–	–	–
	1800	0.3433	23	–	–	–	–	–	–	–
	2000	0.3402	32	–	–	–	–	–	–	–

temperatures as low as 1200–1300°C. In contrast to what is observed in low-sulphur materials (<0.5 wt % S), the profile of the strongest peak, 002, of the ultrafine carbon containing 2.5 wt % S after firing at 900°C becomes asymmetric (Fig. 1a). With increasing treatment temperature, the width of this peak decreases, and its centroid shifts to larger angles. The splitting of the 002 peak shows that the structure of the material becomes nonuniform. The asymmetric peak was deconvoluted into two symmetrical components by the procedure detailed elsewhere [3]. The results are given in the table. After heat treatment at 1200–2000°C, the high-sulphur material consists of large coherently scattering domains (CSDs) with the graphite structure

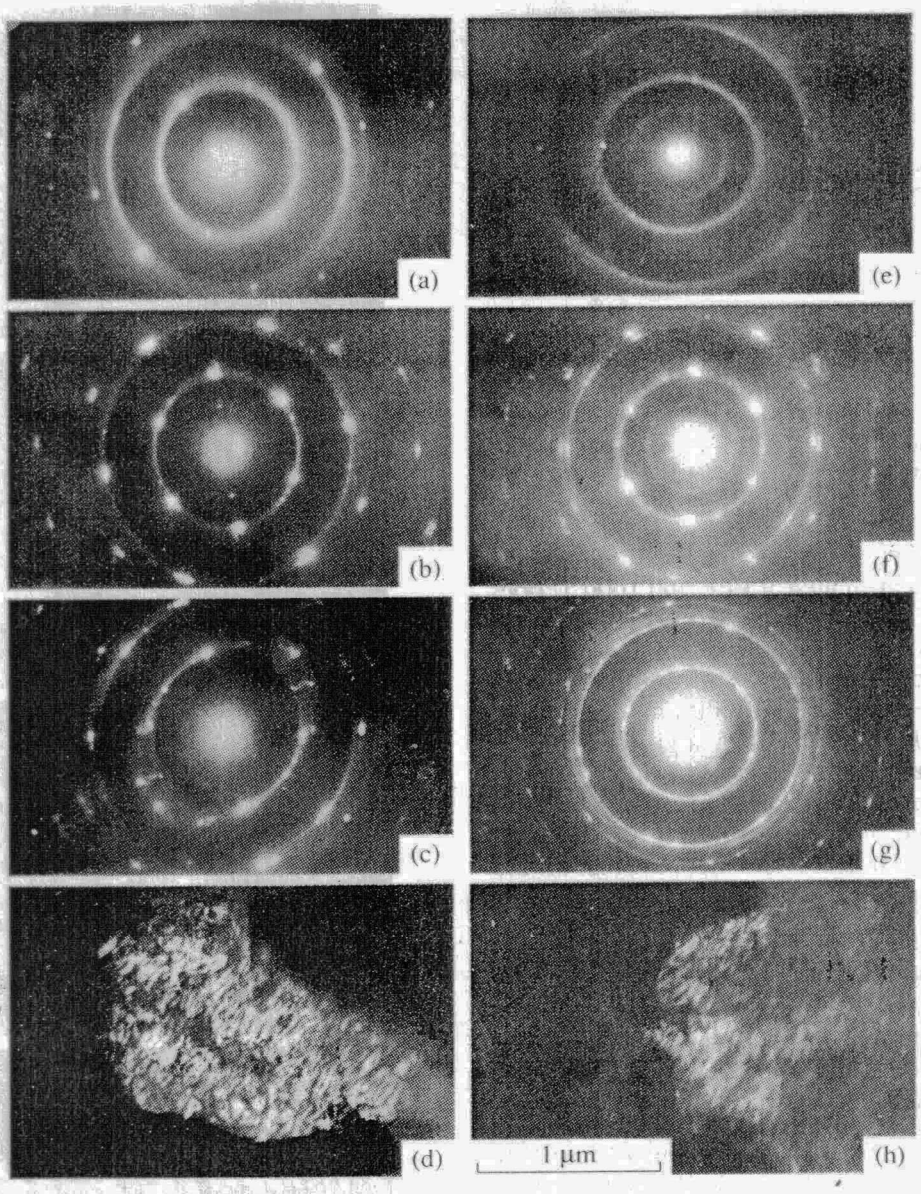

Fig. 2. Microdiffraction patterns and dark-field images of large particles in the 100 reflection of the carbon materials containing (a–d) 2.5 wt % S and (e–h) 0.3 wt % S + 1.5 wt % Cr_2O_3 and heat-treated at (a) 1300, (b, d, e) 1400, (c) 1800, (f, h) 1500, and (g) 2000°C.

