Mechanochemical Synthesis of Magnetic Abrasive Media Fe/SiC, Fe/B$_4$C, and Fe/TiC

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Abstract

Operating characteristics of mechanochemically synthesized powder materials for magnetic abrasive treatment depend on microstructure and elemental distribution within composite particles. X-ray diffraction, high-resolution electron microscopy, and Mössbauer spectroscopy were used to explore Fe/SiC, Fe/B$_4$C, and Fe/TiC mechanocomposites that can be applied as magnetic abrasive working media. Synthesis of iron/abrasive mechanocomposites was carried out in an AGO-2 high-energy planetary ball mill with water cooling under argon. Silicon carbide inclusions of 0.6–5.0 μm size range are homogeneously distributed in composite Fe/SiC particles of 8–110 μm. There is the inter-phase interaction of iron and B$_4$C abrasive in the Fe–B$_4$C system upon mechanical activation. Fe/TiC composites were produced by the two-step mechanochemical synthesis. Fine titanium carbide powders generated in the first step of synthesis during activation with the formation of the high energy titanium–carbon system are mechanochemically fused together with iron powder particles in the second stage. Synthesis of TiC is completed within 4 min of mechanical activation with formation of particles of 0.1–0.5 μm size. The Fe/TiC composites are formed within 2 min of mechanical activation of titanium (IV) carbide with iron.

Key words: mechanochemical reactions, powder metallurgy, abrasives, silicon carbide, boron carbide, titanium carbide, magnetic abrasive materials

INTRODUCTION

Magnetic abrasive treatment (MAT) is a promising method to prepare surfaces of products that are based on magnetic field application and the transfer of the working magnetically-abrasive medium along the surface of the workpiece [1, 2].

Composites with good adhesion between magnetic (iron) and abrasive (SiC, B$_4$C, TiC, *etc.*) components with 60–80 vol. % content of the ferromagnetic component are usually used as the working medium. One of the modern preparation methods for such composites is the intense mechanical treatment of materials in high-energy ball mills, resulting from which powders with a large contact surface are formed. Furthermore, various physicochemical processes are intensified in materials, which facilitates changing their structural-phase state.

The research objective was to explore the effect of modes of mechanical activation (MA) in high-energy planetary ball mills on forming the structure of composite particles of iron/silicon carbide, iron/boron carbide and iron/titanium carbide.

EXPERIMENTAL

Carbonyl iron powders (particle size of 140−50 μm) were used as the metal component. Alpha-SiC powders with the wurtzite structure (40−180 μm), boron carbide (140−180 μm) and titanium carbide (0.1−0.5 μm) produced resulting from mechanical treatment of the stoichiometric mixture of Ti + C for 4 min were utilised as the abrasive ingredient [3].

The volume ratio of the magnetic and abrasive components in the mixture was 60 : 40. That corresponds to mass ratios of Fe/SiC of 80 : 20; those of 83 : 17 and 70 : 30 for Fe/B_4C and Fe/TiC, correspondingly.

Iron/abrasive composites were produced by mechanochemical treatment in an AGO-2 high-energy planetary ball mill with water cooling under argon. The volume of the drum was 250 cm³; the diameter of balls was 5 mm; the ball load was 200 g; treated sample weight was 10 g; the rotation speed of the drums around the common axis was around 1000 rpm [4].

X-ray diffraction measurements of the resulting powders were performed using the D8 Advance diffractometer (Germany) with the characteristic radiation of the copper anode of the Cu$K_{\alpha 1}$ X-ray tube (λ = 1.5406 Å). Phase analysis was carried out using ICDD PDF-2 X-ray diffraction standards database. Calculation and refinement of profile and structural parameters were made using the least squares method with carrying out full-profile analysis of X-ray diffraction patterns in the TOPAZ group utilising the Pawley iterative procedure. Research of microstructural characteristics (crystallite size L and microstresses ε) was carried out using the Double-Voight approach (double Voight), within the scope of which diffraction profiles for crystallite size and microdistortions are described by Voight functions. In order to separate contributions into peak broadening from L the Lorentz function was used and from microstresses ε the Gaussian function.

