

STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Study of Mechanically Synthesized Carbide Fe₇C₃

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Abstract—Magnetic properties and hyperfine interactions in the carbide Fe₇C₃ prepared by mechanical synthesis (MS) of α -Fe in toluene have been studied. It has been found that the boundary of temperature stability of the MS carbide does not exceed 775 K. The Curie temperature of the synthesized phase varies between 509 and 525 K. The Mössbauer experiments (⁵⁷Fe) have demonstrated that the unit cell of Fe₇C₃ contains 32 iron atoms distributed over five types of crystallographic positions with a multiplicity of 4 : 8 : 8 : 8 : 4. The hyperfine interaction parameters have been calculated for each nonequivalent position. It may be conjectured from the specific features of the decomposition at $T \geq 775$ K that the most probable sequence of the phase transitions in the MS carbides Fe–C is $\alpha \rightarrow \theta$, where α is the modified Eckstrom–Adcock carbide Fe₇C₃.

Keywords: iron carbides, mechanical synthesis, Curie temperature, Mössbauer investigations, phase transition

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INTRODUCTION

A study of the catalysis products by the Fischer–Tropsch scheme showed [1] that, along with the known carbide phases, a carbide with the Curie temperature $T_C = 525$ K is formed in the Fe–C system. The presence of a phase with $T_C = 525$ K was also observed in some high-carbon steels upon tempering [2]. However, small volumes and a high dispersion of the precipitates did not allow determining the origin of the magnetically ordered state with an anomalously high temperature T_C in the steels. It was assumed that the growth of the Curie temperature was due to a modification of the orthorhombic cell of the cementite θ -Fe₃C.

An analysis of the experimental data available in the literature showed that in the Fe–C system this carbide is less studied. Even the stoichiometric composition of the phase [3] has not been determined so far. Based on the dependence of the Curie temperature $T_C(c_C)$ in the range of concentrations $25 \leq c_C \leq 33$ at %, it is assumed that the ratio of iron to carbon in this carbide is smaller than in the Hägg χ carbide Fe₅C₂, but is slightly larger as compared to ϵ' -Fe_{2.2}C and approximately corresponds to stoichiometric Fe₇C₃. The identification of the Fe₇C₃ phase becomes still more uncertain because of ambiguous X-ray diffraction data. The crystalline structure of the carbide is considered either in the hexagonal system (the space group $P6_3mc$) [4–7] or in the orthorhombic system (space groups $Pnma$ [8–10]; $Pmn2_1$ [10] or $Pmc2_1$ [3]). The parameters of the unit cell in one and the same group can differ both in size and in the number

and positions of atoms and the occupancy of the crystallographic positions [10].

It is known that, in addition to the FTS process, the Fe₇C₃ phase is formed in a mixture with other carbides under conditions used for the production of synthetic diamonds [6, 10, 11]. The presence of this phase was also observed in crystallized amorphous powders of the nominal composition Fe₇₅C₂₅ synthesized by grinding the initial components in a vacuum [12]. It was noted that, in the single-phase state, Fe₇C₃ was formed during crystallization of amorphous films Fe_{1-x}C_x ($x > 0.32$) synthesized by radio-frequency sputtering [13, 14].

This paper describes the results of investigations of hyperfine interactions and magnetic properties of the carbide Fe₇C₃ synthesized by mechanical grinding of an iron powder in liquid hydrocarbons (toluene C₇H₈). This method was used for the first time to synthesize the cementite Fe₃C in a single-phase state (~90 wt %) [15, 16]. The results of an analysis demonstrated that this method is efficient for production of the θ phase in volumes sufficient for comprehensive investigations at any level. It was found that at the selected parameters of the mechanical synthesis (MS), the single-phase state of the powders exists in a rather narrow time interval. A further increase in the time of the mechanical treatment of the iron powder led to an increase in the proportion of carbides with the carbon concentration higher than that in θ -Fe₃C, probably such as in the Hägg carbide χ -Fe₅C₂ and the Ekstrom–Adcock carbide Fe₇C₃ [17] whose properties have still been mostly unclear so far.

EXPERIMENTAL

A screened iron powder of the analytically pure grade 100 μm in size and household toluene (C₇H₈) were used for the mechanical synthesis of the carbide Fe–C. Five grams of the α -Fe powder were placed in a $\sim 60\text{-cm}^3$ sealed vessel with 30 spheres about 8 mm in diameter. The free volume of the vessel was filled with toluene up to the brim. A tacking made of a composite consisting of tungsten carbide and 6 wt % Co was used to accelerate the process of synthesis. The grinding operation was performed in a Pulverizette-1 centrifugal planetary mill (Fritsch GMBH) with the platform and the vessels rotating at a speed of $\Omega_p = 47$ and $\omega_v = 89\text{ s}^{-1}$, respectively.

The temperature dependence of the dynamic magnetic susceptibility $\chi_{ac}(T)/\chi_{ac}(300\text{ K})$ of the MS carbides at different stages of grinding was studied at temperatures of up to $T = 1075\text{ K}$ in an ac magnetic field with a frequency of $f = 133\text{ Hz}$ and an amplitude $h_{ac} = 400\text{--}800\text{ A m}^{-1}$. The Mössbauer spectra (⁵⁷Fe) of the powders were measured at $T = 300\text{ K}$ in the ⁵⁷Co(Cr) γ -quanta transmission geometry. The model calculations of the Mössbauer spectra and the reconstruction of the probability density function for the hyperfine magnetic fields, $P(H)$, of the synthesized carbides Fe–C were performed using an algorithm realized in the MSTools software [18].

RESULTS AND DISCUSSION

Kinetics of Iron Carbonization during Grinding

The difficulties of identifying the phases in the Fe–C system are customary for nanocrystalline materials. The attempts to use the traditional scheme of X-ray diffraction for exploring the structure of materials with a developed short- and medium-range atomic order point to its limited capacity and require resorting to research methods providing a higher resolution, such as selected-area electron diffraction (SAED) or Mössbauer spectroscopy [3, 14, 19, 20].

Figures 1a–1d show changes in the Mössbauer spectra and the corresponding distributions of the hyperfine interaction fields $P(H)$ in α -Fe after the mechanical treatment for 5, 10, 20, and 30 h. The estimates made from the Mössbauer data demonstrate that the in-synthesis concentration of α -Fe decreases and amounts to less than one-half of the initial iron concentration in 5 h (Fig. 1a) and about 20% in 10 h of grinding (Fig. 1b). It follows from Fig. 1c that the time of mechanical synthesis of $\sim 20\text{ h}$ is sufficient for all the Fe atoms to be in the chemically bound Fe–C state. A comparison of Fig. 1c and Fig. 1d shows that the final stage of grinding (20–30 h) is not followed by any marked changes in the shape of the spectra measured on the synthesized carbide. Insignificant changes in the structure of the corresponding distributions $P(H)$ can be due to both the further carbonization of the Fe–C phase and to a redistribution of the

iron atoms in the unit cell formed during the synthesis process. For definiteness, all the results and their analysis will further refer to the MS Fe–C phase produced after 30-h grinding.

