STUDY OF THE CRYSTALLINE STRUCTURE OF CEMENTITE BY ELECTRON-DIFFRACTION ANALYSIS

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Abstract

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STUDY OF THE CRYSTALLINE STRUCTURE OF CEMENTITE BY ELECTRON-DIFFRACTION ANALYSIS

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The structure of Fe_3C was first studied by Westgren and Phragmén (^{1}), who found the following lattice periods: $a = 4.517$ Å, $b = 5.079$ Å, $c = 6.73$ Å. On the basis of these data, Hendricks (^{2}) determined the space group ($Pbnm$), the positions of the iron atoms, and suggested that the C atoms might be located in octahedral voids at the positions 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Later Westgren (^{3}) confirmed the positions of the Fe atoms found in (^{2}), and, proceeding from crystallogeometrical considerations, showed the possibility of placing the C atom in a general position at the center of a triangular prism formed by Fe atoms. Lipson and Petch (^{4}) carried out an X-ray structural investigation of Fe_3C obtained by reduction of Fe_2O_3 in a stream of CO at a temperature of 550°. The product obtained was not tested for oxygen content. On the X-ray patterns, 30 diffuse lines were observed. Annealing of the powder made it possible to obtain sharper X-ray patterns, but at temperatures above 600° it led to partial decomposition with separation, in the authors' opinion, of the carbide Fe_2C. Therefore the intensities and interplanar spacings were measured on X-ray patterns from different powders. The work mainly confirmed the conclusions of Westgren (^{3}), but sufficient data were not obtained for determining the positions of the C atoms. Thus, the investigations carried out did not yield reliable data for locating the C atoms. In the present work the task was set to solve this question by means of electron diffraction.

In the work, Fe_3C from annealed carbon steel of composition (in %): C 0.79, Mn 0.34, Si 0.24, P 0.014, and S 0.013 was studied. Cementite was separated from the steel by anodic dissolution (^{5}). From the separated precipitate, placed on grids with a collodion support measuring 25×25 mm, transmission electron-diffraction patterns were obtained in an EM-4 electron-diffraction apparatus, and from individual particles—microdiffraction spot electron-diffraction patterns in an electron microscope. In order to eliminate individual reflections on the rings, electron-diffraction patterns were recorded in the electron-diffraction apparatus with continuous rotation of the grid. The intensity of the rings was measured on an MF-4 microphotometer equipped with a logarithmic electronic converter (^{6}). The accuracy of measuring the intensities of medium and strong reflections was about 3%, and of weak ones about 15%. The error in determining

Electron diffraction pattern from isolated cementite particles of annealed carbon steel

Figure 1: Electron diffraction pattern from isolated cementite particles of annealed carbon steel

Spot microelectron diffraction pattern from a cementite particle of annealed carbon steel

Figure 2: Spot microelectron diffraction pattern from a cementite particle of annealed carbon steel

interplanar spacings did not exceed 0.003 Å. Both quantities were determined as the average of 5 measurements on different electron-diffraction patterns.

Recording of electron-diffraction patterns at an angle and analysis of spot electron-diffraction patterns showed that the specimens studied have a plate-like texture. It was established that the habit plane of the Fe_3C crystal is the (001) face. The Fe_3C plates are arranged with this face parallel to the surface of the support, and the z axis of the Fe_3C cell coincides with the direction of the beam. Despite the texture, all reflections of the Fe_3C lattice were observed on the electron-diffraction patterns. A total of 125 reflections were recorded (Fig. 1), which were indexed on the basis of a rhombic lattice. The character of the extinctions of the reflections confirms the space group D_{2h}^{1}—$Pbnm$. The found dimensions of the elemen-

Fig. 1. Electron diffraction pattern from isolated cementite particles of annealed carbon steel

Fig. 2. Spot microelectron diffraction pattern from a cementite particle of annealed carbon steel

of the unit cell fully correspond to the data of ([1]). Forbidden reflections $h00$, $0k0$, $00l$ with odd h, k, and l are present on the electron diffraction patterns; they are clearly visible on spot electron diffraction patterns (Fig. 2).

The presence of texture in the specimens made it possible, from the reflections of the $hk0$ zone, to construct only one projection of the potential onto the (001) plane and to determine the coordinates x and y of the Fe and C atoms. Determination of the coordinate z under these conditions is associated with great difficulties.