The morphology of mechanochemically produced composites, microstructure, and elemental composition were investigated using a Micro 200

microscope (NPO Planar, Minsk) and a Vega II LMU electron microscope with an Ina Energy 350 microanalyser.

Mössbauer spectra were recorded at room temperature using an MS1104 Em plant in transmission geometry utilising a radioactive ^{57}Co(Rh) source with an activity of 50 mCi. The speed range of the relative motion of the source and the absorber was [12, −12] mm/s. Spectrometer calibration was carried out in reference to standard α-Fe absorbent. Spectral analysis was performed using both simulated decoding onto components using Univem MS software and by means of restoring the distribution function of hyperfine parameters of the spectrum with the SPecRelax program.

RESULTS AND DISCUSSION

Fe/SiC

Silicon carbide is characterised by high microhardness (32.4−35.3 GPa). As demonstrated by diffraction research (Fig. 1, *a*), fragmentation of silicon carbide particles proceeds less intensely compared to that for iron due to better strength properties of SiC (for comparison, L_{SiC} ~120 nm, L_{Fe} ~40 nm).

According to X-ray phase analysis (XPA) and SEM (see Fig. 1, *b*), one may conclude about the evolution of the microstructure of composite Fe/SiC particles. Thuswise, both composite Fe/SiC particles and separate species of iron and SiC are present in the mixture activated for 5−10 min. Formed composite Fe/SiC particles, in which milled different-sized (from 1 to 8 μm) solid SiC particles are located in a matrix of less hard iron have a wide size range from 8 to 250 μm. An increase in mechanical activation time to 20 min results in complete iron consumption for the formation of 8−110 μm composite particles containing 0.6−5.0 μm SiC inclusions.

In such a way, the generation process of Fe/SiC composite passes through the following stages: the grinding of initial components with partial generation of composite particles in a wide size range, an increase in the number of composite particles with a decrease in their size characteristics and size reduction of substructural components, and the formation of composite particles in a narrow size range with a homogeneous distribution of components according to phase and size composition.
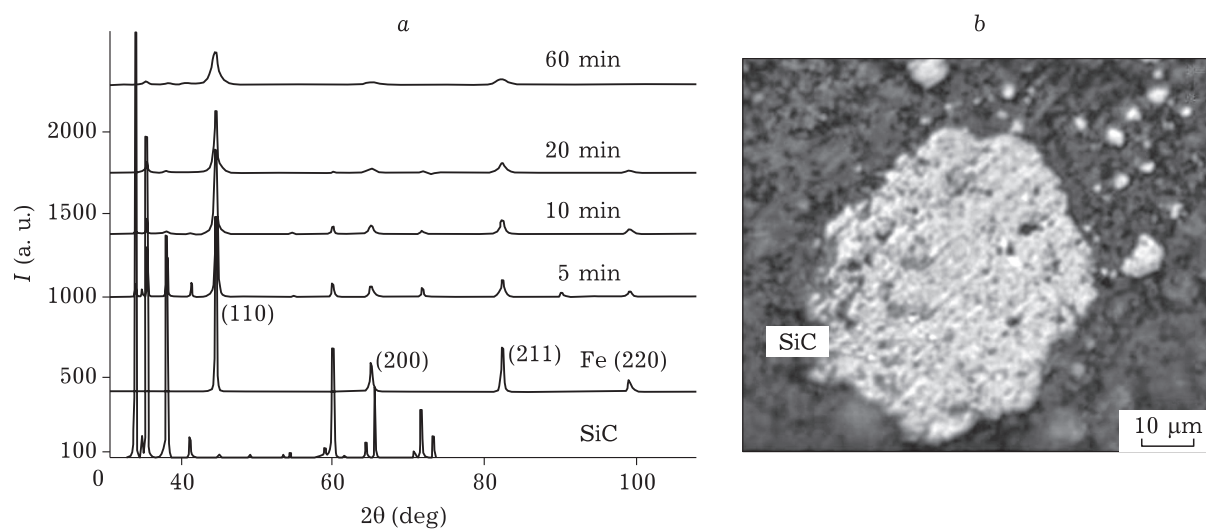
Fig. 1. X-ray diffraction patterns of products of mechanical activation (MA) of a mixture of Fe and SiC with different treatment times (*a*) and SEM image of composite particles produced during MA for 60 min (*b*).