An important portion of the studies on the mechanisms responsible for the formation of Fe–C carbide phases is concerned with the sequence of structural transformations. According to a known scheme, the formation of a mixture of cementite and ferrite in manganese silicon steels upon tempering is due to the interaction between the χ carbide Fe₅C₂ and the martensite [21]. However, the kinetics of the iron carbonization at the initial stages of synthesis points to the preferred formation of local environments with fields $H_{ef} \cong 20$ and 21 T (Fig. 1a, b), which are characteristic of iron atoms in the positions Fe(8d) and Fe(4c) of the θ -Fe₃C orthorhombic cell [19]. Given the optimum parameters of grinding, the formation of atomic configurations of this type becomes a dominant process and ensures synthesizing cementite in the single-phase state [15, 16].

It is seen from Fig. 1a that, along with the local environments mentioned above, the carbonization process leads to the formation of other Fe–C atomic configurations in α -Fe, with the hyperfine fields $H_{hf} \cong 6, 10, 14, 17,$ and 23 T . The concentration of Fe atoms in these configurations increases upon grinding from 17 to 35% (Fig. 1b) and reaches over 60% of the total concentration of iron at the final stage of synthesizing the Fe–C phase (Fig. 1d). The variation in the parameters of the local environment of Fe atoms (the number and the type of nearest neighbors, and their mutual disposition) during the α -Fe carbonization is regularly reflected in the shape of the Mössbauer spectrum and the structure of the distribution of the hyperfine fields $P(H)$.

It follows from Fig. 1d that, without allowance for small Mössbauer contributions in the region $H_{hf} > 25\text{ T}$, the number of component sextets in the spectrum of MS Fe–C phase is no more than six at the fields $6 \leq H_{hf} \leq 23\text{ T}$. For comparison, in an orthorhombic cell of Fe₇C₃ (*Pnma*) the iron atoms are located in five crystallographically nonequivalent positions with the multiplicity of Fe(8d) : Fe(8d) : Fe(4c) : Fe(4c) : Fe(4c) [5, 8–10]. In the monoclinic lattice of the χ carbide Fe₅C₂ (C1₂/c₁), the iron atoms are located in three positions Fe(8f) : Fe(8f) : Fe(4e) [5, 22]. In the triclinic cell of χ -Fe₅C₂ (*P1*), the iron atoms are located in ten positions Fe(2i) [23].

Note in conclusion that the number of the Mössbauer contributions and the structure of the distribution of the hyperfine fields $P(H)$ in the MS Fe–C phase (Fig. 1d) can change upon heating of the samples due to aggregation of the powder and relaxation of stresses, as well as a redistribution of Fe and C atoms within the unit cell because of the carbonization of the MS phase at elevated temperatures. The necessity of the temperature studies is determined also by the fact that all the phases in the Fe–C system at $T > 300\text{ K}$ are

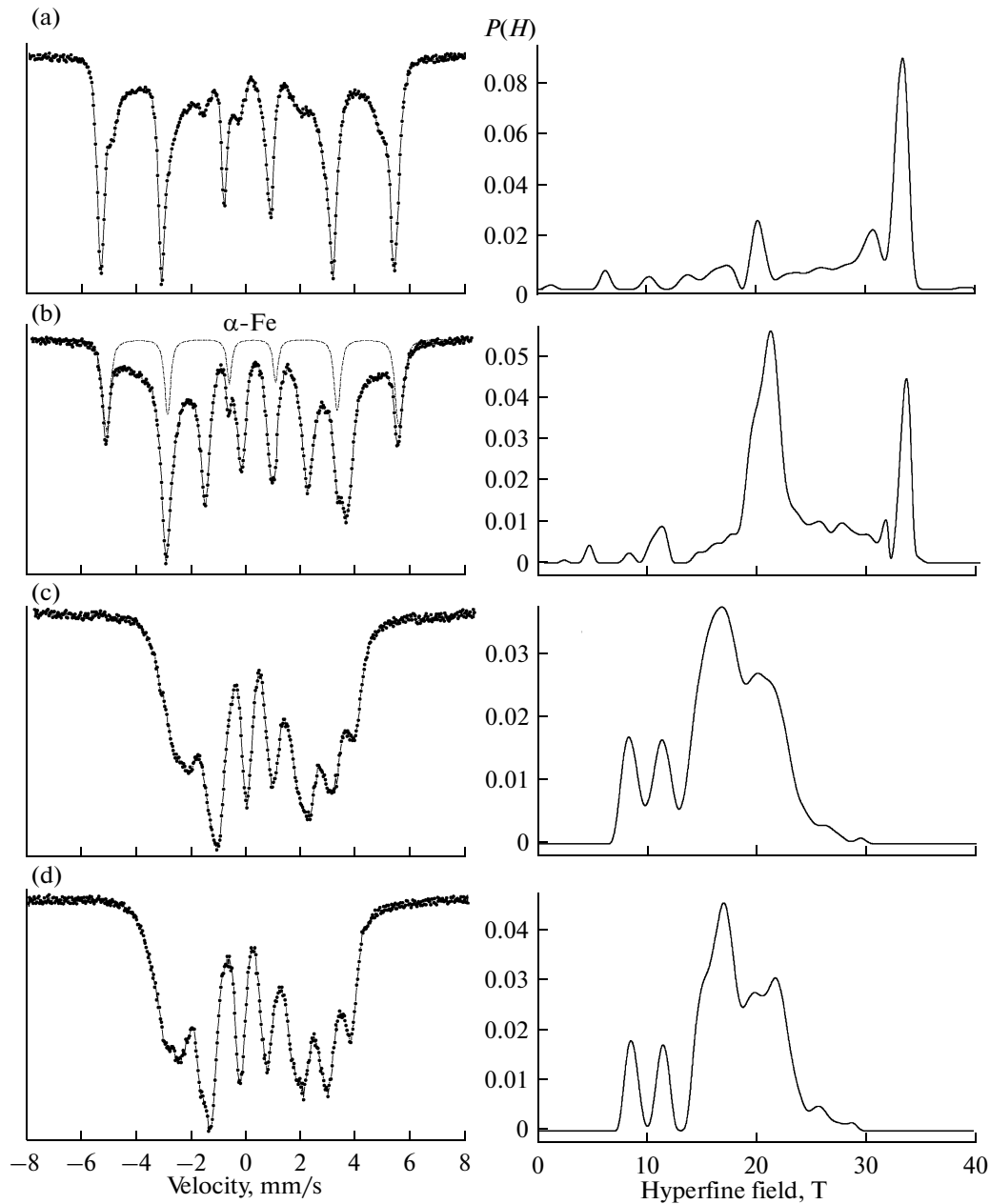


Fig. 1. Variation of the Mössbauer spectra of α -Fe and the corresponding probability density distribution function of hyperfine magnetic fields $P(H)$ during the mechanical synthesis in toluene after grinding for (a) 5, (b) 10, (c) 20, and (d) 30 h; $T_{\text{meas}} = 300$ K.

in a magnetically ordered state at the carbon concentrations $25 \leq c_C \leq 33$ (at %) [19, 20].

