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Peculiarities of the Crystal Structure of the Martensite in Carbon Steels

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The crystal structure of martensite in carbon steels is proposed to consider as a defined system of the lattices blocks. Each block consists of four lattices with carbon atom at the central axis of the block. There are lattices without carbon atoms in steels. Carbon concentration in steel determines the quantity of the blocks with C atom. Edges of the lattices in the blocks and outside them have different sizes that depend on the distance to the block axis with carbon atom. It is necessary to consider the martensitic crystal structure in the carbon steels as pseudotetragonal or pseudocubic. Reasons of the large width of the XRD lines of the martensitic phase in the carbon steels are considered and their explanation is proposed. The number of the *c* edges, which are changed in the same way, determines the diffraction lines width of the martensite in the carbon steels.

Key words: carbon steel, crystal structure, martensite, tetragonality, system of the lattices blocks.

Кристалічну структуру мартенситу вуглецевих сталей запропоновано розглядати як певну систему блоків ґратниць. Кожен блок складається з чотирьох ґратниць із атомом Карбону на центральній осі блоку. В сталі існують ґратниці без атомів Карбону. Кількість блоків визначається концентрацією вуглецю. Ребра ґратниць у блоках і поза ними мають різний розмір залежно від відстані до осі блоку із атомом Карбону. Кристалічну структуру мартенситу у вуглецевих сталях необхідно розглядати як псевдотетрагональну або псевдокубічну. Розглянуто причини великої ширини рентґенівських ліній мартенситної фази вуглецевих сталей та запропоно-

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вано пояснення її виникнення. Ширина рентґенівських ліній мартенситу вуглецевих сталей визначається кількістю ребер *c*, змінених однаковим чином.

Ключові слова: вуглецева сталь, мартенсит, тетрагональність, система блоків ґратниць.

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1. INTRODUCTION

Beginning from the first investigations of the crystal structure of the martensite in steels, it is accepting that martensitic lattice is the body centred tetragonal (b.c.t.) with c/a ratio depending on the carbon concentration [1–4]. It has also set that in steels with (0.1–0.6)% wt. C the martensitic lattice is body centred cubic (b.c.c.). However, until recently nobody has explained how the little number of the carbon atoms, less than 7–8% at. C, may change the body centred cubic structure of iron (Fe_α) to the tetragonal structure. Only recently some works have appeared in which a new approach proposed for describing the crystal structure of the martensite in carbon steels [5, 6].

In this paper, changes in the Fe_α crystal structure under an introduction of the C atoms and manner of describing of the martensitic crystal structure in carbon steels have considered. New explanation of the great width of the diffraction lines of the martensitic phase in steels has also proposed. The number of the lattices with changed c edges in the same way determines the diffraction lines width of the martensite in carbon steels.

2. REAL CRYSTAL STRUCTURE OF MARTENSITE IN CARBON STEELS

Interpretation of the crystal structure of martensite in carbon steels on a basis of an appearance of the doublet splitting of a number of lines in the XRD patterns as tetragonal does not seem to correspond to the real crystal structure of the martensitic phase for next reasons. It known, that steel may contain 0.2–1.7% wt. C or 1–8% at. In the previous investigations it has assumed that C atoms in α-iron arranged in the octahedral pores along $[001]_M$ directions and lattice became tetragonal [2].

Do consider what proceeds when carbon atom introduced into b.c.c. lattice and can this lattice become tetragonal when C atom located at one edge only. Under really concentration of the carbon in steel, there are many b.c.c. lattices without C atoms.

It knows only two types of the tetragonal lattices: simple tetragonal and body-centred tetragonal. When carbon atom places in the octahedral pores of the f.c.c. Fe_γ structure, after transformation the C atom situates on the c lattice edge of the Fe_α b.c.c. structure and this edge increases by a magnitude equal to the diameter of the C atom. The remaining three edges of this lattice also change but significantly less. Thus, the crystal lattice with C atom on one edge distorts but inhomogeneous. This lattice is not tetragonal, better name is pseudotetragonal. There are only as many these lattices as the number of the carbon atoms dissolves actually in steel.

