

## The Effect of Wear of Grinding Tools on the Results of Mechanical Alloying of Fe and Si(C)

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### Abstract

The interaction of the sample with wear products from milling bodies made of stainless steel, tungsten carbide and strengthened ball bearing steel (ShKh15) is investigated by means of Mössbauer spectroscopy, X-ray diffraction and gravimetric measurements. It is stated that under identical conditions the most resistant to wear and the least prone to participate in mechanical alloying is the ShKh15 steel. It is shown that when choosing materials for milling bodies for the investigations of mechanical alloying, one should take into account a condition that provides obtaining reliable information: an increase of the mass of sample under investigation should not exceed 10 % during mechanical treatment.

### INTRODUCTION

At present, mechanical alloying is widely applied as a low-temperature method to synthesize various non-equilibrium phases. High-energy devices with milling bodies made of different materials are used for alloying. A question concerning the purity of the resulting product arises (whether mean chemical composition of the initial mixture corresponds to that of the final product), since the target product is contaminated by wear products of milling bodies. Wear products can interact with sample to be ground; because of this, special attention should be paid to choosing materials for milling bodies in experiments on mechanical alloying. On the other hand, the contamination degree of the sample under treatment and its interaction with wear products may be determined also by the composition of powder mixture under investigation. Really, no substantial contamination was detected in the system Fe – Sn either after mechanical alloying [1] or after mechanical grinding [2]. In the Fe – B system, as this is shown in [3], inconsistency of results

obtained for mechanical activation is explained by the effect of various impurities that get into the sample under treatment. However, it should be noted that the problem connected with contamination during mechanical activation has not received sufficient attention yet.

The goal of the present investigation was to demonstrate that experiments on mechanical activation involving grinding bodies made of various materials require a careful analysis of the purity of ground samples for impurity content and the investigation of the effect of impurities on the results obtained.

Compositions Fe(75)/Si(25), Fe(68)/Si(32) and Fe(68)/C(32) were used for mechanical alloying.

### EXPERIMENTAL

Mechanical alloying of the Fe – Si system was carried out in ball planetary mills with balls and vessels made of the following materials: tungsten carbide (Pulverizette-6 mill), stainless steel 12 % Cr + 8 % Ni, and ShKh15

steel 1 % C + 1.5 % Cr (Pulverizette-7 mill). Mechanical alloying of the Fe – C system was carried out in the Pulverizette-7 mill with balls and vessels made of ShKh15. Mechanical mixtures of iron powder of special-purity grade os. ch. 13-2 (99.98 %), high-purity Si (99.99 %) and spectrally pure graphite were used as initial materials. Grinding was carried out in Ar atmosphere. Grinding time ( $t_g$ ) was varied within the range 1–48 h. Temperature to which the sample, vessels and balls were heated during mechanical treatment did not exceed 60 °C. For each  $t_g$ , the mass of the loaded initial mixture was 10 g. To determine the contamination degree of powders by the wear products of the vessels and balls used for treatment, gravimetric measurements of the sample, vessels and balls were carried out before and after treatment. Contamination of samples with tungsten carbide WC was determined using quantitative phase analysis of X-ray diffraction patterns. To analyze the effect of contamination on chemical and phase composition of the products of mechanical synthesis, X-ray diffraction and Mössbauer spectroscopy were used.

X-ray structural investigations were carried out with a DRON-type diffractometer with  $\text{CuK}_\alpha$  monochromatic radiation. Mössbauer measurements were performed with a YaGRS-4M spectrometer operating in the constant acceleration mode with a  $^{57}\text{Co}$  source in Cr matrix. To obtain an ordered state, some samples of the Fe – Si system were annealed in vacuum after mechanical alloying.

