

Solid State Reactions in the Fe – C System under Mechanical Alloying

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Abstract

The behaviour of $\text{Fe}(100 - x)\text{C}(x)$ systems under mechanical alloying (MA) of elemental components within the concentration range up to $x = 32$ is studied by X-ray diffraction and Mössbauer spectroscopy. At carbon content $x < 20$ the amorphous phase is observed. At $x \geq 20$ the Fe_3C and Fe_7C_3 carbides are formed. For the high-carbon composition $\text{Fe}(68)\text{C}(32)$ the kinetics of solid state reactions is studied. The amorphous phase, Fe_3C cementite and Fe_7C_3 are formed sequentially in MA process. Solid-state reaction mechanism including the penetration of carbon along the grain boundaries of Fe, the formation of amorphous phase and carbides depending on C content and milling time is discussed.

INTRODUCTION

The Fe – C system has been attracting attention of investigators for many years in connection with its exceptional practical importance in particular. Nevertheless, the processes taking place in the system under different actions are still far from being well understood. This is valid for mechanical alloying (MA) processes, too.

A lot of discordant facts concerning phase formation in Fe – C system under MA were reported. The interstitial solid solution was obtained in mixtures with small C content (8.7 at. %) [1]. In the concentration range from 20 up to 50 at. % C the cementite Fe_3C [2–4], or carbide Fe_7C_3 [5], or carbide mixture $\text{Fe}_5\text{C}_2 + \text{Fe}_2\text{C} + \text{Fe}_3\text{C}$ [6] are obtained. However, a complete amorphization was observed in a number of works for the concentration range 20–25 at. % C [7–10]. On the other hand, it was determined [11–13] that the tendency to amorphization of Fe – C system is strengthened when the carbide-forming elements are added. In many works mentioned above, the stainless steel with high content of highly carbide-stabilizing Cr is

used as a milling tool material. Nevertheless, the possibility of contamination of samples by chromium and the effect of this contamination on system's behaviour are not discussed. Besides, the power intensity of the milling devices is not mentioned in these works, which hinders comparative analysis of the results obtained by different investigators.

Taking the above considerations into account, one can state that it is necessary to study phase evolution in the Fe – C system during MA within a broad range of compositions. The experiments of MA should be performed under identical conditions, using milling device of the known power intensity and a wear-resistant milling tool material; contamination level of the obtained samples should be tested. Thus, the purpose of the present work is to study MA processes in Fe – C system for the concentration range up to 32 at. % C with regard to above-mentioned requirements.

EXPERIMENTAL

Mechanical alloying (MA) of elemental powders was carried out in the protective atmos-

phere (Ar) using a planetary ball mill Fritsch P-7 with the power intensity of 2.0 W/g. Vial (volume 45 cm³) and balls (20, diameter 10 mm) were made of ball-bearing steel containing 1.0 mass % C and 1.5 mass % Cr. The total mass of the initial powder loading was $m_0 = 10$ g. Possible contamination of samples by the milling tool material was monitored by the measurement of the powder mass before and after mechanical treatment.

Pure iron (99.99) and pure carbon (99.99 hexagonal graphite) powders with the particle size less than 300 nm were used to form the initial mixtures with atomic ratios Fe(100 - x)C(x), $x = 5$ –32. X-ray diffraction (XRD) studies were carried out with monochromatized CuK $_{\alpha}$ radiation. ⁵⁷Fe Mössbauer spectra were measured at room temperature using a ⁵⁷Co source in Cr matrix.

RESULTS AND DISCUSSION

Milling for 16 h was found to be sufficient for MA completion for any carbon content within the investigated range. Besides, no pronounced contamination of mixtures was observed during milling (mass increment $\Delta m/m_0$ did not exceed 10 %); an exception was the Fe(68)C(32) system, for which $\Delta m/m_0 = 15$ % after grinding for 16 h. However, in this case solid-state reactions were completed within $t_{\text{mil}} = 12$ h with slight mass increment ($\Delta m/m_0 \leq 10$ %). This is why we shall first consider the phase states of all the mixtures after mechanical alloying for 16 h (12 h in the case of Fe(68)C(32)). Then we shall consider the sequence of solid state reactions (SSR) in the case of high-carbon Fe(68)C(32) as the most instructive composition.