Scheme for a change of the f.c.c. lattice into b.c.c. in the carbon steel proposed when C atoms introduced into octahedral pores of the f.c.c. structure and model of arising new lattice offered [5, 6].

According to the Bain reconstruction model [7], it can choose the body centred tetragonal lattice with C atom on the lattice edge in the f.c.c. structure with C atom in the centre of the lattice; the parameters of this lattice are: $a_\gamma = 0.252$ nm and $c_\gamma = 0.356$ nm (Fig. 1, *a*).

During martensitic $\gamma \to \alpha'$ transformation the f.c.c. lattice is reconstructed into b.c.c. one and C atom locates on the c edge (Fig. 1, *b*). If C atom placed only on one c edge, other three edges of this lattice distorted also and instead of the correct b.c.c. or b.c.t. lattice, the distorted lattice arises (Fig. 1, *b*). If C atom locates on one c edge of the martensitic lattice, the size of this edge should increase to a value equal to the sum of diameters of the Fe and C atoms: $c = d_{Fe} + d_C \approx 0.504$ nm. The remaining three edges in this lattice changed also. This distorted lattice cannot be call tetragonal or cubic because lattice has no symmetry of the cubic or tetragonal lattice and looks like as triclinic: all edges have different sizes and angles at the lattice tops differ from 90° (Fig. 1, *b*).

Model of the crystal structure of the martensite in carbon steels for

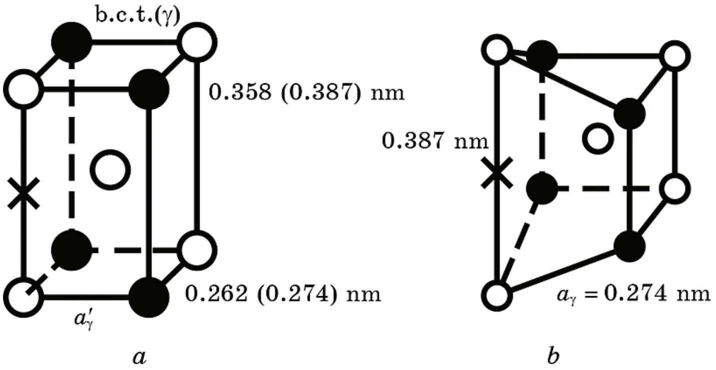

Fig. 1. The b.c.t. lattice (γ-phase) with atom C on c edge (*a*); distorted b.c.t. lattice with atom C on one c edge (*b*) (○ and ● are Fe atoms in the center and at the lattice tops [6].

this case proposed in [5, 6]. The main element of this structure is a block of four distorted b.c.c. lattices. Carbon atom locates on common block edge (axis) (Fig. 2).

In block the *c* edge with C atom is the most increased. Other *c* edges of the lattices forming the block change also but much less (it not shown in Fig. 2). Magnitude of the change depends on the distance to the central edge (axis) with C atom. Diagonally disposed edges are less increased. The evaluation shows that carbon concentration in this block is 11.1% at. (2.48% wt.). The total C concentration in the steel determines the number of blocks with only one C atom in block in the crystal structure of martensite.

Next evaluations have carried out.

1. Concentration of carbon in steel under various numbers of the lattices nearest to the block (Appendix 1).
2. Quantity of the blocks in the volume of 10^6 lattices at different carbon concentrations (Appendix 2).
3. Angular distance between XRD peaks $(200)_M$ and $(002)_M$ at different carbon concentrations (Table 1).
4. Angular position of $(002)_M$ diffraction line at different size of the *c* parameter (Table 2).

Depending on the number of the lattices without C atoms around the block, carbon concentration may change from 11.11% at. (2.48% wt.) for structure of only blocks up to 2.43% at. (0.46% wt.) to the structure consisting of one block and twenty lattices without carbon atom around it (Appendix 1). The first case (only blocks in the crystal structure) is unrealistic since the carbon concentration in steel and in martensitic phase does not exceed 1.7–1.8% wt.