Fe/B₄C

Mechanochemical synthesis of iron-abrasive composites (Fe/B$_4$C) was explored by XPA. When MA is increased the intensity of diffraction peaks of α-iron (bcc) is substantially decreased and their width is increased. The broadening of X-ray reflections for α-Fe indicates both a decrease in crystallite sizes and an increase in internal microstresses (Fig. 2).

Upon further MA, X-ray diffraction profiles of the α-iron phase are insignificantly changed resulting from the interfacial interaction of iron and B$_4$C abrasive.
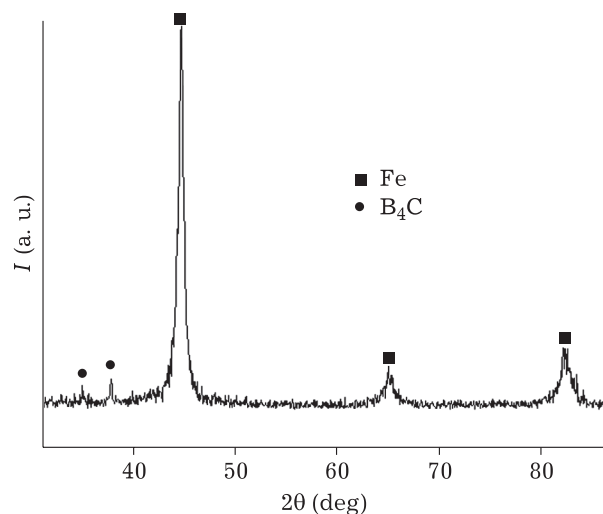
Furthermore, the intensity of diffraction peaks is substantially reduced during MA and they almost do not exceed the background after 40 min. In the initial step of MA (to 20 min) of a mixture of Fe and abrasive, the decomposition rate of abrasive particles is higher than that for iron. The average crystallite size L_{B_4C} of abrasive reaches 150 nm at the MA for 40 min. Diffraction peak profiles of the iron phase of the mechanically activated mixture of Fe and abrasive remain unchanged when mechanical activation time is less than 20 min.

Fe/TiC

According to XPA, iron powder addition to titanium (IV) carbide followed by combined MA for 2 min leads to the formation of the Fe/TiC composite (Fig. 3). The lattice parameter of iron is increased to a_{Fe} = 2.874 Å, whereas that of titanium(IV) carbide is decreased (a_{TiC} = 4.296 Å). The average size of iron crystallites (L_{Fe}) is around 29 nm. An increase in the level of microstresses to ε = 1.768 may indicate a significant concentration of defects, whereas a decrease in the lattice parameter of TiC (a_{TiC}) is due to a small size of crystallites (L_{TiC} = 4.6 nm) [5].

Multicomponent composite particles are formed resulting from mechanochemical synthesis. The topological and composite short-range order therein determines their properties in many respects. Figure 4, *a* presents the Mössbauer spectrum of the Fe/TiC composite. The spectral profile is a superposition of spectra of various local structures of iron, such as crystal phases,
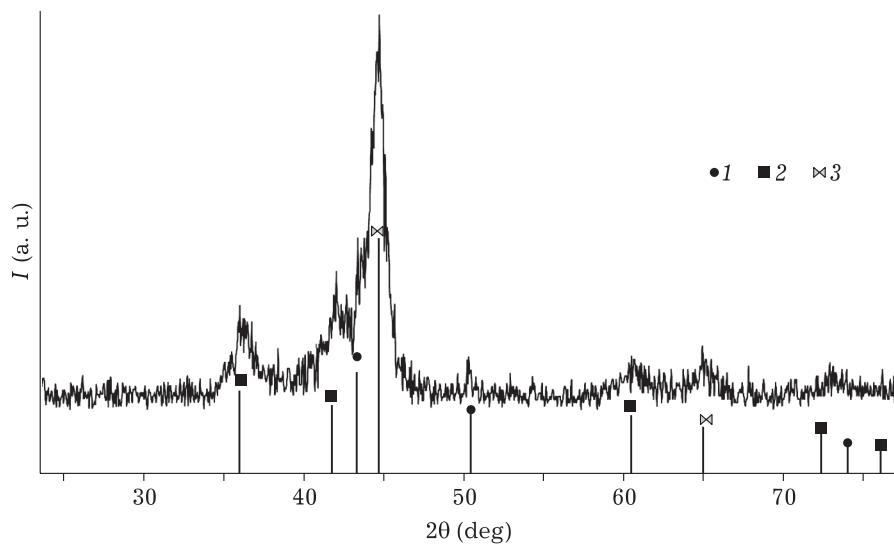

Fig. 2. X-ray diffraction pattern of the Fe/B$_4$C composite produced resulting from MA of a mixture of Fe and B$_4$C for 40 min.