Comparison of the change in the mean values $I/\rho d^2$ with the f- and f^2-curves of iron according to ([7]) indicated the dynamic character of electron scattering. Therefore the transition from intensities to amplitudes was carried out according to the formula ([7])

$$\Phi_{hkl} = \frac{I_{hkl}}{d_{hkl}^2 \rho}.$$

Fig. 3. Projection of the potential of cementite of annealed carbon steel. Solid isolines are drawn every 100 Å, dashed ones every 50 Å

Figure 3: Fig. 3. Projection of the potential of cementite of annealed carbon steel. Solid isolines are drawn every 100 Å, dashed ones every 50 Å

Fig. 4. Interatomic distances in the cementite molecule

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The experimental amplitudes obtained, normalized to volts according to (^{8}), are given in Table 1. The calculated values are given with a temperature correction ($B = 0.5$).

Fig. 3. Projection of the potential of cementite of annealed carbon steel. Solid isolines are drawn every 100 Å, dashed ones every 50 Å.

From the experimental amplitudes a Fourier projection of the potential onto the (001) plane was constructed. The signs of the amplitudes were calculated from the atomic coordinates found in (^{3}) and refined atomic factors (^{9}, ^{10}). Three projections were constructed, including a difference synthesis; however, the placement of the C atom in the general position according to (^{3}, ^{4}) was not confirmed. Therefore projections were constructed from amplitudes whose signs were calculated on the basis of the position of the C atom in an octahedral void at position 000. On the two constructed projections a peak is clearly indicated at position 000, corresponding to the C atom (Fig. 3).

Fig. 4. Interatomic distances in the cementite molecule.

The positions of the peaks were calculated by the method of Buse. The following atomic coordinates were obtained: 8Fe $x_1 = 0.338$, $y_1 = 0.169$; 4Fe $x_2 = -0.178$, $y_2 = 0.030$; 4C $x_3 = 0$, $y_3 = 0$. The root-mean-square error in determining the coordinates of the Fe atoms according to calculation (^{7}) was 0.001 Å.

Figure 4 shows the interatomic distances in the Fe_3C molecule, calculated from the found coordinates x and y (the coordinate z was taken according to Westgren). The Fe–C bond length is on average 1.86 Å, which is considerably smaller than the value 2.03 Å obtained in (^{4}), which is apparently overestimated.

If the Fe–C bond length in austenite is calculated, a value of 1.97 Å is obtained, coinciding with the data of (^{11}, ^{12}), in which it was experimentally confirmed that C in austenite is located in octahedral pores and is a cation. Therefore it may be expected that in Fe_3C it will be still smaller. However, the Fe–C bond length in Fe_3C is probably somewhat greater than 1.86 Å, as a result of which some Fe atoms are displaced from their ideal positions. In particular, this is indicated by the appearance of forbidden reflections, which cannot be attributed to secondary electron scattering. If significant secondary scattering occurred, then the calculated values there should have been more experimental intensity values. The data obtained show that this is not observed. Nor were sufficiently intense reflections found that do not correspond to the orthorhombic lattice.

Table 1

$hk0$	Φ_{calc}, V	Φ_{exp}, V	$hk0$	Φ_{calc}, V	Φ_{exp}, V	$hk0$	Φ_{calc}, V	Φ_{exp}, V
110	+1.81	0.17	400	−1.96	2.02	440	+0.71	1.03
020	+1.26	1.66	330	−4.37	3.94	350	+1.00	3.23
200	−4.70	4.70	240	+0.46	0.47	160	+0.71	1.65
120	−4.55	4.15	410	−2.70	2.35	530	+1.64	1.08
210	+6.47	6.70	420	+1.11	0.97	260	−0.80	1.09
220	+0.83	0.60	150	+0.04	0.17	450	+0.49	0.76
130	+4.97	4.20	340	+0.02	0.46	600	+2.78	3.13
310	−0.93	1.07	430	−0.60	0.39	610	−0.14	0.35
230	+0.79	0.57	250	−1.16	0.93	360	−0.28	0.06
320	−0.48	0.55	510	+0.83	0.72	540	−1.79	1.22
040	+0.36	0.88	520	+1.30	1.39			
140	+4.26	3.90	060	+3.00	4.00			

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