## RESULTS AND DISCUSSION

### Analysis of the change in sample mass

Figure 1 shows the data on relative changes of sample mass ( $\Delta m/m_0$ ) depending on time of mechanical treatment (alloying). One can see in Fig. 1, a that the largest mass increase is observed in the Fe(75)/Si(25) mixture when the vessels and balls made of tungsten carbide and stainless (SL) steel are used. Strengthened ball bearing steel is more stable to wear: at  $t_g \leq 10$  h,  $\Delta m/m_0 = 0$ . It is also important to note that the observed  $\Delta m/m_0$  values are determined mainly by the wear of balls and, to a less extent,

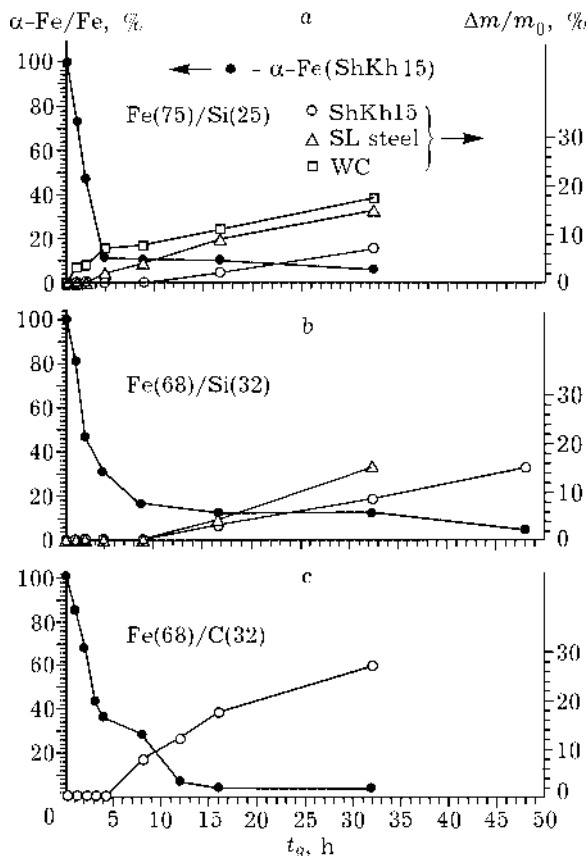


Fig. 1. Dependencies of the relative mass increase ( $\Delta m/m_0$ ) and relative content of  $\alpha\text{-Fe}$  ( $\alpha\text{-Fe/Fe}$ ) in the milled mixture on the milling time.

of vessel. The data for the Fe(68)/Si(32) mixture (see Fig. 1, b) confirm the advantage of ShKh15 steel in comparison with stainless steel. However, the wear of ShKh15 steel increases sharply when the composition of the initial mixture is changed. One can see comparing Fig. 1, b and c that at  $t_g = 16$  h  $\Delta m/m_0$  for Fe(68)/C(32) is about an order of magnitude larger than that for Fe(68)/Si(32) mixture.

In each specific case, it is necessary to answer the question concerning the interaction of wear products with the sample under treatment. Figure 1 shows time dependencies of the relative content of unreacted iron ( $\alpha\text{-Fe/Fe}$ ) in the case when ShKh15 steel is used; these dependencies were obtained by mathematical processing of the Mössbauer spectra of ground mixtures. We described the processing details in [4]. Three stages can be distinguished in the behaviour of  $\alpha\text{-Fe/Fe}$  mixture depending on  $t_g$ : 1) a sharp decrease of  $\alpha\text{-Fe/Fe}$ , which is a direct evidence of the mechanical alloying of

iron with silicon or carbon; 2) the appearance of a plateau which is most clearly seen for the Fe(68)/Si(32) system within the  $t_g$  range from 8 to 32 h (see Fig. 1, b); in general, the appearance of the plateau coincides in time with the increase of sample mass after grinding; 3) decrease of  $\alpha\text{-Fe}/\text{Fe}$  to 0 when  $Dm/m_0 \approx 10\%$ . In our opinion, the third stage points directly to the mechanical alloying of the sample under treatment with the wear products. We performed a detailed analysis of the interaction of wear products with sample under treatment using the data of X-ray diffraction and Mössbauer spectroscopy.

### The Fe – Si system

First of all, we must make preliminary remarks on the estimation of Si content in a mechanically alloyed  $\alpha\text{-Fe}(\text{Si})$  supersaturated solid solution (SSS).

The concentration dependence of the bcc lattice parameters of the ordered Fe – Si alloy and that disordered by ball milling is well studied within a wide concentration range. An ordered alloy disorders during the milling time of 8 h when contamination is virtually absent. Within the concentration range from 13 to 33 at. % of Si, the disordered Fe – Si alloys have a decreasing linear dependence of the lattice parameter on concentration. On ordering by the  $D0_3$  type, the bcc lattice parameter decreases, though the linear dependence on concentration conserves. Thus, the Si concentration may be determined by the lattice parameter to an accuracy of 0.5 at. %.