(d'_{002} = 0.3374 nm) and ultrafine carbon with d''_{002} decreasing from 0.3513 to 0.3425 nm, and the *c*-axis CSD size, L_c, increasing from 12 to 43 nm. The relative content *G* of graphite is 18% after heat treatment at 1400°C and reaches a maximum value of about 50% at 1600°C. After treatment at 2000°C, the content of graphite does not exceed 15%, and, after treatment at ≥2200°C, the material becomes single-phase.

In the material containing 1.5 wt % S, the two phases coexist in a narrower temperature range—between 1500 and 1800°C. The graphite content in the material heat-treated at 1500 and 1600°C is 14 and 16%, respectively; at higher temperatures, *G* drops to ≈1%.

TEM examination shows that the grain size of the material heat-treated at 1200–2000°C is very nonuniform. The electron-diffraction patterns of the samples heat-treated at 1200–1300°C (Fig. 2a) show diffraction spots from graphite superimposed over broad rings. After heat treatment at 1400°C, the intensity of the spots increases sharply, indicating that the CSD size grows. The dark-field image taken in the 100 strong reflection from graphite (Fig. 2d) reveals large CSDs embedded in the carbon matrix with $L_c \simeq 10$ nm.

To study the effect of iron on the graphitization of high-sulphur carbon, fine iron particles (10 wt %) or iron oxide (1–10 wt %) were added to the material. As is clear from the table, iron decelerates the formation of graphite particles at 1200–1600°C in the carbon mate-

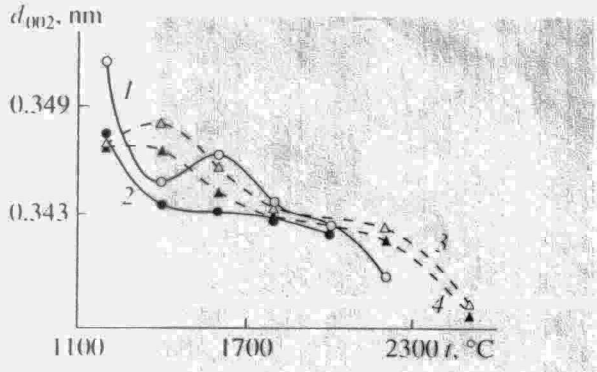

Fig. 3. (*1*, *3*) d''_{002} and (*2*, *4*) d_{002} spacings as a function of heat-treatment temperature for the carbon materials containing (*1*, *2*) 2.5 wt % S and (*3*, *4*) 2.5 wt % S + 10 wt % Fe.

rial containing 2.5 wt % S. The content of graphite in the carbon matrix heat-treated at 1400 and 1600°C does not exceed 15 and 20%, respectively. The latter value is smaller than that for the iron-free material by almost a factor of two. In addition, the introduction of 10 wt % iron broadens the transition of ultrafine carbon to graphite up to 2500°C (Fig. 1b). A high iron content intensifies the formation of coarse graphite particles with a rather perfect structure ($\Delta d/d$ = 0.003) above 1800°C (table). After heat treatment at 1200–1600°C, the d_{002} value determined from the centroid of the observed peak and d''_{002} are higher in the samples containing iron. With increasing heat-treatment temperature, d_{002} in these samples decreases more slowly than that in the iron-free material (Fig. 3). The effect of fine-particle Fe_2O_3 (10 wt %) on the structural transformations in the range 1400–2500°C in the carbon material containing 2.5 wt % S is similar to that of Fe.

In samples prepared from cokes containing 1.5 wt % S and doped with 1 wt % Fe_2O_3, d_{002} is also independent of heat-treatment temperature in the range 1400–1600°C (table). The G value in these samples is smaller than that in iron-free samples by almost a factor of two. The two-phase range (1400–1600°C) of the samples containing Fe_2O_3 is narrower and lies at lower temperatures than that of the iron-free material (1500–1800°C).