Results of Temperature Measurements

Figure 2 shows the change in the temperature dependence of the relative susceptibility $\chi_{\text{ac}}(T)/\chi_{\text{ac}}(300 \text{ K})$ of the MS Fe–C phase after 30-h grinding as a function of the temperature of subsequent heating. It follows from Fig. 2 (curve 1) that, upon heating, the MS phase undergoes the only transformation at the transition temperature $T_C = 509(5)$ K. Since the

$\chi_{\text{ac}}(T)/\chi_{\text{ac}}(300 \text{ K})$ dependence does not exhibit a feature near $T_C = 487(3)$ K characteristic of the transition of the cementite, which is most stable phase in the Fe–C system [19], into the paramagnetic state, then it is either absent in the MS phase or its concentration is lower than the sensitivity of the measuring setup. The value of $\Delta\chi_{\text{ac}}/\Delta T$ in the region of the magnetic transition is ~ 0.05 for curve 1, pointing to the presence of microinhomogeneities in the structure of the synthesized phase. The absence of a signal from the sample at $550 \leq T \leq 600$ K indicates that the MS carbide is magnetically single-phase.

The $\chi_{ac}(T)/\chi_{ac}(300\text{ K})$ dependences of the MS Fe–C phase after heating to 625 and 775 K are shown in Fig. 2 (curves 2 and 3, respectively). The state produced upon heating was fixed by water quenching. As in the previous case, it can easily be shown that at the preset conditions of the heat treatment the carbide is still a single-phase material, but is more homogeneous. It follows from Fig. 2 that heating leads not only to an increase in the homogeneity of the MS-phase microstructure, but also to a rise of the magnetic-ordering temperature. The Curie temperature, which is near 509 K in the carbide after its mechanical synthesis, elevates to 515(3) K after heating to 625 K, and reaches $T_C = 525(3)$ K after the phase is heated under these conditions to 775 K. In accordance with the concentration dependence of T_C in the Fe–C system, the rise of the Curie temperature of the carbide upon heating may indicate that the process of an additional temperature-induced carbonization is activated in the synthesized Fe–C phase. The temperature $T_C = 525$ K is limiting and corresponds to the maximum possible concentration of carbon in the MS phase under the heating conditions employed. The attempts to increase the carbon concentration by holding at 775 K or by increasing the heating temperature lead to the decomposition of the mechanically synthesized phase and the release of a considerable amount of carbon, which is condensed as carbon black in the cold end of the measuring ampoule.

The temperature $T_C = 518$ K was determined in one of the pioneering papers concerned with the susceptibility in the Fe–C system and was stated to be the Curie temperature of the Hägg χ carbide Fe₅C₂ [24]. However, no substantiations were given for this inference. It was conjectured from a systematic analysis of the pooled data of Mössbauer experiments and magnetic measurements known by the beginning of the 1980s that in the context of $\varepsilon' \rightarrow \chi \rightarrow \theta$ transformations, the formation of Fe_yC phases ($2.5 < y < 3$) with the Curie temperature in the region of $495 \leq T_C \leq 518$ K in the Fe–C system is due to an excess concentration of C atoms or their deficit with respect to stoichiometric θ -Fe₃C or χ -Fe₅C₂ [20]. However, the analysis performed cannot be viewed as complete without discussing the fundamental issues of nonequivalent positions, in which the excess atoms of carbon are located in the unit cells of these phases, and the place of the carbide Fe₇C₃ in the sequence of the phase transitions and its properties in the case of a carbon deficit, i.e., in the region of compositions $2.3 < y < 2.5$.

The Mössbauer spectra and the corresponding distributions of the hyperfine fields $P(H)$ for the MS carbide after synthesis and subsequent heating to 625 and 775 K are shown in Figs. 3a–3c, respectively. A comparison of the spectra of the MS Fe–C carbide in Fig. 3 demonstrates that their shapes differ substantially from the shape of the Mössbauer spectra of the Hägg carbide χ -Fe₅C₂ in the region of $2.09 \leq y \leq 2.46$

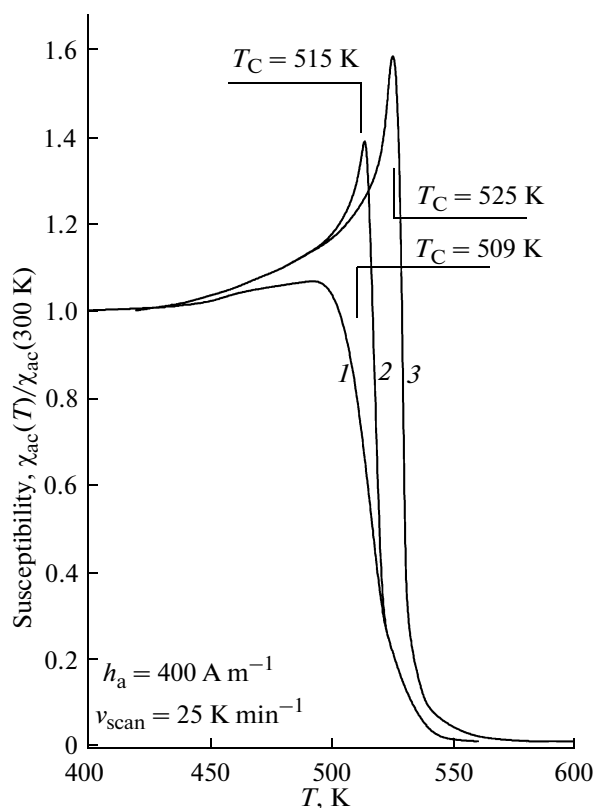


Fig. 2. Temperature dependence of the susceptibility $\chi_{ac}(T)/\chi_{ac}(300\text{ K})$ for the MS carbide Fe–C after grinding in toluene for 30 h (curve 1); and after heating to 625 (2) and 775 K (3).

[14, 19], but they approach the spectra characteristic of the carbides Fe₇C₃ synthesized by the crystallization of amorphous Fe_{1-x}C_x ($x \geq 0.45$) films, or amorphous powders having the nominal composition of Fe₅₀C₅₀, or powders synthesized under conditions used for the production of synthetic diamonds [13, 25].

It follows from Fig. 3 that the shape of the spectra of the carbide under study is generally preserved and, as distinct from the Curie temperature, weakly depends on the conditions of the subsequent heat treatment. A comparison of the $P(H)$ distributions shows that the heating temperature has the greatest effect on the low-field part of the distribution. As can be seen from Fig. 3, the portion of the Mössbauer contribution with a field $H_{hf} \cong 8.5$ T diminishes upon heating and becomes negligibly small above 775 K.