More precise estimation of Si content in the alloys near the  $D0_3$  stoichiometry (25 at. % Si) can be obtained with the help of the Mössbauer spectroscopy. There are only two magnetically split components with different hyperfine magnetic fields (HMF) in the ordered stoichiometric  $\text{Fe}_3\text{Si}$  alloy: one is from the Fe atoms with 8 Fe atoms in nearest environment (HMF at Fe nuclei  $H_0 = 312$  kOe) and another from the Fe atoms with 4 Si and 4 Fe atoms in nearest environment ( $H_4 = 200$  kOe). When Si content decreases, there appear components with 3, 2 and 1 Si atoms in the nearest environment of Fe in Mössbauer spectrum, a sharp

concentration dependence of intensity of components  $P_4(H_4)$  and  $P_3(H_3 = 250$  kOe) having been found [7, 8], which allows one to estimate the Si content with high accuracy. The data from the X-ray diffraction and Mössbauer spectroscopy give the Si content in ordered alloys with an error of 0.2 at. %.

Thus, having taken a concentration dependence of the lattice parameter of uncontaminated ordered and disordered Fe – Si alloys as a reference, we can estimate Si content in the samples under study with high accuracy by the X-ray diffractational data on the lattice parameter. Besides, for an alloy with Si content near 25 at. % annealed to the  $D0_3$  ordering, the Si content may be easily estimated by the ratio between intensities  $P_k$  of components of the Mössbauer spectrum (where  $k$  denotes the number of Si atoms in the nearest environment of Fe atoms). Two samples of the stoichiometric composition  $\text{Fe}_{75}\text{Si}_{25}$  obtained with a usual technique were taken as a primary standard: one was annealed to the complete  $D0_3$  ordering and another was milled during 8 h after annealing (Pulverizette-7 mill, the ShKh15 steel, Ar).

To compare with a primary standard, the Fe(75)/Si(25) mixtures under study were annealed after mechanical alloying to the maximum ordering according to the scheme: 800 °C (1 h) @ slow cooling down to 500 °C @ exposure at 500 °C during 4 h.

**Fe(75)/Si(25).** The data on Si content in the samples mechanically alloyed and annealed to the maximum ordering and in the primary-standard  $\text{Fe}_3\text{Si}$  alloy are presented in Table 1.

In the milled primary-standard  $\text{Fe}_{75}\text{Si}_{25}$  alloy, Si content was found to be 25.0 at. %, which was indicative of the absence of sample contamination after grinding during 8 h in the ShKh15 steel. The annealing of this alloy (the  $\text{Fe}_3\text{Si}$  state) provided a high-accuracy confirmation of the absence of contamination by the products of wear of the balls and vial. The X-ray pattern (Fig. 2), Mössbauer spectrum and the HMF distribution function  $P(H)$  (Fig. 3) entirely correspond to the data known from the literature. Si content in the ordered state was estimated as  $(25.0 \pm 0.2)$  at. % from the intensity of the component  $P_4(H_4) = 0.66$  (Fig. 4) and the bcc lattice parameter 0.2826 nm.

TABLE 1

Si content in mechanically alloyed samples Fe(75)/Si(25), in the milled primary standard Fe<sub>75</sub>Si<sub>25</sub> and in the annealed to the D0<sub>3</sub> type alloys from the data of the X-ray diffraction (XRD) and Mössbauer spectroscopy (MS)

Sample	Time of treatment, h	SL steel	WC	ShKh15
Fe(75)/Si(25)	8	—	$\frac{25.0(0.2836)}{23.4(0.2829) / 23.5}$	$\frac{23.0(0.2845)}{24.4(0.2837) / 24.2}$
	16	$\frac{20.0(0.2846)}{22.3(0.2832) / 22.5}$	$\frac{23.5(0.2840)}{22.2(0.2832) / 22.1}$	$\frac{23.5(0.2840)}{23.7(0.2829) / 23.8}$
	32	$\frac{21.0(0.2844)}{21.3(0.2834) / 21.8}$	$\frac{22.0(0.2848)}{20.1(0.2837) / 20.2}$	$\frac{22.0(0.2843)}{22.8(0.2838) / 23.2}$
Fe <sub>75</sub> Si <sub>25</sub>	8			$\frac{25.0(0.2837)}{24.9(0.2826) / 25}$

Note. Numerator – after mechanical treatment (XRD), denominator – after annealing (XRD/MS). The numbers in brackets show the bcc lattice parameter.