Compositional behaviour of mechanosynthesis

Figure 1 shows the XRD patterns of the products of mechanical alloying of the system Fe(100- x)C(x) as a function of x . Up to $x = 15$ only the broadened bcc peaks are observed. Their positions point to the invariance of the lattice parameter which is equal to that of the pure α -Fe. However, as carbon content increases to $x = 15$, the increase of (110) reflection should

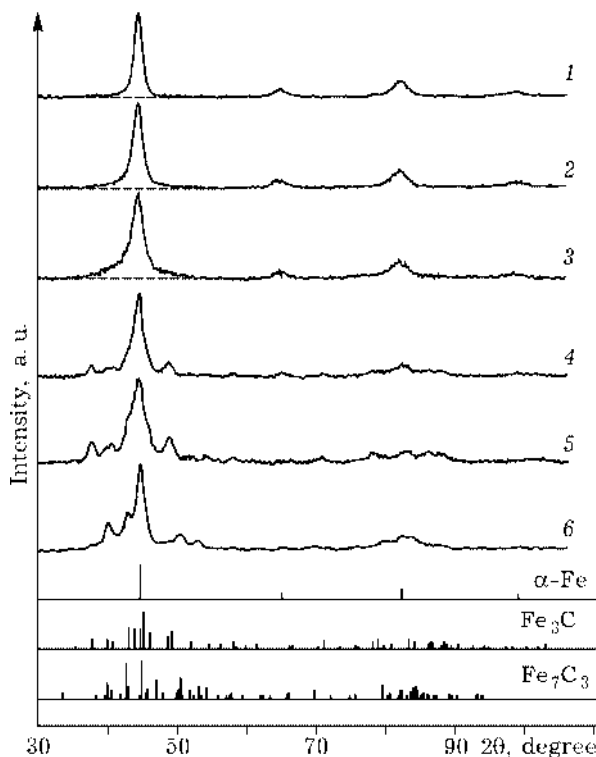


Fig. 1. XRD patterns of mechanically alloyed Fe(100 - x)C(x) system as a function of the composition of initial mixture (x). Milling time: 16 h (12 h for $x = 32$); $x = 5$ (1), 10 (2), 15 (3), 20 (4), 25 (5), and 32 (6). Diffraction patterns of the detected phases are also shown.

der intensity looking like amorphous halo takes place. For $x = 20$ the reflections of Fe₃C carbide (cementite) appear. They emerge more sharply in pattern of the Fe(75)C(25) composition. However, for $x = 32$ the reflections change, which can be interpreted in terms of higher-carbon Fe₇C₃ carbide formation.

Figures 2 and 3 show the ⁵⁷Fe Mössbauer spectra for the same samples. Already beginning from $x = 5$ the Mössbauer spectra are distinguished from the spectrum of pure α -Fe (see Fig. 2). A new magnetically split component with very broad lines appears. The subspectrum with broad lines points to the existence of formations in which carbon atoms are distributed chaotically around Fe atoms. The joint consideration of the Mössbauer and XRD data drives to conclusion that an amorphous Fe - C phase is formed in mixtures with $x < 20$.

The results of Mössbauer spectra fitting are shown in Table 1. As x increases, the fraction of the relative area of the amorphous phase subspectrum increases reaching a maximum (70 %) for Fe(85)C(15). The efficient magnetic field on

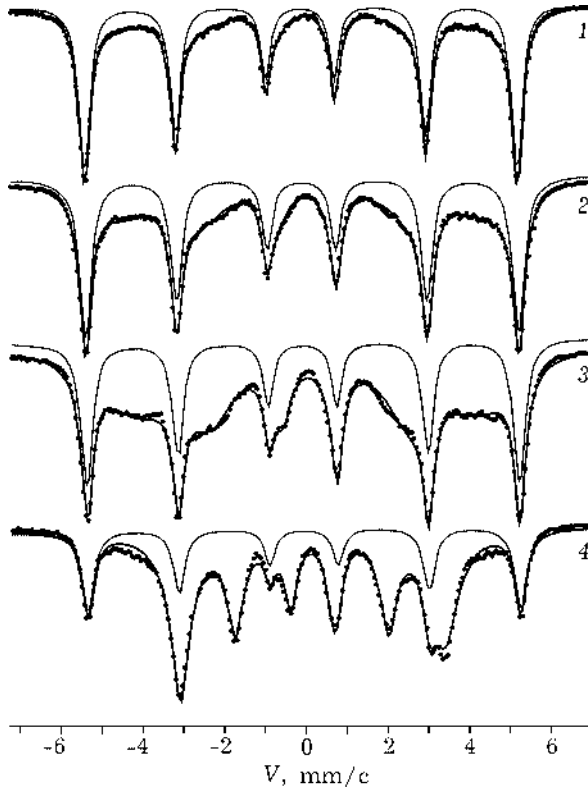


Fig. 2. Mössbauer spectra of the products of mechanical alloying in the $\text{Fe}(100 - x)\text{C}(x)$ system as a function of initial mixture composition ($x = 5-20$). Milling time: 16 h; $x = 5$ (1), 10 (2), 15 (3), and 20 (4).