The origin of the low-field contributions to the $P(H)$ distributions in the Fe–C system has not been clearly understood. When analyzing the hyperfine interactions in amorphous Fe_{1-x}C_x films ($0.19 \leq x \leq 0.49$), it was assumed that $P(H)$ contained additional contributions in the region $H_{hf} \cong 0.38\langle H \rangle$ ($\langle H \rangle$ being the average field) caused by quadrupole interactions in this system [13]. The use of the method for the restoration of $P(H)$ distributions for carbides Fe–C is not quite correct also because of the piecewise-linear dependence of the iso-

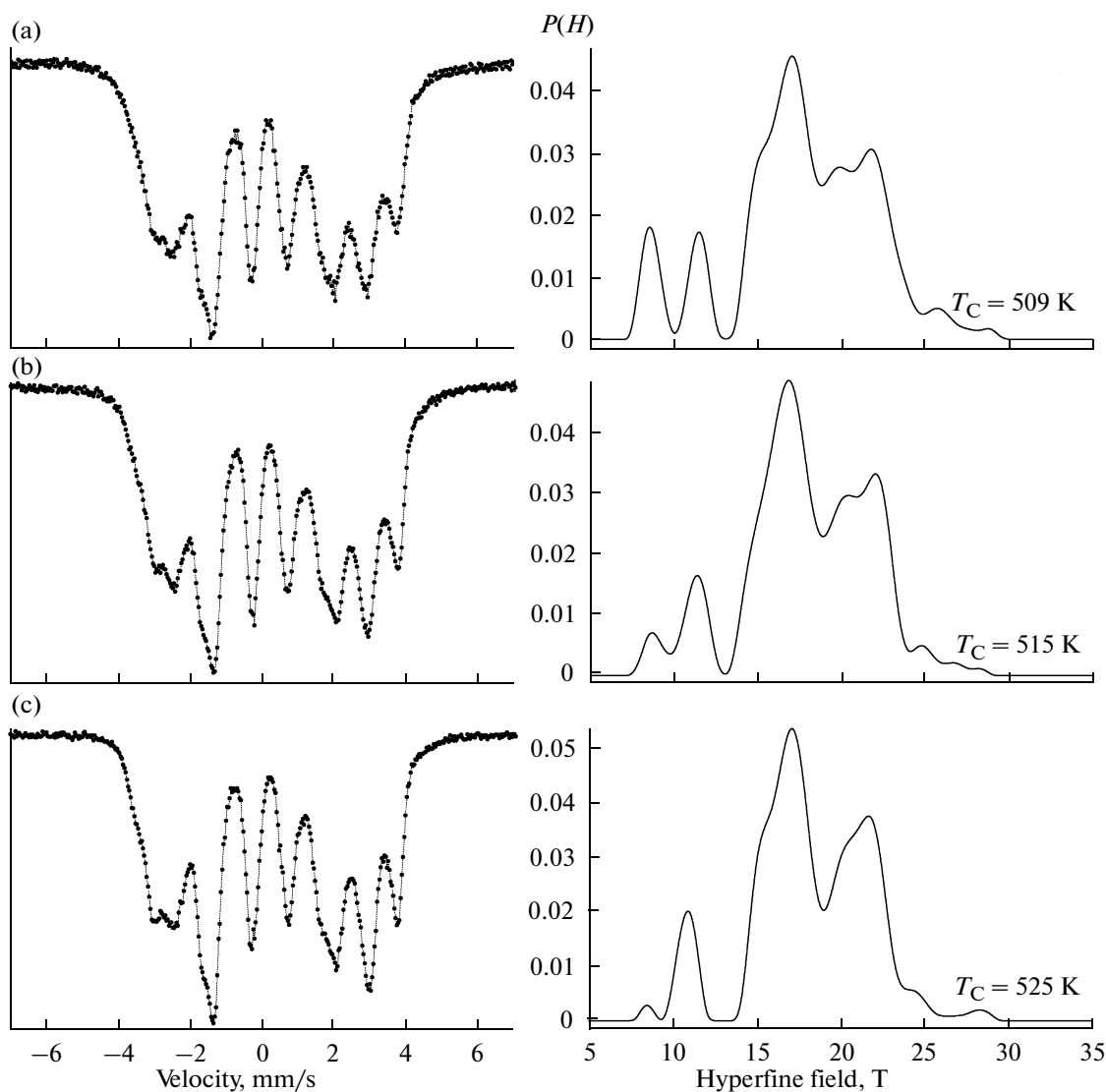


Fig. 3. Mössbauer spectra and the corresponding distributions of the hyperfine fields $P(H)$ in the MS carbide after (a) 30-h grinding, (b) heating to 625 K, and (c) heating to 775 K; $T_{\text{meas}} = 300$ K.

mer shift on the carbon concentration with a knee near $x_r \cong 0.32$. However, the calculation of $P(H)$ as a function of the sum of $p(H_i)$ shows [18] that the feature in the $IS(c_C)$ dependence does not influence the number of the Mössbauer contributions to the distribution for the carbide under study. Thus, it follows from Fig. 3 and from the earlier remarks that the number of sextets determining the experimental spectra of the MS Fe–C carbide is no less than five, at least for the carbide after heating to 775 K (Fig. 3c).

Calculations of the Mössbauer Spectra of the MS Fe–C Carbide

The exceeding of the interval of the confidence parameters ($N_{\text{obs}} - N_{\text{clc}}$) revealed for the experimental spectra of the synthesized Fe–C carbide with respect

to those found from the restored $P(H)$ distributions suggests the need to perform model calculations, in which constraints known from other experiments are imposed on the varying parameters of the hyperfine interaction. However, any data on the Mössbauer parameters of the carbide Fe_7C_3 , which have been calculated based on five constituent sextets, have not been reported in the literature. It was noted that the shape of the spectrum of the carbide Fe_7C_3 that was synthesized by crystallization of amorphous $\text{Fe}_{1-x}\text{C}_x$ films in the region of $x > x_r$ was independent of the carbon concentration at $T = 300$ K and was described by three broad sextets with the field values $H_1 = 24.8(3)$, $H_2 = 21.2(3)$, and $H_3 = 16.7(1)$ T, which were close to the hyperfine fields calculated for Fe_7C_3 synthesized under a high pressure and temperature [13, 25].

Table 1. Calculated values of the hyperfine interaction parameters ($T = 300$ K) for the MS carbide Fe–C after 30-h grinding of an iron powder in toluene, heating in a vacuum (10^{-1} Pa) to 675 and 775 K, and subsequent quenching in water

Sample	Parameter	Partial Mössbauer sextets ($T = 300$ K)				
		p_1	p_2	p_3	p_4	p_5
MS, 30 h ($T_C = 509$ K)	H_{hf} , T	22.6	20.6	17.5	15.5	10.7
	IS , mm/s	0.33	0.23	0.22	0.19	0.56
	QS , mm/s	−0.10	0.07	−0.04	0.02	−0.05
	f_{Fe} , %	15.4	22.2	29.5	21.6	11.3
MS + 675 K 0.25 h ($T_C = 525$ K)	H_{hf} , T	22.7	20.9	17.7	15.8	10.2
	IS , mm/s	0.29	0.26	0.20	0.20	0.45
	QS , mm/s	−0.11	0.05	−0.01	0.07	−0.05
	f_{Fe} , %	13.3	23.4	27.6	25.6	10.1
MS + 775 K ($T_C = 525$ K)	H_{hf} , T	22.9	21.1	17.9	16.3	10.4
	IS , mm/s	0.30	0.24	0.18	0.18	0.44
	QS , mm/s	−0.18	0.05	−0.04	0.08	−0.10
	f_{Fe} , %	12.5	27.8	23.8	28.8	7.1
Fe ₅ C ₂ [14]	H_{hf} , T	—	21.7(1)	18.1(1)	—	10.0(4)
	IS , mm/s	—	0.25(2)	0.19(2)	—	0.15(2)
	QS , mm/s	—	—	—	—	0.07(2)

Note: IS is taken relative to α -Fe; $QS = 1/4e^2qQ[1/2(3\cos^2\Theta - 1)]$. The measurement errors of the hyperfine field ΔH_i , isomeric shift $\Delta(IS)$, quadrupole splitting $\Delta(QS)$, and the relative contribution of a Mössbauer sextet Δf_i do not exceed 0.2 T, 0.02 mm/s, and 1.5%, respectively.