After heat treatment at 1800°C, fairly large ($L_a \geq$ 1 μm) graphite particles are found by TEM in ultrafine carbon containing 10 wt % iron. These particles are larger than those observed in iron-free samples and have a rather perfect structure, as evidenced by the presence of moiré patterns in dark-field images (Fig. 4d) and Kikuchi lines in microdiffraction patterns. It is likely that, at high heat-treatment temperatures, iron is uniformly distributed over the carbon material. Distinct islands ≈10 nm in size, occasionally decorating boundaries of graphite particles, are observed in cross-sectional micrographs of the samples heat-treated at

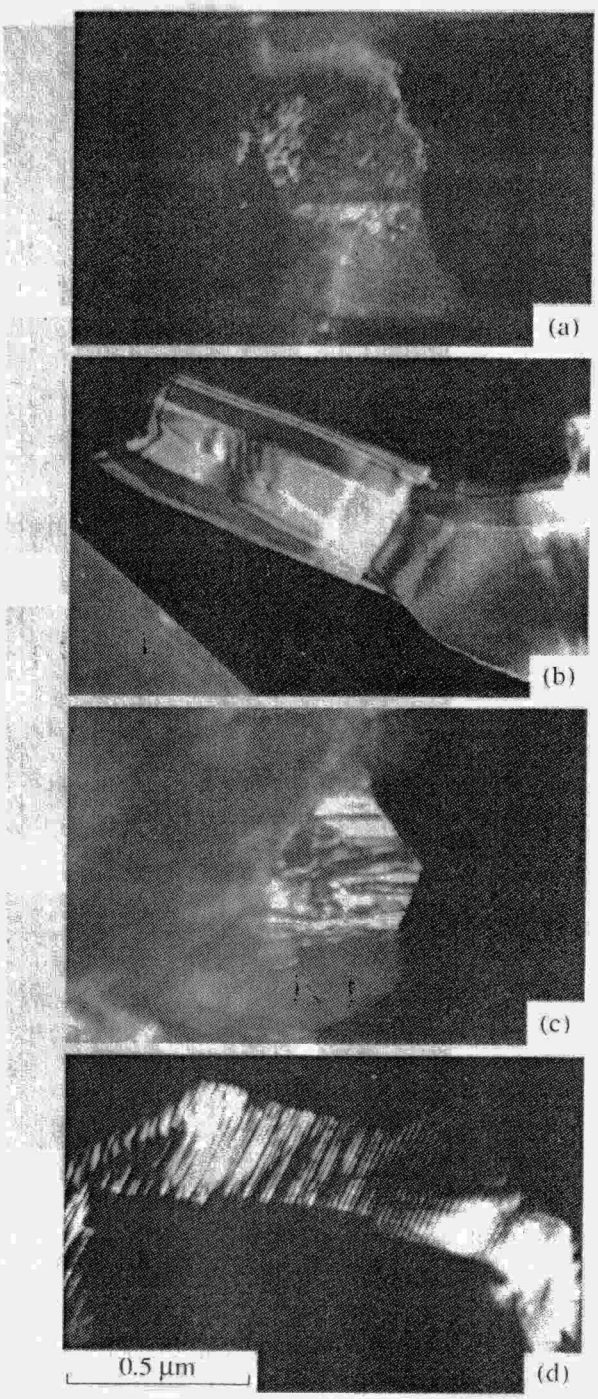

Fig. 4. Dark-field images taken in the 100 reflection from graphite: carbon materials containing (a, c) 2.5 wt % S and (b, d) 2.5 wt % S + 10 wt % Fe and heat-treated at (a, b) 1800 and (c, d) 2500°C.

2400°C (Fig. 5). Dark-field images of these islands are formed by reflections from iron carbide.