Fig. 3. X-ray diffraction pattern of the Fe/TiC composite after MA for 2 min: *1* − CFe$_{15.1}$, cubic, *Fm-3m* [52-0512]; *2* − TiC, cubic, *Fm-3m* [32-1383]; *3* − Fe, cubic, *Im-3m* [06-0696].
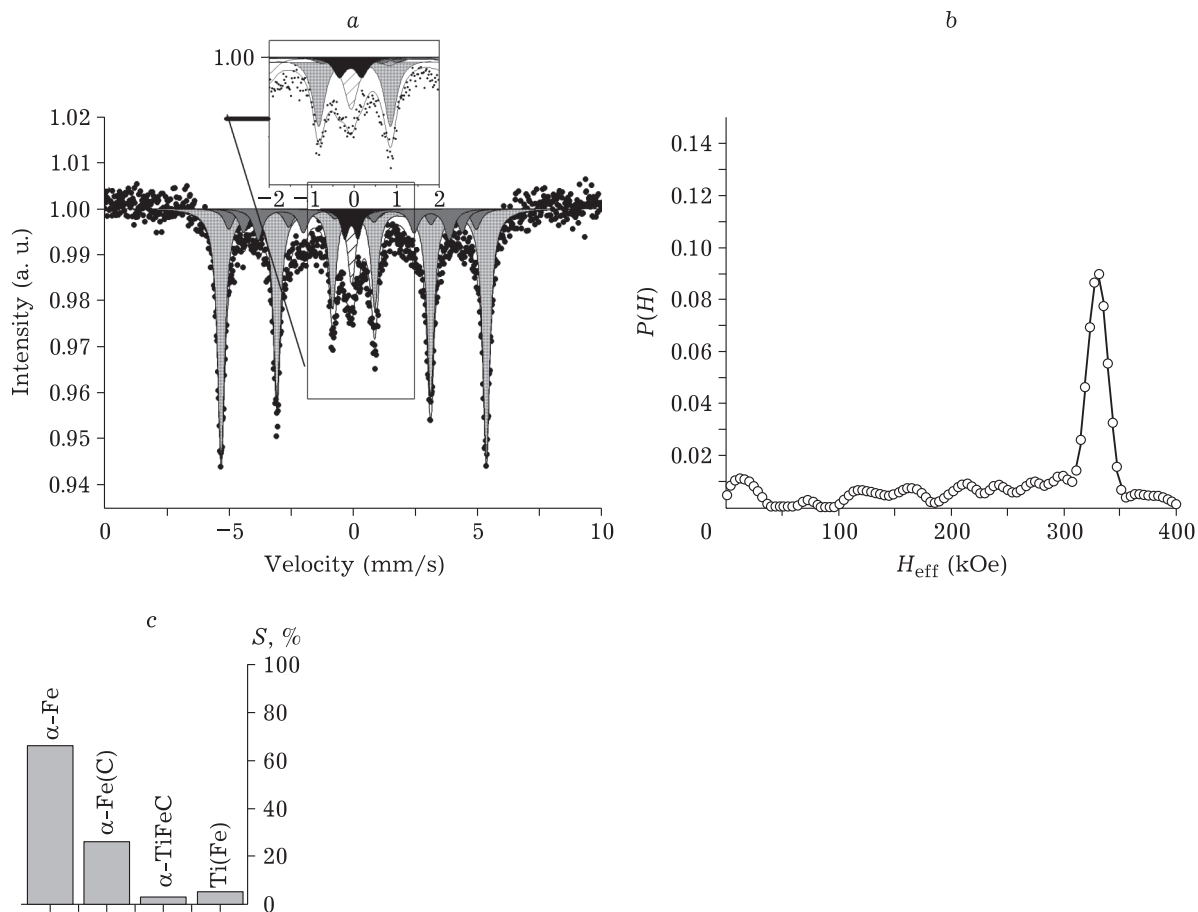

Fig. 4. Mössbauer spectrum of the Fe/TiC composite with model decoding components (*a*), distribution function of hyperfine fields, *P(H)* (*b*), and composite phase composition (*c*).