It can see also that one C atom belongs to a few lattices: to 4 lattices when C concentration is 2.48% wt. (only blocks in the crystal structure) and to 24 lattices when C concentration is 0.46% wt. (Appendix

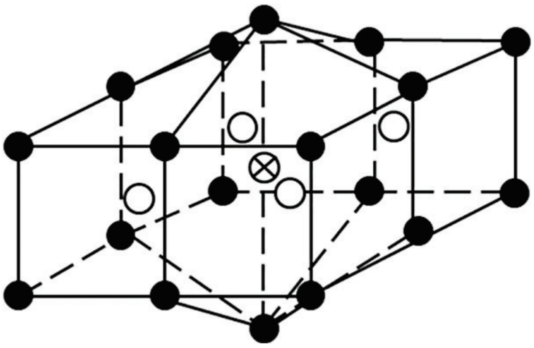

Fig. 2. Block of four lattices with one enlarged *c* edge on which C atom is located (× is C atom, ○ and ● are Fe atoms in the center and at the tops of lattices) [6].

TABLE 1. Evaluation of the angular distance between diffraction peaks. $(200)_M$ and $(002)_M$.

Reflection $(200)_M$ ($Fe_{K\alpha}$ radiation, $\lambda = 0.194$ nm)

C, % wt.	a, nm	d, nm	sinφ	φ	Δφ—angle distance between $(200)_M$ and $(002)_M$ peaks
0.2	0.2858	0.1429	0.6788	42°45′	0°30′
0.8	0.2849	0.1424	0.6809	42°55′	1°53′
1.4	0.2840	0.1420	0.6831	43°15′	3°22′

Reflection $(002)_M$ ($Fe_{K\alpha}$ radiation, $\lambda = 0.194$ nm)

C, % wt.	c, nm	d, nm	sinφ	φ	Δφ—angle distance between $(200)_M$ and $(002)_M$ peaks
0.2	0.2885	0.1442	0.6724	42°15′	0°30′
0.8	0.2955	0.1477	0.6565	41°02′	1°53′
1.4	0.3026	0.1513	0.6411	39°53′	3°22′

TABLE 2. Angle position of the diffraction line $(002)_M$ at different values of c parameter ($Fe_{K\alpha}$ radiation, $\lambda = 0.194$ nm).

c_M, nm	sinφ	φ	Δφ	
0.362	0.5359	32°26′	5°12′	c_{max}
0.342	0.5673	34°34′		
0.322	0.6025	37°04′		
0.302	0.6424	39°58′		
0.292	0.6644	41°38′		
0.286	0.6783	42°43′	5°5′	$a_{Fe\alpha}$
0.318	0.6335	37°38′		$c_{average}$

1). This C atom influences differently on the changes of the edges sizes in the nearest lattices. Thus, the crystal lattices of the martensite cannot be tetragonal because the lattice edges are different.

For the volume of 10^6 lattices the number of blocks and the number of neighbouring lattices without C atoms evaluated for the real carbon concentrations in martensite of steel (Appendix 2). It established also, how many lattices without C atoms are per one block consisting four lattices with C atom on the central edge (block axis). It found that 46 lattices without C atoms should be located around one block at concentration 1% at. C (0.22% wt.). In the case of 8% at. C (1.79% wt.) only two (2.25) lattices without C atoms are adjacent to one block. For real concentration of 5% at. C (1.12% wt. C) should be six lattices without C atoms around one block with C atom.

Under ordered arrangement of the C atoms in the crystal structure periodic changes in the size of *c* edges depending on the distance to the axis of the block with carbon atom and changes in the corresponding interplanar distances should be observed. As result of these changes distorted lattices have appeared. These lattices can be defined as pseudotetragonal but in no case as tetragonal, because lattice edges in these lattices have different sizes, only one C atom is on one *c* edge in some lattices and angles between [100], [010] and [001] directions change also and are not equal 90°.