The mechanical alloying of Fe(75)/Si(25) in SL steel during  $t_g = 16$  and 32 h which gives a large mass increment  $Dm/m_0$  (see Fig. 1, a), changes the Si content significantly (see Table 1). The Mössbauer spectrum of these samples after annealing contains an intensive component  $P_3(H_3)$  (see Figs. 3 and 4). A comparison between Si contents in the annealed and milled samples shows that at  $t_g = 16$  h the formation

of the SSS is not completed yet (Si content increases after annealing), whereas at  $t_g = 32$  h the process comes to a close. However, absence of the component from the unreacted  $\alpha$ -Fe in the Mössbauer spectra of the Fe(75)/Si(25) mixture milled for 16 and 32 h in the SL steel and the Si content of 20–21 at. % are a direct indication of the intensive mechanical alloying of the milled sample with the products of wear of the balls and vial made of the SL steel.

In the case of milling with vial and balls made of WC, time  $t_g = 8$  h is found to be large enough for the formation of the SSS with 25 at. % Si to complete, the component from the unreacted  $\alpha$ -Fe being absent in Mössbauer spectrum. As the WC-wear products contain no Fe, one may conclude that during this stage ( $t_g = 8$  h) no interaction occurs between the sample and the wear products. However, the increase of the time  $t_g$  up to 16 and 32 h results in a considerable decrease of Si content in the SSS, indicating the interaction between the sample and the wear products. Unexpected were the results on the annealed samples from the Mössbauer spectroscopy and X-ray diffraction. The Mössbauer spectrum of the sample after the mechanical treatment during 8 h and the subsequent annealing contains the  $P_3(H_3)$  component (see Fig. 3) which is indicative of a Si-content decrease (see Fig. 4) dur-

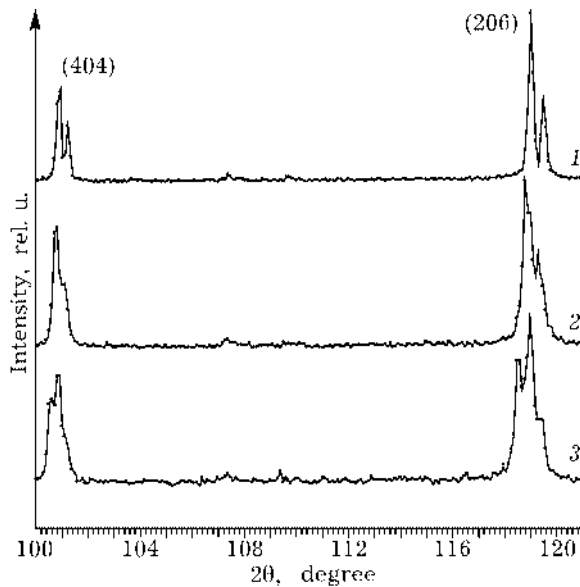


Fig. 2. The X-ray diffraction patterns of the annealed primary standard (Fe<sub>3</sub>Si) alloy (1) and of the Fe(75)/Si(25) mixtures after the mechanical alloying during 16 (2) and 32 h (3) with the use of the ShKh15 steel.