Fe nuclei in the amorphous phase decreases, and the isomeric shift increases, which points to the increase of C concentration. The line width increases significantly. At the same time, the parameters of α -Fe subspectrum remain unchanged within the error, with an exception of line width, which slightly increases as x increases. A new sextet with substantially different parameters appears for $x = 20$ instead of the amorphous phase subspectrum (see Table 1 and Fig. 2). The line width changes espe-

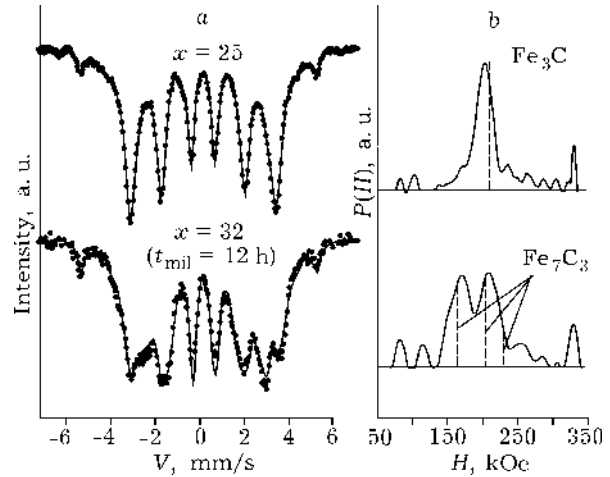


Fig. 3. Mössbauer spectra (a) and $P(H)$ functions (b) of mechanically alloyed $\text{Fe}(75)\text{C}(25)$ (for 16 h) and $\text{Fe}(68)\text{C}(32)$ (for 12 h) systems.

cially sharply being decreased from 2.3 mm/s for $x = 15$ to 0.8 mm/s for $x = 20$. The parameters of this sextet are close to the known parameters [14, 15] for non-deformed cementite spectrum ($H = 209$ kOe, isomeric shift $d = 0.2$ mm/s with reference to α -Fe and quadrupole splitting $DE_Q = 0.1$ mm/s). Therefore, we assume (in accordance with XRD data) that the obtained phase is cementite. The difference of its Mössbauer parameters from those of non-deformed cementite parameters is due to distortions caused by mechanical actions. As the carbon content increase up to $x = 25$ (see Fig. 3) the cementite fraction rise almost to 100 %. At $x = 32$ the Mössbauer spectrum may be interpreted as the appearance of the Fe_7C_3 carbide. The reference data of the hyperfine fields for non-deformed Fe_3C [14, 15] and Fe_7C_3 [16] are shown in Fig. 3, b as dashed lines, along with hyperfine field distribution functions $P(H)$. Similarly to the case of cementite

TABLE 1

Mössbauer parameters of the products of mechanical alloying in $\text{Fe}(100 - x)\text{C}(x)$ system

x	f , %	$\langle H \rangle$, kOe	d , mm/s	DE_Q , mm/s	G , mm/s
5	37 ₅	296 ₃	0.13 ₄	-0.05 ₃	1.8 ₁
10	50 ₅	279 ₃	0.12 ₄	-0.03 ₃	1.9 ₁
15	70 ₅	263 ₃	0.14 ₄	-0.02 ₃	2.3 ₁
20	63 ₅	203 ₃	0.19 ₄	0.01 ₃	0.82 ₅

Notes. 1. f is the area fraction, $\langle H \rangle$ is average effective field, d is isomeric shift with reference to α -Fe, DE_Q is quadrupole splitting, G is line width of amorphous (Fe_3C for $x = 20$) phase subspectrum. 2. Error in the last digit is shown.

phase, we suppose that slight mismatch of these data with the maximums of $P(H)$ functions is explained by distortions caused by mechanical actions.

Thus, an intermediate conclusion can be made on the basis of the results presented above. The MA in the $\text{Fe}(100 - x)\text{C}(x)$ system results in the formation of the amorphous phase ($x \notin 20$), cementite when $x = 20\text{--}25$ and carbide Fe_7C_3 in the case of $x \gg 30$.