In the case of the disordered arrangement of C atoms on three possible *a, b, c* edges, blocks also appear and axes of the blocks may arrange in [100], [010] or [001] direction by the random manner. In this case the edges *a, b* or *c* with one C atom change by the same extent and have equal sizes. Changes of the remaining edges depend on the distance to the edge with C atom (axis of block). Since in this case all three directions [100], [010] or [001] are equivalent, *a, b, c* parameters are averaged over the martensitic crystal and 'averaged' lattice will be 'cubic'. The parameters of these lattices differ a little from the b.c.c. lattice parameter of the α-iron. In this case, no diffraction line splitting observes on the diffraction patterns and the doublets are absent but the lines broaden nevertheless; this is the case of so-called cubic martensite. However, this crystalline structure of martensite must define as pseudocubic since edge sizes in the lattices of the blocks and in neighbouring lattices are different.

Thus, difference between ordered and disordered arrangement of the carbon atoms in the crystal structure of martensite in steels and accordingly between so-called 'tetragonal' and 'cubic' martensite consists in only one. In the case of the 'tetragonal' martensite, the blocks with atom C on *c* axis (Fig. 2) are located mainly along one direction [001]. In the case of the 'cubic' martensite the blocks are located along all three directions [100], [010], [001] arbitrary and this leads to an averaging of all three lattice parameters *a, b, c* to one average parameter *a*.

For carbon concentrations 0.2, 0.8 and 1.4% wt. positions of two XRD lines $(200)_M$ and $(002)_M$ estimated and angular distance between the peaks of these lines determined. It turned out that for steel with 1.4% wt. C this distance is 3°22′ (Table 1).

3. REASONS OF THE DIFFRACTION LINES BROADENING OF THE MARTENSITE IN CARBON STEEL

Broadening of the diffraction lines of martensite in carbon steels can reach 10–12° (Fig. 3). It needs to consider reasons of this great broadening.

Various methods for an evaluation of these quantities and different explanations have proposed. Until now, broadening of the diffraction line of the martensite in steels has explained quite simply: during transformation of the initial γ-phase into the martensitic α'-phase the micro stresses arise and coherent scattering regions of 30–70 nm in value appear in the martensitic crystals. However, XRD studies have carried out on the extracted powders of the martensite in steel (1.0% wt. C) showed that even in this case, when influence of the micro stresses on the diffraction lines width excluded, the lines remain quite broad [9]. Thus, not all X-ray line broadening stipulated by the stresses and coherent scattering regions. There are some other reasons.

It proposed above to represent the crystal structure of the martensite in carbon steels as consisting of the blocks containing four b.c.c. lattices with carbon atom on the axis of block and the b.c.c. lattices without carbon atoms around it. All lattices, both in the blocks and near them, have changed edges with the sizes depending on the distance to the axis of the block. This leads to the periodic changes in the interplanar distances that depend on the number of the blocks in the crystal structure and on the number of the lattices without C atoms; these changes depend on the carbon concentration in steel. As a result there are definite 'sets' of these distances for given type of the reflections (for example, $(002)_M$), that lead to an appearance of the wide diffraction line. In fact, this 'line' consists of a number of the overlapping diffraction reflections conforming to a definite set of the interplanar distances and correspondingly changed *c* parameters.

The angular positions of the $(002)_M$ diffraction line ($Fe_{K\alpha}$ radiation, $\lambda = 0.194$ nm) calculated for *c* parameters in the interval 0.286–0.362 nm (Table 2).