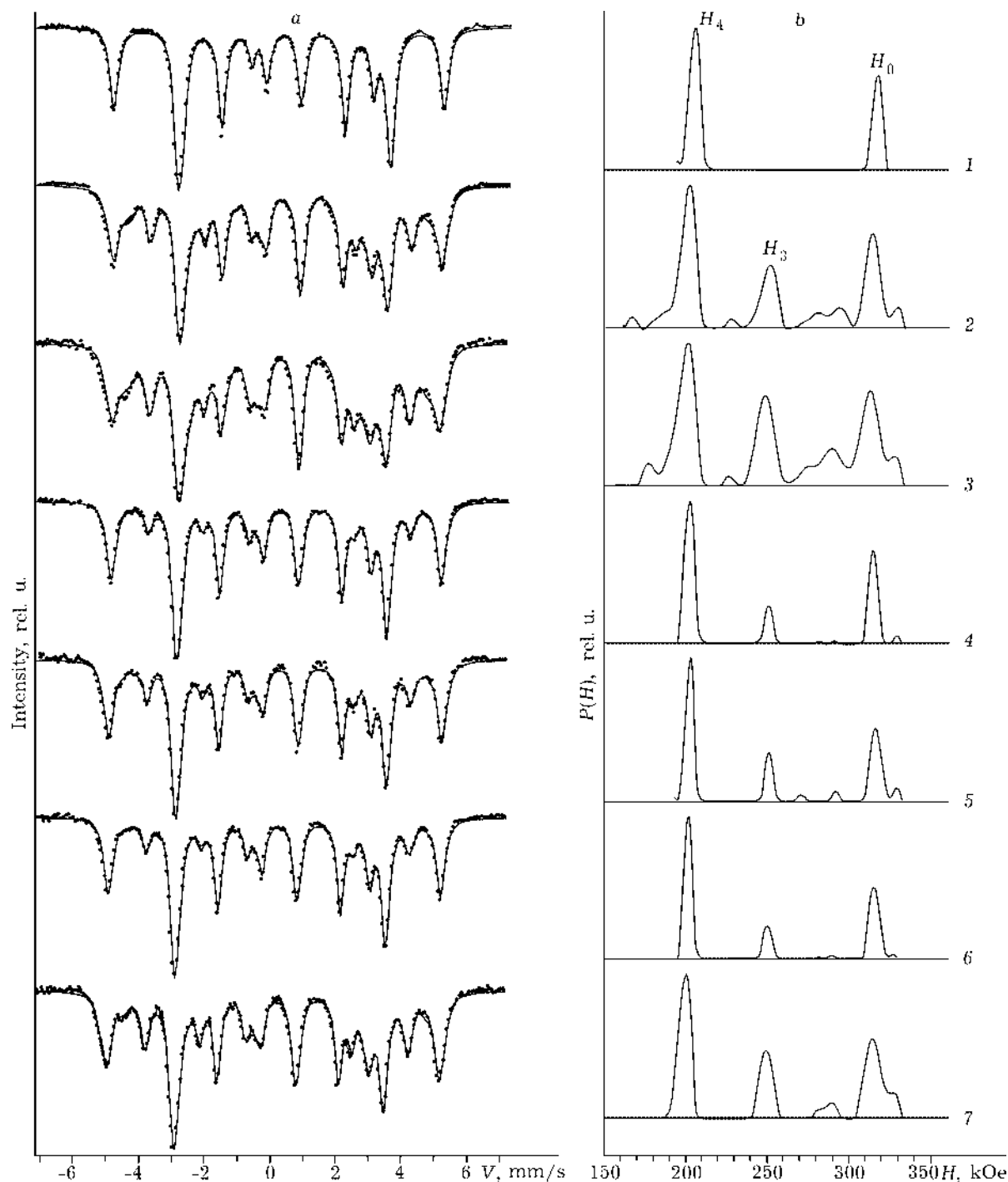


Fig. 3. The Mössbauer spectra (a) and the corresponding functions of the hyperfine magnetic field distribution  $P(H)$  (b) of the primary standard ( $\text{Fe}_3\text{Si}$ ) alloy and the mechanically alloyed  $\text{Fe}(75)/\text{Si}(25)$  samples after annealing to the maximum ordering: 2, 3 – SL steel, 16 and 32 h; 4, 5 – ShKh15 steel 16 and 324 h; 6, 7 – WC 8 and 16 h, respectively.

ing annealing. As a whole, for the case of WC vial and balls, all annealed samples prove to have lesser Si content in comparison with that of the samples after the mechanical alloying. To account for the results obtained, we infer that, starting from a definite stage of the me-

chanical alloying, there is a selective chemical interaction between WC and Si causing a decrease of Si content in the SSS. During annealing the interaction increases and exists even in those samples ( $t_g = 8$  h) where WC was a non-interacting impurity.