Kinetics of mechanical alloying

The whole sequence of solid state reactions in Fe – C system can be conveniently considered with the example of high-carbon $\text{Fe}(68)\text{C}(32)$ composition. The XRD patterns of $\text{Fe}(68)\text{C}(32)$ system during MA are shown in Fig. 4. For milling up to 3 h, there are only broadened bcc reflexes of $\alpha\text{-Fe}$ and halo from amorphous structure close to the (110) reflection. Further, the cementite Fe_3C and carbide Fe_7C_3 with orthorhombic structure appear sequentially. The latter is observed most clearly at $t_{\text{mil}} = 12$ h (see Fig. 1). The measurements of $\alpha\text{-Fe}$ lattice parameter show that it does not change during the whole milling process of while the clearly discernible peaks of bcc phase (up to $t_{\text{mil}} = 8$ h) exist. The grain size and microstrains were determined from the analysis of XRD line profile. The superfine grain (about 4 nm) was revealed as early as at $t_{\text{mil}} = 1$ h. At further

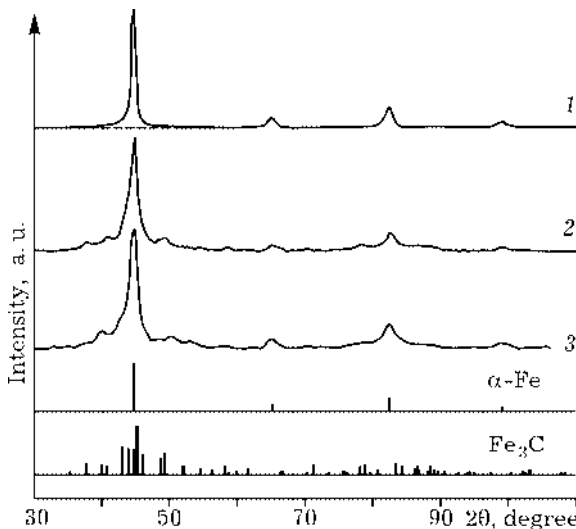


Fig. 4. XRD patterns of $\text{Fe}(68)\text{C}(32)$ system as a function of milling time. t_{mil} , h: 2 (1), 4 (2), and 8 (3).

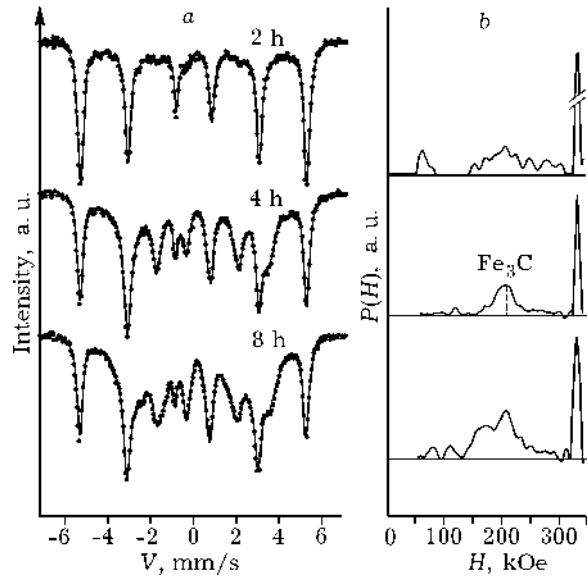


Fig. 5. Mössbauer spectra (a) and $P(H)$ (b) of mechano-synthesis products in $\text{Fe}(68)\text{C}(32)$ system as a function of milling time.

milling the grain size does not change. The lattice microstrains gradually increase up to 0.15 % after milling for 6–8 h.

Mössbauer spectra and the functions $P(H)$ retrieved from them are shown in Fig. 5. After milling for short time intervals $t_{\text{mil}} \notin 3$ h, the major contribution into the spectrum is made by the component from pure $\alpha\text{-Fe}$. Nevertheless, it is possible to make the conclusion about the beginning of Fe and C MA with the amorphous phase formation basing on the arrangement of the spectrum relative to non-resonance level (it is shown by horizontal line) and the presence of hyperfine field distribution widely ranged from 140 to 300 kOe. At $t_{\text{mil}} \approx 3$ h the Mössbauer spectrum shows an additional sextet, and at $t_{\text{mil}} \approx 8$ h (see Figs. 5 and 3) the complex spectrum of the Fe_7C_3 carbide is detected.