The angular distance for the reflections corresponding to these parameters reaches 10° and this value practically coincides with the dif-

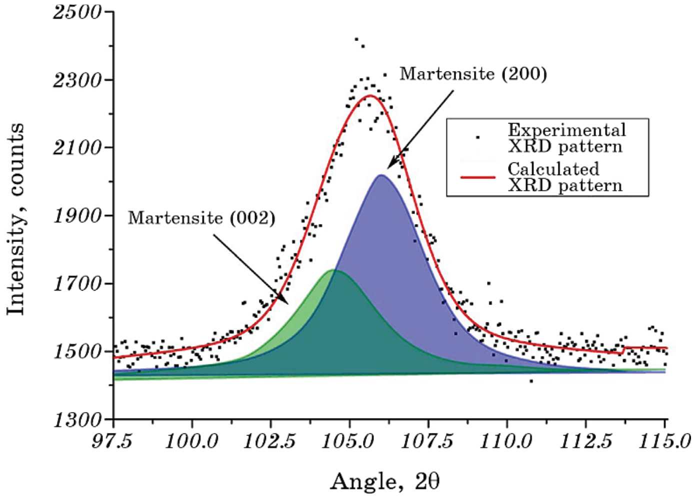

Fig. 3. XRD line for steel with 0.45% wt. C [8].

fraction line width observed experimentally in the different works. For example, the angular width of the $(200)_M$–$(002)_M$ martensitic lines in steel with 0.45% wt. C is near 12° [10], a doublet width of the lines $(211)_M$–$(112)_M$ in Fe–0.97 C–6.3 Mn (% wt.) steel reaches 10° [11]. Other examples of a great width of the martensitic diffraction lines in steels may also give.

Thus, evaluations have shown that there is a set of the c_M parameters in the crystal structure of the martensite in steel at a given carbon concentration caused by the edge changes and the distortions of the lattices during formation of the martensitic phase and an appearance of the corresponding interplanar spacing. The number of the blocks defines a quantity of the parameters of one or another size for given carbon concentration in steel. Intensity of the individual diffraction line of definite 'set' depends on the quantity of the equally changed lattices edges and corresponding interplanar distances; a magnitude of the particular interplanar spacing defines a position of the diffraction lines.

Thus, observed coincidence of the calculated and experimental diffraction line widths confirms proposed model of the crystal structure of the martensite in carbon steels: this structure consists of the blocks with C atoms at the axes of the blocks and the lattices without carbon around the blocks but with edges sizes changed differently.

Thus, martensitic lattice of the carbon steels is not tetragonal. This lattice has only one C atom at the common edge of four lattices (at the axes of bocks), has different sizes of the lattice edges and angles at the lattice tops differ from 90°. It is necessary to define this lattice as distorted tetragonal or pseudotetragonal and there is no need to determine so-called degree of the tetragonality c/a.

4. DISCUSSION

When the crystal structure of the martensite in carbon steels considers some questions arise, requiring discussion and solution. To what extent the doublets of the diffraction lines appearing on the XRD patterns of the martensitic phase in steels reflect the tetragonality of the crystal lattice. What really determines large, 10–12°, diffraction line width of the martensitic α'-phase in the carbon steels? The main question is: how 3–8% at. carbon atoms, embedded in several octahedral pores of the b.c.c. lattices of the α'-phase (and only at one edge of some lattices), may change the body-centred cubic lattices to the body-centred tetragonal lattices.

For a long time these questions did not even arise although investigations of the crystal structure of the martensite in carbon steel have begun in the twenties of the last century and continue with different intensities to date.

The conclusion about tetragonality of the martensite in the carbon steels and b.c.t. lattice drew on a basis of an appearance of the doublet splitting of the martensitic diffraction lines in the XRD patterns. However, as shown by the analysis carried out in this work, an amount of the carbon that remains during martensitic transition $Fe_\gamma \to Fe_\alpha$, is not suffice to change the f.c.c. crystal structure of the parent phase into the b.c.t. martensitic structure. Carbon atom during $\gamma \to \alpha$ transformation locates at one edge only of the b.c.c. lattice (in some octahedral pores) and changes this edge to the size $d_{Fe} + d_C = 0.5036$ nm (d_{Fe} and d_C are the diameters of the iron and carbon atoms). Edge sizes of the lattices where no C atoms change also but on the different magnitude that depends on the distance to the edge with C atom. In the result of the martensitic transition, the lattice with one C atom at one edge only and with different sizes of other edges is formed from f.c.c. lattice of the parent γ-phase. It is not possible to call this lattice tetragonal. The distorted b.c.c. lattices without C atoms arise near.