The fitting parameters in the zero approximation for all the experimental spectra of the MS carbide were obtained by the consecutive subtraction of the tentative constituents of the sextets from the calculated spectrum upon achieving the level at which the confidence interval was not exceeded. The parameters determined by this procedure for each Mössbauer sextet were used for the final calculations of the experimental spectra of the MS carbide on the assumption that the intensities of the lines in each of the sextets were described by the ratios of 3 : 2 : 1 : 1 : 2 : 3. The results of the spectrum calculations for the carbides after their synthesis and heating to 675 and 775 K are given in Table 1 and in Fig. 4.

It follows from Table 4 that the calculated experimental spectra of the MS carbide differ from the spectra of Fe₇C₃ and Fe₅C₂ [13, 14] not only in the number, but also in the magnitudes of the hyperfine interaction parameters. If the synthesized carbide Fe–C is indeed

a crystalline Fe₇C₃ phase, it may be thought that the five sextets present in the experimental spectra of the MS carbide are determined in the space group $Pnma$ by five crystallographically nonequivalent positions of iron atoms in an orthorhombic unit cell with a multiplicity $8d_1 : 8d_2 : 4c_1 : 4c_2 : 4c_3$ [5, 8–10]. However, the values of f_i for the partial sextets p_i correspond to $f_1 : f_2 : f_3 : f_4 : f_5 \cong 4 : 8 : 8 : 8 : 4$, pointing to the fact that this supposition is more justified if an MS-carbide unit cell contains 32 iron atoms, which correspond to the chemical formula Fe₇C₃, rather than 28 iron atoms, as in the case of Fe₈C₃.

Evaluating Concentration of Bound Carbon in the MS Carbide

The concentrations of the components in the MS Fe–C carbide could be easily found from a chemical analysis if the synthesized carbide were a single-phase

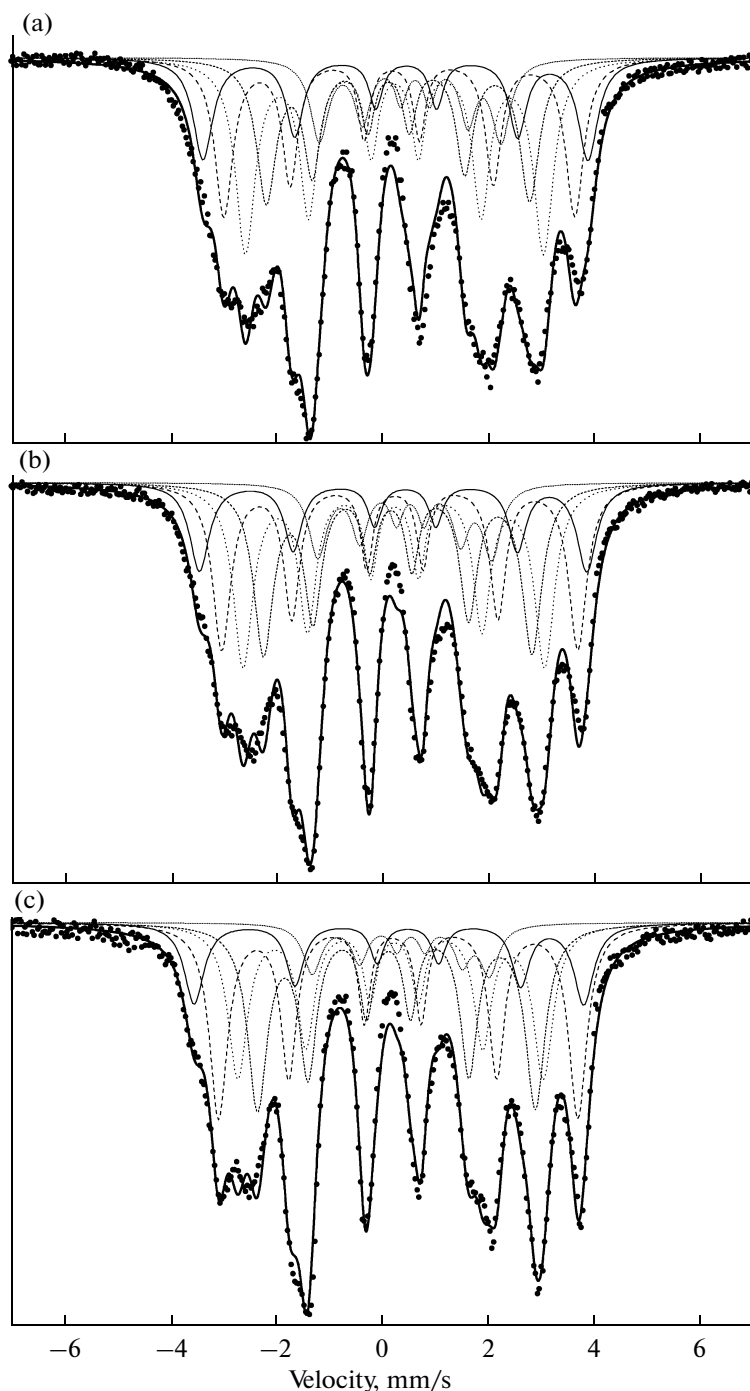


Fig. 4. Calculated Mössbauer spectra for the carbide Fe–C: (a) after mechanical synthesis, (b) after heating to 625 K, and (c) after heating to 775 K; the dots denote the experimental data; the thick line is the envelope for the five constituent Mössbauer sextets; $T_{\text{meas}} = 300$ K.

material not only in the magnetic respect and all the carbon atoms, as the iron atoms, in it were in the chemically bound state. For example, a thermogravimetric analysis (TGA) of a multiphase Fe_7C_3 sample (≤ 54 wt %), which was produced by the FTS method, showed that, out of 22 wt % C, the concentration of chemically bound carbon Fe–C in the carbide unit

cells was not over 4.3 instead of 8.4 wt % expected for stoichiometric Fe_7C_3 [3]. The reasons for such a low concentration of carbon bound to Fe atoms in the structure of the FTS sample was not discussed by the author of [3]. However, it follows from the TGA curve that the carbide under study was held for over 20% of the measurement time at temperatures (780–980 K),

Table 2. Evaluated concentrations of carbon in carbides Fe_{1-x}C_x: $y = \frac{1-x}{x} = \frac{6}{m} \sum_{i=1}^m \frac{1}{S_i(LC)_i}$, where (LC)_i denotes the partial linkage coefficients determined in accordance with [20]