TABLE 1

Mössbauer spectra parameters (H_{eff}, δ, Δ G, and S are hyperfine ring field, isomer shift, quadrupole splitting, line width, and relative subspectrum area, respectively) for mechanically activated Fe/TiC composites

Sample	H_{eff}, kOe ±2	δ, mm/s ±0.003	Δ, mm/s ±0.003	G, mm/s ±0.003	S, % ±1	Phase
Fe/TiC	331	0.004	0.001	0.35	66	α-Fe
	309	0.093	−0.270	0.45	7	Fe(C,Ti)/
	273	0.100	0.020	0.45	8	disordered grain
	238	0.110	−0.200	0.45	11	boundaries and interfaces
		−0.090	0.530	0.35	3	α-TiFeC
		−0.080		0.40	5	Ti(Fe)

and also intergranular and interphase boundaries. Effects of disordering and non-stoichiometry become apparent in lines broadening and the appearance of distributions of hyperfine parameters of the spectrum. Its magnetically split portion with the distribution of ultrathin magnetic fields and the central non-magnetic broadened component stand out. Figure 4, *b* demonstrates the result of restoring distribution function of hyperfine fields P(H). The recovery of the function was carried out to separate contributions of different local ordering or the surrounding of iron atoms in magnetic particles. The main peak near H_{eff} = 330 kOe and several weaker peaks (309, 273, and 238 up to 100 kOe) correspond to the bcc phase of α-Fe (66 %) and disordered states (~26 %) on inter-grain boundaries or defect surfaces of iron particles.

Analysing the spectrum reveals two components that are non-magnetic at room temperature (see Fig. 4, *b*, inset). They are 1) a doublet with parameters close to α-TiFeC [6, 7] (Table 1) and 2) a singlet that may correspond to the Ti(Fe) solid solution [8] or the γ-Fe(C) phase.

CONCLUSION

The identification of interfacial atomic structure and element distribution plays a key part in understanding Fe/SiC, Fe/B$_4$C, and Fe/TiC systems. Direct information regarding chemical interaction depth and range may be obtained from Mössbauer data susceptible to the local surrounding of iron atoms.

An opportunity to mechanochemical producing of nanostructured Fe/SiC, Fe/B$_4$C, and Fe/TiC composites to be used as magnetic abrasive media without creating high pressures and temperatures has been demonstrated.

REFERENCE

1 LaRoux K. Gillespie, Mass Finishing Handbook. Chapter 20: Magnetic-Abrasive Finishing. NY: Industrial Press, 2006. P. 371−401.

2 Khomich N. S., Magnitno-Abrazivnaya Obrabotka Izdeliy, BNTU, Minsk, 2006.

3 Lyakhov N., Grigoreva T., Šepelák V., Tolochko B., Ancharov A., Vosmerikov S., Devyatkina E., Udalova T., Petrova S., *J. Mater. Sci.* 2018. Vol. 53, Is. 19. P. 13584−13591.

4 Avvakumov E. G., Mekhanicheskiye Metody Aktivatsii Khimicheskiykh Protsessov, Nauka, Novosibirsk, 1986.

5 Gusev A. I., Nanokrisallicheskiye Materialy: Metody Polucheniyai Svoystva, Izd-vo UrO RAN, Yekaterinburg, 1998.

6 Follstaedt D., Ќnapp J., Picraux S. T., *Appl. Phys. Lett.* 1980. Vol. 37. P. 330−333.

7 Follstaedt D., Yost F., Pope L. E., Ќnapp J. A., *Appl. Phys. Lett.* 1983. Vol. 43. P. 358−360.

8 Stupel M., Ron M., Weiss B., *J. Appl. Phys.* 1976. Vol. 47. P. 6−12.