Imaging of the crystal structure of the martensite in carbon steels as a system of the blocks of four lattices with carbon atom at common *c* edge (axis of block) and b.c.c. lattices without C atoms around it allows describe the real crystal structure of the martensite quite well. This explains an appearance of the doublets of a number of the diffraction lines on the XRD patterns and great width of these lines. In the blocks common *c* edge with C atom has the largest size and is an axis of the block.

The total carbon concentration in steel determines the number of the blocks in the structure of the martensite. The evaluation (Appendix 2) showed that with a change in C concentration from 0.22 to 0.6, 1.06 or 1.65% wt. the number of the carbon-free lattices around the blocks with C atom changes from 46 to 13, 6 or 2 lattices, respectively. It should also be taken into account that in the lattices without carbon atom the sizes of *c* edges are different and the greater distance of the separate *c* edge is from axis of the block the lesser it changes.

For the better understanding and explanation of the martensitic crystal structure in the carbon steels it is needed to take into account the conception of the carbon atom ordering proposed and considered in [12, 13]. As shown by a number of the experimental investigations [11, 14, 15] ordering of the C atoms really occurs and, depending on the heat treatment and cooling rate, both ordering of the carbon atoms and disordered state may occur in the martensite of the steels. In the case of an ordered arrangement of the C atoms the axes of the blocks are located in one direction [001] and a state arises that can be called pseudotetragonal. In the disordered state of the C atoms the axes of the blocks are randomly located along all three directions [100], [010] or [001] of the b.c.c. lattice and the cubic (pseudocubic) martensite structure is formed in the result.

Representation of the martensitic crystal structure in the carbon steels as a set of the orderly arranged blocks with the C atoms at their axes and surrounding carbon-free lattices, defined as pseudotetragonal, furnishes also the explanation of an appearance of the martensitic diffraction lines doublets in the X-ray diffraction patterns and their large (10–14°) width. Such being the case an appearance of the doublets has a simple explanation.

In the crystalline structure of the martensite there are enough large ‘sets’ of the edges with different sizes (and different interplanar distances), since not every lattice contains C atoms and the edges of the lattices change by the different magnitude in a dependence on the distance to the block axis. At each specific C concentration in a steel there is a predominant ‘set’ of the edges of the identical size and the corresponding interplanar spacing which provides proper reflection at an certain angle. The remaining changed edges and the corresponding interplanar distances bring about to an appearance of the reflections at other angles. As a result, certain ‘set’ of the reflections and broad diffraction lines appear in the XRD patterns. Described processes occur in the case of the ordering of the C atoms in the martensite of steels.

With disordered arrangement of the C atoms and an arbitrary orientation of the blocks there are also the edges of the different sizes but there is no predominant set of the edges of the same sizes. They distributed over the volume of the martensitic crystal randomly. In this case, there are no doublets of the X-ray lines, only diffraction line broadening observes.

Calculated width of the diffraction line $(002)_M$ in the case of simultaneous presence of the edges with $c_M = 0.362$ nm and $c_M = 0.286$ nm (and other intermediate c_M values) in the martensitic crystals is 10°17′ (Table 2) that is quite good coincides with the experimentally observed width of this reflection 10–12°.

Thus, a representation of the martensitic crystal structure in the carbon steels as a set of the blocks with the C atom at block axes and the lattices around them without carbon atoms but with changed edges allows well describe the real crystal structure of the martensite in the carbon steels. This explains also an appearance of so-called cubic martensite and such effects on the XRD patterns as doublets of the diffraction lines and broadening of these lines.