Sample	Site occupancy factor (SOF)					$y = (1-x)/x$	x	Chemical formula
	S_1	S_2	S_3	S_4	S_5			
1	2	3	4	5	6	7	8	9
Fe ₇ C ₃ or Fe ₈ C ₃ ($S_i = 1$)	1	1	1	1	1	$\frac{2.299}{2.220}$	$\frac{0.303}{0.313}$	Fe _{0.697} C _{0.303} Fe _{0.687} C _{0.313}
MS 30 h (8d : 8d : 4c : 4c : 4c)	0.537	0.777	2.065	1.513	0.793	$\frac{2.726}{2.660}$	$\frac{0.268}{0.273}$	Fe _{0.732} C _{0.268} Fe _{0.727} C _{0.273}
MS 30 h (4 : 8 : 8 : 8 : 4)	1.228	0.888	1.180	0.865	0.906	$\frac{2.297}{2.181}$	$\frac{0.303}{0.314}$	Fe _{0.697} C _{0.303} Fe _{0.686} C _{0.314}
MS + 675 K 0.25 h (4 : 8 : 8 : 8 : 4)	1.062	0.937	1.105	1.022	0.810	$\frac{2.329}{2.231}$	$\frac{0.300}{0.310}$	Fe _{0.70} C _{0.30} Fe _{0.69} C _{0.31}
MS + 775 K (4 : 8 : 8 : 8 : 4)	0.999	1.110	0.952	1.152	0.571	$\frac{2.433}{2.347}$	$\frac{0.291}{0.299}$	Fe _{0.709} C _{0.291} Fe _{0.701} C _{0.299}

Note: The values in the numerator and the denominator of each fraction were obtained for the sets of the coefficients (LC)_i 2, 2, 3, 3, 4 and 2, 2, 3, 4, 4, respectively.

which were higher than the limiting possible temperature of the phase stability amounting to ≈ 775 K for the carbide Fe₇C₃ produced by mechanical synthesis.

An original method based on Mössbauer data for evaluating the concentration of carbon in FTS Fe–C samples was used for the characterization of O carbides Fe_yC (2.2 \leq y \leq 2.4) [20]:

$$y = \frac{1-x}{x} = \frac{6}{m} \sum_{i=1}^m \frac{1}{S_i(LC)_i}, \quad (1)$$

where x is the carbon concentration; m is the number of positions of iron atoms in a unit cell; $S_i = f_i/f_0$ is the factor characterizing the occupancy of the i th position by Fe atoms; and (LC)_i are the linkage coefficients [26].

The value of m corresponds to the number of sextets in the experimental spectra ($m = 5$). In the case of 32 iron atoms in the orthorhombic cell of the MS carbide, the values of f_0 are 12.5 and 25 at % Fe for the crystallographic positions 4c and 8d, respectively. As distinct from the cementite and the Hägg carbide, in which the coefficients (LC)_i are 2 and 2 and 2, 2, and 4 for two and three positions of Fe atoms in the unit cells of θ -Fe₃C and χ -Fe₅C₂, respectively, the partial coefficients (LC)_i in the MS carbide are unknown, but they can be found from the dependence on the hyperfine field H_{hf} as 2, 2, 3, 3, and 4 [20]. The calculated values for y and x are given in Table 2.

It follows from Table 2 that the carbon concentration in the MS carbide decreases upon heating and, in general, contradicts the dependence $T_c(x)$ for Fe_{1-x}C_x at 0.25 \leq x \leq 0.33. However, still more surprising is the coincidence of the concentration regions of 0.291 \leq x \leq 0.308, which were calculated from (1) for the MS car-

bide under study and for the carbides χ -Fe₅C₂ produced by crystallization from amorphous Fe_{1-x}C_x films at $x_c \leq 0.32$ [14]. It might be supposed that the detected discrepancies are connected with an uncertainty of (LC)₄ in the fields of 15 \leq $H_{\text{hf}} \leq 17$ T [20]. The use of the coefficients (LC)_i as 2, 2, 3, 4, 4 leads to some displacement of the calculated concentrations x in the MS carbide into the region 0.299 \leq x \leq 0.313, but all the features determined for the previous set of (LC)_i are preserved.

Thus, the revealed contradictions between the experimental and calculated data for the MS carbide can be sufficient to question the validity of the methods used for calculating the concentration of bound carbon in the Fe–C system from both the thermogravimetric values and the Mössbauer data, at least until we know the methods for separating the effects related to the number of iron and carbon atoms in the nearest environment of the resonance ⁵⁷Fe core and the available local displacements of atoms within the unit cell of a given type [27, 28].

Specific Features of the MS Carbide Decomposition

Since the concentration ranges of the carbides Fe_{1-x}C_x are determined ambiguously, additional information about the properties of the MS carbide can be derived from investigations of the specific features of its decomposition upon heating and holding at $T \geq 775$ K. Figure 5 shows the effect of different heat treatment regimes on the variation of the relative susceptibility of the MS Fe–C phase after 30-h grinding. Note that these investigations essentially replicate the known experiments [24], but differ from them by the use of water quenching (Fig. 5a) and cooling of the

