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Anomalous Effect of Graphite on the Degree of Wear of Copper Milling Bodies of the Mechanochemical Reactor*

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Abstract

The anomalous effect of graphite on the degree of wear of copper milling bodies was studied quantitatively. It was shown that mechanical activation of the system diamond–graphite–silicon with copper milling bodies led to the formation of copper-containing semi-products and stable coatings on the surface of milling bodies.

Key words: diamond, mechanical activation, mechanochemical reactors, milling bodies, abrasive reaction wear, effect of graphite

INTRODUCTION

Previously [1–3], we considered in detail the phenomenology and applied aspects of the abrasive reaction wear (ARW) of the substances under treatment [1] and the material of milling bodies [2, 3] in planetary mills. The applied value of nanosized ARW is most clearly pronounced in case when diamond is used as the abrasive material [2–5]. On the other hand, such substances as diamond, graphite and silicon possess a number of unique properties and they are widely used in various areas [4, 5]. For example, diamond is characterized by the highest abrasive and heat conducting properties. Graphite serves as the basis for many functional materials including lubricants, while silicon crystals are the basis for electronics in general. The problem of processing substandard natural diamonds and the wastes of silicon production to obtain high-technology materials and coatings for various purposes is also relevant. The wear of materials in mechanochemical reactors is principal for the development of new ARW technologies for obtaining of functional materials.

In [5] we noted for the first time the effect of graphite on the acceleration of the wear of copper material of milling bodies during mechanical activation (MA) of the mixture of diamond and graphite. In the present work we carried out the quantitative investigation of graphite effect on the acceleration of wear of milling bodies during MA of the system diamond–graphite–silicon in a Pulverisette 6 planetary mill (Fritsch, Germany) with copper hardware.

EXPERIMENTAL

The planetary Mono Mill Pulverisette 6 with specially manufactured duralumin cylinders with seals made of vacuum rubber was used for MA. Copper sheets 3, 2 and 1 mm thick, subjected to annealing in vacuum, were used to line the inner walls of cylinders and to prepare the mobile milling bodies. Internal sidewalls were made of the sheets 2 and 1 mm thick, while caps, side walls and mobile milling bodies shaped as parallelepipeds with the average sizes $6 \times 6 \times 3$ mm were made of 3 mm thick sheets. Before facing, the surface of cop-

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per hardware was cleaned by successive treatment with nitric acid and deionised water. After facing, the internal dimensions of the cylinders were: height 7.4 cm, diameter 8.0 cm, volume 370 cm^3. Before experiments, rolling of the copper mobile milling bodies was carried out until they got the shape of extended or oblate ellipsoid of rotation [6]. At the same time, sealing of copper sheet joints was performed according to the following programme of treatment in the mill (with cylinder overturn at each indicated frequency of carrier rotation):

– 280 min^{-1}, MA for 7 min, pause for 1 min, reverse (backward rotation of the carrier), two repetitions, total MA time 28 min;

– 350 min^{-1}, MA for 4 min, pause for 1 min, reverse, two repetitions, total MA time 16 min;

– 420 min^{-1}, MA for 2 min, pause for 1 min, reverse, two repetitions, total MA time 8 min;

– 490 min^{-1}, MA for 1 min, pause for 1 min, reverse, two repetitions, total MA time 4 min.

Total time of rolling treatment was 56 min.

Initial abrasive materials were natural diamond micropowder (State Standard GOST 9206–80, nominal size 1.5–0.5 μm, total admixture content not more than 1 mass %), specially pure powdered graphite of MG-OSCh grade [7] and graphite of Alfa Aesar Co. with purity 99.9995 %, and carbonyl grade silicon. For correct comparison of experimental results, the same MA mode was chosen for all the systems under study:

– 280 min^{-1}, MA for 7 min, pause for 1 min, reverse, one repetition, total MA time 14 min; 350 min^{-1} under the previous conditions; cylinder overturn and repetition of the conditions; total treatment time 56 min^{-1}.

– MA for 2 min under the same conditions at the rotation frequency of 420 and 490 min^{-1}; 560 min^{-1}, pause for 1 min, reverse, one repetition, total MA time 4 min; cylinder overturn and repetition of the indicated conditions; total treatment time 64 min.

So, the final time of MA was 120 min. Cylinder overturn provided uniform wear of copper hardware of milling bodies. The samples obtained after MA were studied using the standard X-ray phase analysis method (XPA) [1–5, 8, 9]. Carbonyl-grade silicon was used as a standard.