5. CONCLUSIONS

1. At real carbon concentrations (0.1–1.7% wt.) the crystalline structure of the martensite in carbon steels should be presented as consisting of the blocks of 4 lattices with C atom at the central block axis, surrounded by the lattices without C atoms. The concentration of carbon in the steel determines the number of the blocks, the distances between them and the number of the lattices without C atoms around these blocks. The higher C concentration the greater number of the blocks

and the smaller number of the lattices without C atoms are. The crystal structure of martensite in the carbon steel necessary determines as pseudotetragonal or pseudocubic.

2. The sizes of the *c* edges of the distorted martensitic lattices depend on the distance to the axis of the block containing carbon atom. Quantity of the equally changed *c* edges (and appropriate interplanar distances) determines intensity of the corresponding diffraction lines; a value of the identical *c* edges defines an angular position of the diffraction lines.

3. Really determined by the XRD method the parameters of the martensitic crystal lattice in carbon steels, using position of the diffraction line maximum, are some average values and do not correspond to the real crystal structure of the martensite in steels. Since martensitic lattice is not tetragonal really, c/a ratio does not characterize the crystal structure of the martensite in steel. However, this ratio can use for an evaluation of the C concentration in steels.

4. Experimentally observed martensitic diffraction line width of the carbon steel depends on the number of the lattices with changed *c* edges.

APPENDIX 1

Concentration of the carbon in steel under various quantities of the lattices adjacent to the block.
Block – 4 lattices,
8 Fe atoms + 1 C atom, total 9 atoms.
C concentration: 11.11% at. – 2.48% wt.
Block + 4 lattices around in horizontal plane, total 8 lattices.
16 Fe atoms + 1 C atom, total of 17 atoms.
C concentration: 5.88% at. – 1.31% wt.
Block + 4 lattices above and 4 lattices below, total 12 lattices.
24 Fe atoms + 1 C atom, total of 25 atoms.
C concentration: 4% at. – 0.89% wt.
Block + 8 lattices around in horizontal plane, total 12 lattices.
24 Fe atoms + 1 C atom, total of 25 atoms.
C concentration: 4% at. – 0.89% wt.
Block + 8 lattices around in horizontal plane + 4 lattices above and 4 lattices below, total 20 lattices.
40 Fe atoms + 1 C atom, total 41 atoms.
C concentration C: 2.43% at. – 0.54% wt.
Block + 12 lattices around in horizontal plane + 4 lattices above and 4 lattices below, total of 24 lattices.
48 Fe atoms + 1 C atom, total of 49 atoms.
C concentration: 2.04% at. – 0.46% wt.

APPENDIX 2

The number of the blocks at the different carbon concentration.
Volume: 100 × 100 × 100 lattices = 1000000 lattices.
1% at. (0.22% wt.).
1 atom C per 100 atoms Fe.
Real concentration: 0.99% at. (0.22% wt.).
1000000 lattices: 2 000000 atoms Fe and 20000 atoms C.
20000 blocks – 80000 lattices, out of blocks 920000 lattices.
One block + 46 lattices round.
3% at. (0.67% wt.).
3 atoms C per 100 atoms Fe.
Real concentration: 2.91% at. (0.65% wt.).
1000000 lattices: 2000000 atoms Fe and 60000 atoms C.
60000 blocks – 240000 lattices, out of blocks 760000 lattices.
One block + 13 lattices round.
5% at. (1.12% wt.).
5 atoms C per 100 atoms Fe.
Real concentration: 4.76% at. (1.06% wt.).
1000000 lattices: 2000000 atoms Fe and 100000 atoms C.
100000 blocks – 400000 lattices, out of blocks 600000 lattices.
One block + 6 lattices round.
8% at. (1.79% wt.).
8 atoms C per 100 atoms Fe.
Real concentration: 7.41% at. (1.65% wt.).
1000000 lattices: 2000000 atoms Fe and 160000 atoms C.
160000 blocks – 640 000 lattices, out of blocks 360000 lattices.
One block + 2 (2.25) lattices round.

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