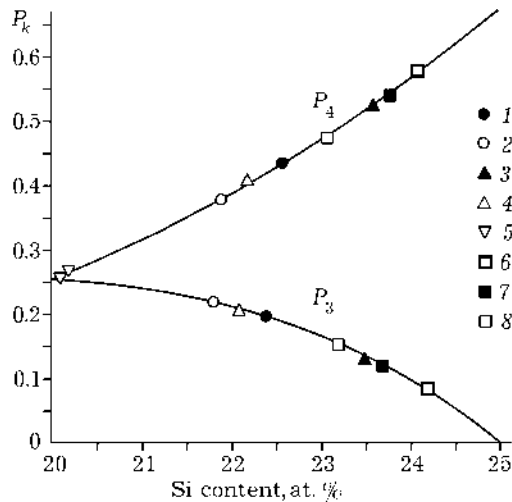


Fig. 4. Theoretical concentration dependencies of the probabilities of the local atomic configurations with 4 ( $P_4$ ) and 3 ( $P_3$ ) Si atoms in the nearest environment of a Fe atom in the Fe – Si alloys ordered according to the  $D0_3$  type (lines). The experimental data for the annealed Fe(75)/Si(25) mixtures after the mechanical alloying with the use of different material for the vial and balls: 1 – SL st., 16 h; 2 – SL st., 32 h; 3 – WC, 8 h; 4 – WC, 16 h; 5 – WC, 32 h; 6 – ShKh15 st., 8 h; 7 – ShKh15 st., 16 h; 8 – ShKh15 st., 32 h.

The following results were obtained for the ShKh15 steel. With  $t_g = 8$  h, the formation of the SSS does not complete, which is proved by the presence of the component from the unreacted  $\alpha$ -Fe in Mössbauer spectrum of the milled sample,  $Dm/m_0=0$  (see Fig. 1, *a*), and an increase of Si content after annealing (see Table 1). The closest to the process completion was the sample after milling for  $t_g = 16$  h. The X-ray pattern (see Fig. 2), Mössbauer spectrum and  $P(H)$  function (see Fig. 3) of this sample after annealing are similar to those of the primary standard alloy  $Fe_3Si$ . The Si content in the mechanically alloyed sample with the use of the ShKh15 steel ( $t_g = 16$  h) may be estimated as being in the range from 23.5 to 23.8 at. % (see Table 1). However, the increase of  $t_g$  up to 32 h leads to a decrease of Si content in the milled sample down to 22 at. %. The X-ray diffraction pattern of the sample after annealing (see Fig. 2) evidences a two-phase state that shows up clearly in the form of (405) and (206) lines (the indices of reflections are given for the  $D0_3$  superstructure cell). The intensity of the  $P_3(H_3)$  component raises in the Mössbauer spectrum and  $P(H)$  function.

The data presented allow us to make some preliminary conclusions. As far as the complete-

ness of conversion (the SSS formation) is concerned, the WC was the best material. However, large magnitudes of  $Dm/m_0$  and the possibility of interaction between the sample and the WC-wear products during mechanical alloying, which increases with annealing, require many precautions in the usage of this material. The stainless steel is absolutely unsuitable in this case. The most wear-resistant and least prone to participation in the mechanical alloying with the sample under study is the ball bearing steel.

**Fe(68)/Si(32).** The advantage of the ShKh15 steel as compared to the SL steel clearly manifests itself in studies of the mechanical alloying in Fe(68)/Si(32). The results of the X-ray and Mössbauer studies of this system are presented in detail in our work [4]. Here we give only those results which bear a direct relation to contamination.

Figure 5 gives the time dependences of the bcc lattice parameter  $a$  of the SSS for the use of SL and ShKh15 steels. It is distinctly seen that, for the ShKh15 steel,  $a(t_g) \gg \text{const}$  at  $t_g$  ranging from 4 to 48 h and equals 0.2825 nm. According to [5] this magnitude corresponds to the Si content of 30 at. %, *i. e.* close to that of the initial mixture. For the SL steel, the minimum value of  $a = 0.2834$  nm is achieved at  $t_g = 8$  h and further it rises up to 0.2838 nm at  $t_g = 32$  h, which corresponds to the Si content of 26 and 23 at. %, respectively. The Mössbauer data for the case of mechanical treatment with the BB steel are given in Fig. 6. One can clearly see the component from  $\alpha$ -Fe in the Mössbauer spectrum and function  $P(H)$  for  $t_g = 32$  h that, according to Fig. 1, *b*, results from the