As one can see, the phase composition evolution of the high-carbon mixture is generally similar to the sequence of phase states of the final product obtained at increase of the C content in initial mixture (see the previous section). This fact indicates that a common mechanism of MA in Fe – C system within a broad concentration interval exists.

Let us consider the probable mechanisms of mechanosynthesis of iron and carbon. The invariance of lattice parameter being equal to

that of pure α -Fe testifies that no interstitial supersaturated solid solution of carbon in a body of α -Fe grains is formed. The presence of super-equilibrium carbon in interstices of iron lattice would give the additional Mössbauer components due to C atoms in close vicinity of Fe atoms, as it takes place in case of quenched martensite [17]. However, broad distribution $P(H)$ (see Fig. 5), halo not far from (110) diffraction peak (see Fig. 4) and anomalously rapid grain refinement observed for samples with $t_{\text{mil}} \leq 3$ h indicate the effect of carbon presence in α -Fe. The carbon atoms can penetrate into iron along the grain boundaries and dislocation cores. The carbon atoms can penetrate into Fe crystallites probably by the interstitial diffusion as well, but they must be immediately adsorbed on dislocations. It is known that the dislocations and other lattice defects are more preferable positions for carbon atoms in iron than normal interstices: the heat effect of carbon transfer from the latter positions in the former ones is $\Delta H_C^d = -27.5$ kJ/mol of carbon [18]. It is possible to estimate equilibrium distribution of carbon in these positions. If C_d and C_i are concentrations of carbon in defects and interstices, respectively, then $C_d / C_i = \exp(-\Delta H_C^d / (RT)) \approx 1000$ at representative process temperature of $T = 473$ K. At such relation, it is clear that the carbon amount residing in defects can be very high and is restricted only to the amount (density) of these defects in spite of the fact that $C_i \leq 0.095$ at. % (the limitary interstitial concentration in α -Fe). With regard to high-defective nanocrystalline state, it is possible to expect that almost all the carbon atoms entering α -Fe will be arranged in defects such as grain boundaries and dislocations, and consequently the lattice parameter will not change.

According to the present notions [19–21], the nanocrystalline state obtained by severe deformation is characterized by both an almost defect-free grain body and a great extent of non-equilibrium large-angle grain boundaries saturated with defects. The elastically distorted interfacial area 1.0–1.5 nm deep exists near the nanograin boundary. We assume that carbon having a very small miscibility in undistorted bcc Fe penetrates into nanocrystal-

line iron along interfacial areas where it forms an amorphous phase.

The carbide Fe_3C is formed just when C concentration in the interfacial areas achieves $\gg 25$ at. %. It is known [18, 22] that places of carbide nucleation in steels are usually the grain boundaries where carbon concentration is the greatest. Carbon penetrating along the new boundaries (α -Fe/ Fe_3C boundaries) provides the increase of cementite amount. However, as the carbon content increases over the Fe_3C stoichiometry, it becomes unstable. Then the reaction proceeds by the pathway involving the formation of Fe_7C_3 carbide. The Fe_7C_3 fraction reaches almost 100 % at $t_{\text{mil}} = 12$ h (see Fig. 5). It should be noted that the enthalpy of carbide formation in Fe – C alloy is $-26.0 \dots -28.4$ kJ/mol of carbon [18], which is close to ΔH_C^d . This means that an energetic driving force of carbide formation is absent. In other words, carbide precipitation is hindered even in places of their most probable formation (on defects).

The carbides are formed by crystallization of the amorphous phase when the carbon concentration in the latter approaches the carbide stoichiometric concentration. In $\text{Fe}(100 - x)\text{C}(x)$ with small carbon content ($x < 20$), the C concentration in the amorphous phase is small and consequently the carbides are not formed. The Fe_3C and Fe_7C_3 carbides are formed when $x \geq 20$.

CONCLUSIONS

The study of mechanical alloying in $\text{Fe}(100 - x)\text{C}(x)$ system over the wide C content range up to 32 at. % C reveals a common sequence of solid-state reactions:

Fe – C \otimes Amorphous phase for $0 < x < 15$;

Fe – C \otimes Amorphous phase \otimes Fe_3C
for $20 \leq x \leq 25$;

Fe – C \otimes Amorphous phase \otimes Fe_3C \otimes Fe_7C_3
for $x = 32$.

Mechanism of mechanical alloying is connected with carbon diffusion along nanograin boundaries of iron.

Acknowledgements

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