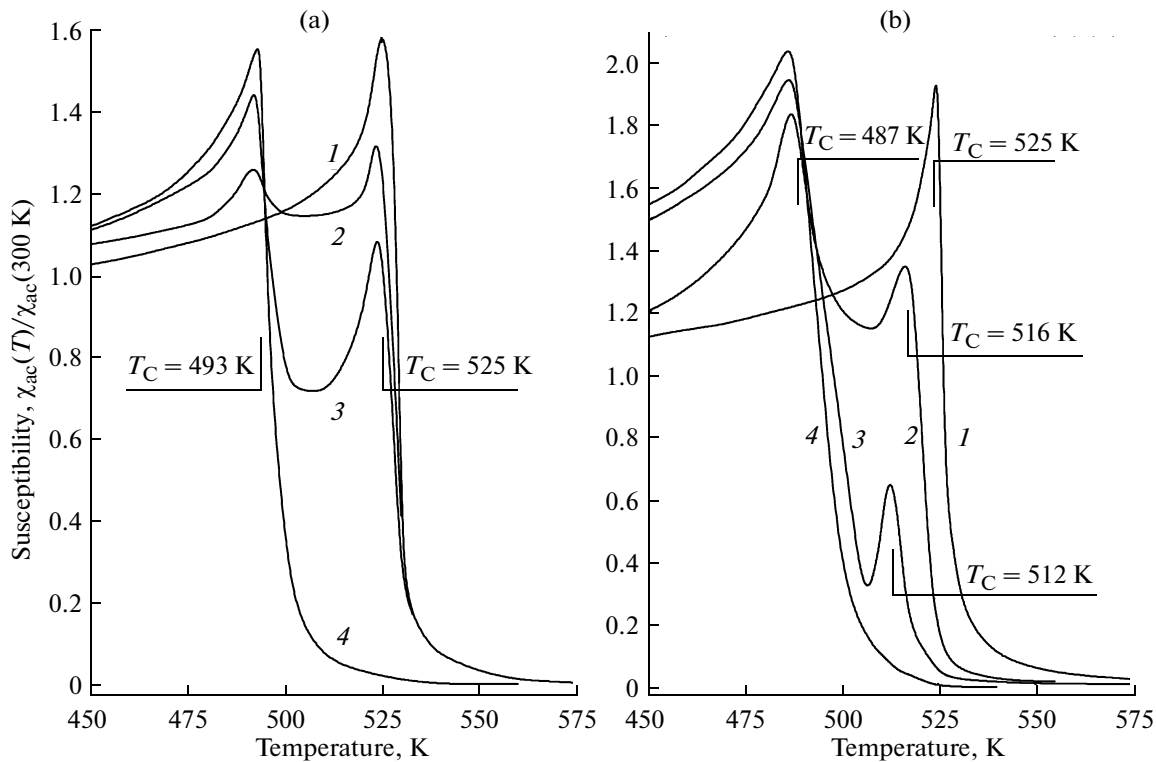


Fig. 5. Effect of different heat treatment regimes on the relative susceptibility $\chi_{ac}(T)/\chi_{ac}(300\text{ K})$ of the MS Fe–C phase: (a) after 30-h grinding: (a) (1) heating to 775 K and subsequent water quenching; (2) annealing for 5 min at 775 K; (3) annealing for 15 min at 775 K; and (4) annealing for 15 min at 925 K. (b) The MS Fe–C phase after heating and cooling in a furnace from (1) 775, (2) 825, (3) 875, and (4) 925 K.

samples in a fast-response furnace of the measuring cell after the switching-off of the furnace (Fig. 5b).

It follows from Fig. 5 that the MS phase becomes unstable at $T \geq 775\text{ K}$ and decomposes irrespective of the cooling conditions. The degree of instability of the MS phase increases with increasing temperature or holding time. Heating to $T \cong 925\text{ K}$ probably is sufficient for completing the decomposition process in the carbide under study. As can be seen from Fig. 5, the difference in the cooling rate affects the Curie temperature of the newly precipitated Fe–C phases, whose T_C is 487(3) and 493(3) K after cooling in the furnace and water quenching, respectively. Since from the viewpoint of the Mössbauer spectroscopy the phases formed upon the MS-carbide decomposition are identical and have the hyperfine interaction parameters approaching those of $\theta\text{-Fe}_3\text{C}$ [19], at this stage of the investigations it can be assumed that $T_C \cong 493\text{ K}$ is determined by the presence of excess carbon in the cementite [20].

An analysis of the specific features of the MS-phase decomposition makes it possible to arrive at some assumptions, which may be fundamental for understanding the mechanism by which carbides are formed in the Fe–C system in general. It was already noted that, according to the known scheme, a mixture of cementite and ferrite in manganese silicon steels dur-

ing their tempering is formed due to the interaction of the χ carbide and the martensite [21]. If it is assumed that the MS carbide under study indeed is the $\chi\text{-Fe}_5\text{C}_2$ phase, then from Fig. 5 it follows that the cementite precipitates in the absence of martensite. The presence of $\alpha''\text{-(Fe)C}$ was detected during a partial decomposition of $\theta\text{-Fe}_3\text{C}$ upon heating to 1075 K and subsequent cooling in the furnace. The variation of the $\chi_{ac}(T)/\chi_{ac}(300\text{ K})$ dependence during a “heating–cooling” cycle in the region of $1000 \leq T \leq 1025\text{ K}$ for the sample under study does not differ from the temperature hysteresis observed in the U15 steel after annealing at 925 K for 1 h and subsequent water quenching.

According to another scheme, the mechanism of cementite formation is determined by the interaction between the χ carbide and the hexagonal phase $\varepsilon\text{-Fe}_3\text{C}$ ($P6_322$) [3]. However, the realization of this scheme also seems to be doubtful, at least in the MS carbides under study, since a phase with $T_C \cong 650\text{ K}$ was not found in the samples.

Another conjecture is more general and is related to the coexistence of the carbides $\chi\text{-Fe}_5\text{C}_2$ and Fe_7C_3 in the Fe–C system. According to the concept of the $\varepsilon' \rightarrow \chi \rightarrow \theta$ transformations, the MS carbide that decomposes at $T \geq 775\text{ K}$ can be identified as the Hägg χ carbide if a mechanism by which additional posi-

tions for the location of iron and carbon atoms in the ratio of Fe : C = 2.5 can be determined for the monoclinic cell ($C1_2/c_1$) of the χ -Fe₅C₂ phase or a solid solution on its basis. This problem does not exist for the concept of $\varepsilon' \rightarrow \varepsilon \rightarrow \theta$ transformations, where ε is the Eckstrom–Adcock carbide Fe₇C₃. It was shown [10, 30] that all the structural models of the ε carbide are isotypic and can be generalized in the context of an “averaged” model with a limiting number of iron and carbon atoms $n_{\text{Fe}} = 40$ and $n_{\text{C}} = 24$ distributed in the space group $Pnma$ on seven and five crystallographically nonequivalent positions of the rhombohedral cell, respectively. In this universal unit cell, the θ phase Fe₃C corresponds to 25 at % and the χ carbide Fe₅C₂ corresponds to less than 44 at % of the maximum permissible number of iron and carbon atoms. An “intermediate” variant of the concept— $\varepsilon' \rightarrow \varepsilon \rightarrow \chi + \varepsilon \rightarrow \theta$ —is also known [3]. However, the absence of the phases ε -Fe₃C and χ -Fe₅C₂ in the samples under study with the hyperfine interaction parameters indicated in the literature [13, 19, 20] does not confirm the possibility that this concept is accomplished in the MS Fe–C carbides produced under the mechanical-synthesis conditions used in this work.

The “either–or” dilemma with respect to the χ and ε carbides Fe–C, which has not been solved so far in Mössbauer experiments, can be tried by the tools of the electron microscopy. An analysis of the crystalline structure of FTS carbides Fe–C showed convincingly [3] that the identification of a particular type of unit cells in the carbides refers to standard problems of the SAED method.

CONCLUSIONS

The paper describes the results of a study on the hyperfine interactions and magnetic properties of the Eckstrom–Adcock carbide Fe₇C₃ (ε phase) produced by mechanical synthesis using an iron powder in toluene. The unquestionable advantages of this method over the other synthesis techniques include the technical simplicity in combination with an efficient production of the carbides in a state close to the single-phase state. A considerable amount of the synthesized ε phase was sufficient for comprehensive investigations. It was found that the temperature stability boundary of the MS carbide was no higher than 775 K. The Curie temperature T_{C} of the ε phase changed between 509 and 525 K. The data of the Mössbauer experiments (⁵⁷Fe) demonstrated that the unit cell of Fe₇C₃ contains 32 iron atoms distributed over five crystallographic positions with the multiplicity of 4 : 8 : 8 : 8 : 4. The hyperfine interaction parameters were calculated for each nonequivalent position. The specific features of the decomposition at $T \geq 775$ K suggested that the most probable sequence of the phase transitions in the MS carbides Fe–C is $\varepsilon \rightarrow \theta$, where ε is the modified Eckstrom–Adcock carbide Fe₇C₃.