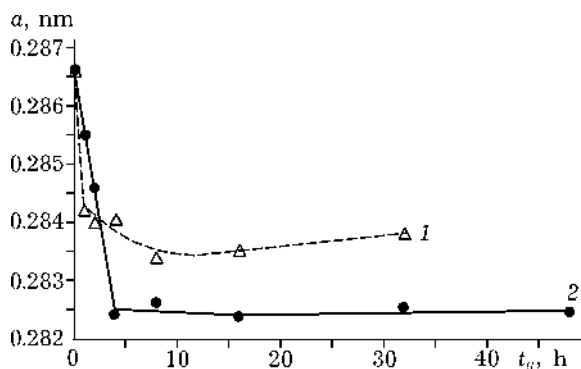


Fig. 5. Dependencies of the bcc lattice parameter of the super-saturated solid solution  $\alpha$ -Fe(Si) in the Fe(68)/Si(32) mixture on the time of mechanical alloying with the use of the vial and balls fabricated from the SL steel (1) and ShKh15 steel (2).

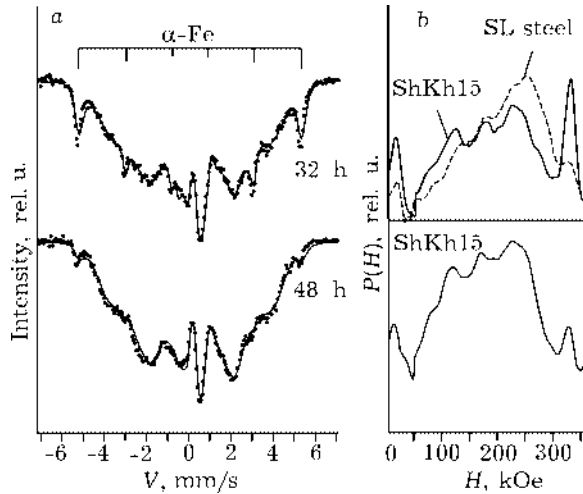


Fig. 6. The Mössbauer spectra (a) and functions  $P(H)$  (b) of the Fe(68)/Si(32) mixture mechanically alloyed with the use of the ShKh15 steel. The dashed line shows the  $P(H)$  for this mixture with the use of the stainless steel.

wear products ( $Dm/m_0 = 10\%$ ). Taking into account the fact that the Si content in SSS comprises 30 at. % at  $t_g = 32$  h, we can conclude that there is no interaction between the products of the ShKh15 steel wear and the sample at this stage. On the other hand, a comparison of the  $P(H)$  functions (see Fig. 6) for the ShKh15 steel (solid line) and the SL steel (dashed line) evidences a substantially smaller contribution from  $\alpha\text{-Fe}$  for the SL steel and a shift of the broad distribution of the  $P(H)$  function to a region of larger HMF values. At  $Dm/m_0 = 15\%$  for the LS steel after  $t_g = 32$  h, one may assert that the LS steel wear products take an intensive part in the mechanical alloying with the sample reducing the effective Si content of 32 at. % in initial mixture down to 24 at. % in the mechanically alloyed sample.

Nevertheless, Fig. 6 shows that the increase of  $t_g$  up to 48 h leads to a sharp decrease in contribution from  $\alpha\text{-Fe}$  for the ShKh15 steel usage. At  $Dm/m_0 = 15\%$  (see Fig. 1, b) one may conclude that the ShKh15 steel begins to mechanically alloy with the sample under study.

#### The Fe – C system

Study of the mechanically alloyed Fe(68)/C(32) samples exhibits that, for some elements (C), the balls and vial made of the ShKh15 steel may also undergo an essential wear (see

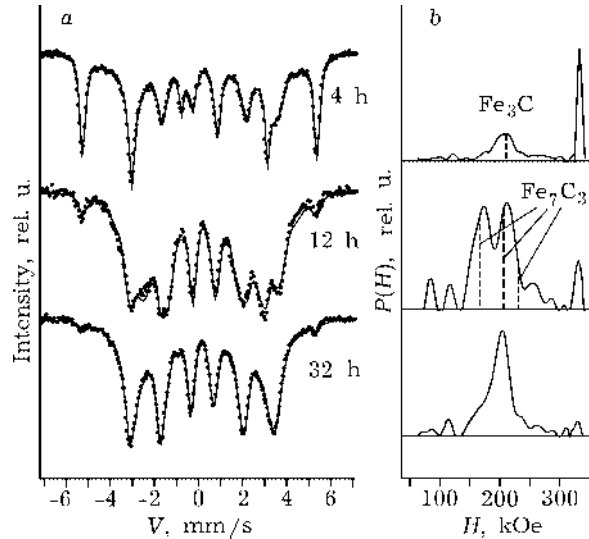


Fig. 7. The Mössbauer spectra (a) and functions  $P(H)$  (b) of the Fe(68)/C(32) mixture against the time of mechanical alloying with the use of the ShKh15 steel.