The structural transformations in the carbon material containing chromium differ substantially from those in the samples containing iron or no additives. We consider the effect of chromium by the example of the samples

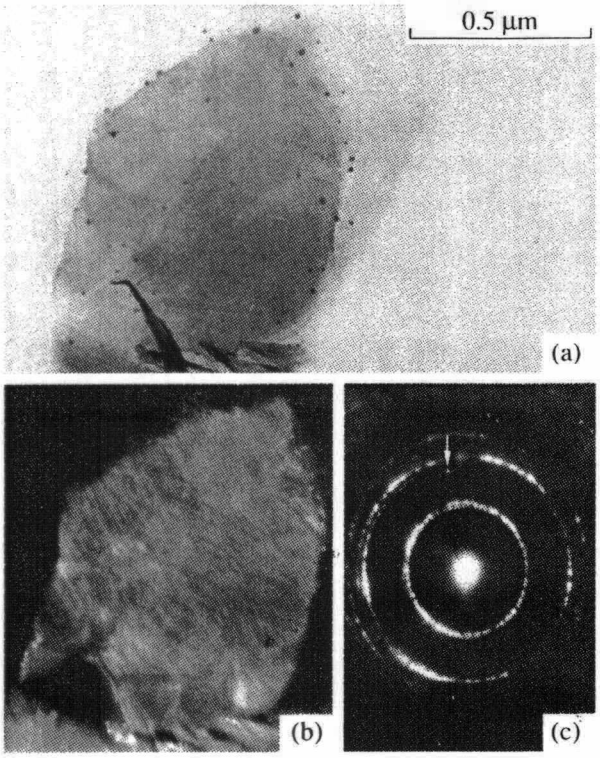

Fig. 5. (a) Bright-field image and (b) dark-field image taken in the reflection indicated by the arrow in the microdiffraction pattern (c). The images indicate the presence of iron carbide islands in the carbon material containing Fe_2O_3 and heat-treated at 2400°C.

prepared from low-sulphur (0.3 wt %) cokes. The 002 reflections of low-sulphur carbon heat-treated at 1400–2000°C are rather symmetrical, and the material is uniform in phase composition and grain size. With increasing heat-treatment temperature, d_{002} decreases, and L_c increases (table). The addition of 1.5 wt % Cr_2O_3 slightly increases the average size of CSDs. However, the XRD peaks remain symmetrical after heat treatments in the entire temperature range examined. Fine-particle chromia additions (1.5 wt %) substantially intensify the structural transformations at low temperatures (1400–1800°C), resulting in an asymmetric shape of the 002 peak (Fig. 1c). Fairly large—up to 100 nm in the *c*-axis direction—particles with the graphite structure are formed in the Cr_2O_3-containing sample even at 1400°C. Their content attains $G \simeq 5\%$. With increasing heat-treatment temperature, L_c of the carbon matrix increases from 20 to 40 nm. The G value increases to 8% at 1600°C and decreases at higher heat-treatment temperatures. After treatments at $t \geq 1900$°C, graphite particles are missing, and the material is rather uniform in phase composition and grain size.

Similar to those of high-sulphur carbon, the microdiffraction patterns of the low-sulphur chromium-containing carbon samples heat-treated at 1400°C often contain diffraction spots superimposed over broad rings (Fig. 2e). After heat treatments at 1500 and 1600°C, such patterns are observed more frequently, and the intensity of the spots is higher. The dark-field images taken by diffraction spots reveal large particles formed at relatively low temperatures (1500°C) in the ultrafine carbon matrix.

Thus, two phases differing in CSD size, d_{002}, and $\Delta d/d$ are observed in the high-sulphur carbon material after heat treatments at 1500–1800°C. The average L_c of the newly formed phase exceeds 100 nm after heat treatment at a temperature as low as 1500°C, and $\Delta d/d$ is less than 0.002 over the entire temperature range. The d'_{002} value is close to that of graphite. With increasing treatment temperature, the L_c of the carbon matrix increases from 10 to 40 nm.

The addition of chromia intensifies the formation of large graphite particles in low-sulphur carbon at 1400–1600°C. As a result, both the low- and high-sulphur carbon materials become nonuniform in phase composition and grain size. The formation of large particles in the rigid matrix at relatively low temperatures, at which diffusivity of carbon is low, is likely to give rise to internal stresses. High concentrations of graphite particles in the carbon matrix cause the formation of micro- and macrocracks. This process is similar to that occurring in the rigid matrix of C–SiC composites owing to the formation of $CaCO_3$ crystals [5]. The addition of iron results in an almost twofold decrease in the content of graphite formed in the high-sulphur material upon heat treatment at 1400–1600°C, thus improving the performance of the graphitized carbon material.

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