REFERENCES

1. H. C. Eckstrom and W. A. Adcock, “A New Iron Carbide in Hydrocarbon Synthesis Catalyst,” *J. Am. Chem. Soc.* **72** (2), 1042–1043 (1950).
2. S. Murphy, J. A. Whiteman, and J. H. Woodhead, “Iron Carbides in Tempered Steels,” in *Crystalline Solids* (Institute of Metals, London, 1969), pp. 72–77.
3. H. E. du Plessis, *The Crystal Structures of Iron Carbides*, <http://hdl.handle.net/10210/421>.
4. F. H. Herbstein and J. A. Snyman, “Identification of Eckstrom–Adcock Iron Carbide as Fe₇C₃,” *Inorg. Chem.* **3** (6), 894–896 (1964).
5. S. Nagakura and S. Oketani, “Structure of Transition Metal Carbides,” *Trans. Inst. Iron Steel Jpn.*, No. 5, 265–294 (1968).
6. A. A. Zhukov, L. E. Shternberg, V. A. Shalashov, et al., “Pseudohexagonal Fe₇C₃ Iron Carbide and Fe₃C–Fe₇C₃ Eutectics in Fe–C System,” *Izv. Akad. Nauk SSSR, Met.*, No. 1, 181–183 (1973).
7. H. L. Yakel, “Crystal Structures of Stable and Metastable Iron-Containing Carbides,” *Int. Met. Rev.* **30** (1), 17–40 (1985).
8. R. Fruchart and A. Rouault, “On the Existence of Twins in the Isomorphous Orthorhombic Carbides Cr₇C₃, Mn₇C₃, Fe₇C₃,” *Ann. Chim. Paris* **4** (3), 143–145 (1969).
9. M. A. Rouault, M. P. Herpin, and M. R. Fruchart, “Crystallographic Study of Carbides Cr₇C₃ and Mn₇C₃,” *Ann. Chim. Paris*, **5** (6), 461–470 (1970).
10. A. A. Putyatin, “On the Crystal Structure of Fe₇C₃ Carbide,” *Sverkhtverd. Mater.*, No. 4, 22–29 (1990).
11. S. Naka, A. Tsuzuki, and S. I. Hirano, “Diamond Formation and Behaviour of Carbides in Several 3d-Transition Metal–Graphite Systems,” *J. Mater. Sci.* **19**, 259–262 (1984).
12. S. J. Campbell, G. M. Wang, A. Calka, et al., “Ball Milling of Fe₇₅C₂₅: Formation of Fe₃C and Fe₇C₃,” *Mater. Sci. Eng., A* **226–228**, 75–79 (1997).
13. E. Bauer-Grosse and G. Le Caër, “Structural Evolution of Sputtered Fe_{1-x}C_x Films for 0.19 < x < 0.49,” *Philos. Mag. B* **56** (4), 485–500 (1987).
14. G. Le Caër and E. Bauer-Grosse, “Aperiodic Carbides Formed by Crystallization of Amorphous Fe–C Alloys,” *Hyperfine Interact.* **47**, 55–67 (1989).
15. V. A. Barinov, E. P. Elsukov, and L. V. Ovechkin, “Method of Obtaining Cementite Powder,” *USSR Inventor’ Certificate No. 1 678 525*.
16. E. P. Yelsukov, V. A. Barinov, and L. V. Ovechkin, “Synthesis of Disordered Fe₃C Alloy by Mechanical Alloying of Iron Powders with Liquid Hydrocarbon (Toluene),” *J. Mater. Sci. Lett.* **11**, 662–663 (1992).
17. E. P. Elsukov, V. A. Barinov, and L. V. Ovechkin, “Mechanochemical Synthesis of Iron Carbides by Milling Iron Powder in Toluene,” in *Proc. I Int. Conf. on Mechanochemistry (ICM-93)* (Cambridge Inter. Science, 1994), vol. 2, pp. 63–66.
18. V. S. Rusakov, *Mössbauer Spectrometry of Locally Inhomogeneous Systems* (Almaty, 2000) [in Russian].
19. G. Le Caër, J. M. Dubois, and J. P. Senateur, “Etude par spectrométrie Mössbauer des carbures de fer Fe₃C et Fe₅C₂,” *J. Solid State Chem.* **19**, 19–28 (1976).

20. G. Le Caër, J. M. Dubois, et al., "Characterization by Mössbauer Spectroscopy of Iron Carbides Formed by Fischer–Tropsch Synthesis," *J. Phys. Chem.* **86** (24), 4799–4808 (1982).
21. M. Dirand and L. Afqir, "Identification structurale précise des carbures précipités dans les aciers faiblement alliés aux divers stades du revenu. Mécanismes de précipitation," *Acta Metall.* **31** (7), 1089–1107 (1983).
22. J. J. Retief, "Powder Diffraction Data and Rietveld Refinement of Haegg-Carbide Fe_5C_2 ," *Powder Diffraction* **14**, 130–132 (1999).
23. H. E. Plessis, J. P. R. de Villers, and G. J. Kruger, "Redetermination of the Crystal Structure of Fe_5C_2 Haegg Carbide," *Z. Kristallogr.* **222** (5), 211–217 (2007).
24. E. I. Cohn and L. J. E. Hofer, "Mode of Transition from Haegg Iron Carbide to Cementite," *J. Am. Chem. Soc.* **72** (10), 4662–4664 (1950).
25. G. Le Caër, P. Matteazzi, E. Bauer-Grosse, et al., "Mössbauer Study of Mechanical Alloying in Fe–B and Fe–C Alloys," *J. Phys. Paris* **51**, C4, Suppl. no. 14, C4-151–C4155 (1990).
26. E. Parthe and J. M. Moreau, "Crystal Chemical Considerations on Rare-Earth–Transition Metal Compounds R_xT with $x > 1$ ($T = \text{Co, Rh, Ni, Pd}$)," *J. Less-Common Met.* **53** (1), 1–24 (1977).
27. M. E. Lines, "Hyperfine Fields in Iron–Metalloid Ferromagnetic Metals," *Solid State Commun.* **36** (5), 457–460 (1980).
28. V. A. Barinov, V. A. Tsurin, S. I. Novikov, et al., "Short-Range Atomic Order in Fe_2B Powders," *Fiz. Met. Metalloved.* **103** (5), 497–508 (2007) [*Phys. Met. Metallogr.* **103** (5), 470–480 (2007)].
29. V. A. Barinov and V. T. Surikov, "Short-Range Atomic Order in Metastable Fe_{23}B_6 Phase," *Fiz. Met. Metalloved.* **105** (3), 262–270 (2008) [*Phys. Met. Metallogr.* **105** (3), 245–253 (2008)].
30. E. Bauer-Grosse, J. P. Morniroli, C. Frantz, and G. Le Caër, "Defects in Fe_7C_3 Type Carbide Formed during the Crystallization of Amorphous High Carbon Alloys and Their Relations with Amorphous State," *J. Phys. Paris* **43**, C9, Suppl. no 12, C9-285–C9-288 (1982).