Fig. 1, c), and the wear products may participate in the mechanical alloying. The results of the X-ray and Mössbauer study will be published in detail in our paper [9].

Figure 7 presents the Mössbauer spectra and the  $P(H)$  functions of the Fe(68)/C(32) samples after 4, 12 and 32 h of mechanical treatment. The 4 h sample is largely composed of an  $\alpha\text{-Fe}$  and the  $\text{Fe}_3\text{C}$  carbide (cementite). After 12 h of treatment, the main component corresponds to the  $\text{Fe}_7\text{C}_3$  carbide, and the 32 h sample again consists of the  $\text{Fe}_3\text{C}$  carbide. Time dependencies of the carbide content are shown in Fig. 8. When they are compared with the dependence of  $Dm/m_0$  on  $t_g$  (see Fig. 1, c), one may con-

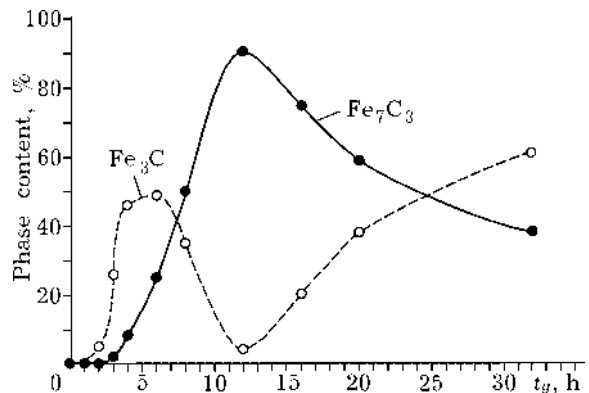


Fig. 8. The evolution of the  $\text{Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  contents in the Fe(68)/C(32) mixture as a function of the time of mechanical alloying with the use of the ShKh15 steel.

clude that at  $t_g \in 12$  h the results of the study reflect processes occurring mainly in the initial mixture. However, a drastic decrease of the unreacted  $\alpha$ -Fe from 30 to 4 % (at  $t_g = 8$ –12 h) and  $Dm/m_0 = 12$  % (see Fig. 1, c) are indicative of the mechanical alloying of the ShKh15 steel wear products with the sample. As far as the formation of  $Fe_7C_3$  carbide (30 at. % C) concerned, an additional iron from the BB steel favours the effective decrease in carbon content in mixture from 32 to 30 at. %. Therefore, at  $t_g = 12$  h an almost 100 % content of this carbide is obtained.

However, the observed reverse transformation  $Fe_7C_3 \rightarrow Fe_3C$  at  $t_g > 12$  h bears no relation to the mechanical alloying in the Fe – C system at atomic ratio 68 : 32, being a result of the mechanical alloying of the  $Fe_7C_3$  carbide with the products of wear of the balls and vial made of the ShKh15 steel.

## CONCLUSION

To obtain reliable results on the microscopic mechanisms of solid-phase reactions during mechanical alloying one must carefully take into account numerous factors that may affect the solid-phase reactions (environment, temperature, and so on). Among them, a special place is taken by the wear of the grinding tools (vial and balls for the ball planetary mills), as the wear products can also take part in the solid-phase reactions thus distorting the actual picture.

The examples of the mechanical alloying of iron with *sp*-elements (Si and C) presented in the paper show that each specific case requires a combined usage of the experimental techniques to make conclusions on the effect

of the products of the grinding-tool wear. Nevertheless, a row of overall conclusions may be done for practical purposes.

Among the materials considered (tungsten carbide, stainless steel and ball-bearing steel) the most wear-resistant and least prone to interaction with the sample under study is the ball bearing steel containing 1 mass % C and 1.5 mass % Cr.

The first stage of the mechanical-alloying study must involve careful gravimetric measurements of the sample, vial and balls before and after milling. The authors' experience suggests that the change in the sample mass should not exceed 10 % to obtain a reliable information.

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