The wear degree and, as a consequence, the quantitative composition of the composites were determined by means of gravimetry as a difference between the masses of copper hardware before and after experiment, and also by means of sample pyrolysis under atmospheric conditions. Under heating to 900 °C, diamond and graphite burn out, while silicon and copper are oxidized according to equations

$Si + O_2 = SiO_2$

$2Cu + O_2 = 2CuO$

For example, if the mass of copper-silicon composite is m, then

$m = m_{Si} + m_{Cu}$

After oxidation, the mass of the sample will increase to m^*:

$m^* = (m_{Si}M_{SiO_2}/M_{Si}) + (m_{Cu}M_{CuO}/M_{Cu})$

where M stands for molecular masses of the corresponding reagents. Substituting

$m_{Cu} = m - m_{Si}$

we determine silicon content of the sample:

$m_{Si} = M_{Si}(m^*M_{Cu} - mM_{CuO})/(M_{SiO_2}M_{Cu} - M_{Si}M_{CuO})$

RESULTS AND DISCUSSION

The following results were obtained in the experiments on mechanical activation of a number of systems using the copper hardware for milling bodies.

Diamond. The weighted portion was 4.192 g. The total mass of copper milling bodies was m_{Cu} = 132.583 g, the number of milling bodies was N = 146, average radius $R = (3m_{Cu}/4N\pi\rho)^{1/3}$ = 0.289 cm, where ρ = 8.960 g/cm^3 is copper density. After experiment, the mass of milling bodies was 132.339 g. The mass of copper sheet sidewall 1 mm thick was 120.286 g before experiment and 119.962 g after experiment. Initial masses of copper caps were 135.923 and 133.599 g before experiment, 136.069 and 133.768 g after experiment, respectively. So, a decrease in the mass of copper hardware after experiment is only 0.253 g.

After MA, 3.794 g of copper-diamond powdered intermediate product (composite) was taken out; a very firm grey copper-diamond coating was obtained on the surface of copper sidewall. The data of XPA of composite sample recorded with the ground powder of the reference substance (reference content 12 %) are presented in Fig. 1. The appearance of graphite lines is connected with partial graphitization of diamond during MA proceeding at the

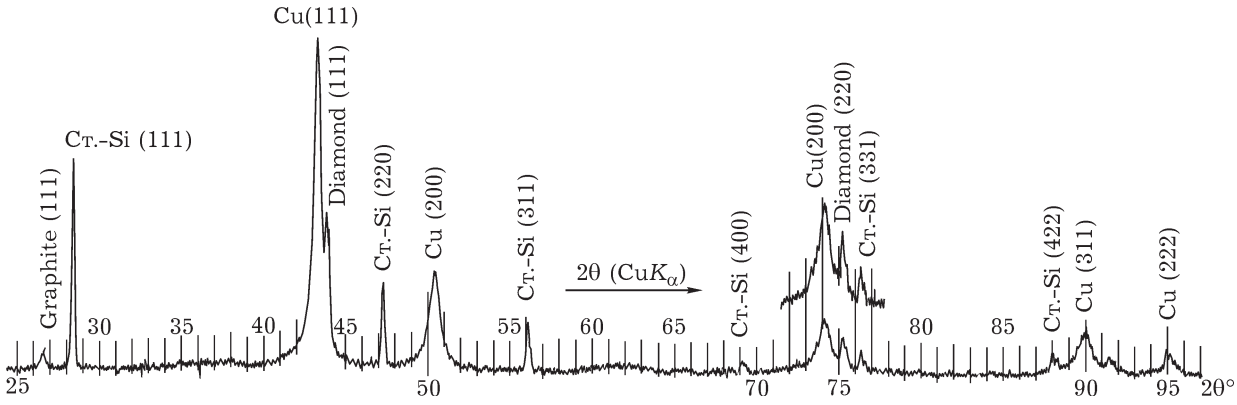

Fig. 1. XPA data for the copper-diamond composite within the 2θ reflection angle range 25–97° (CuK_α) and the lines of reference (Re is carbonyl-grade silicon). Within the angle range 2θ = 72–77°, the lines obtained with the amplification of the sensor signal are shown.

impact-friction contacts of particles at temperatures above 1000 °C [5, 10, 11].

To determine microdeformations (ε) and the size (D) of the blocks of coherent scattering for the particles (crystallites) of copper (Cu), diamond (d) and graphite (gr) in the composite, we used the methods described in [8, 9]. As a result of treatment of the data shown in Fig. 1, the following results were obtained: D_{Cu} = 246 Å ≈ 25 nm, ε_{Cu} = 0.0021 (0.21 %), relying on separate reflections D_d (220) ≈ 38 nm; D_{gr} (111) ≈ 24 nm. Copper content of the composite was equal to 63.3 mass %. Therefore, the missing amount of diamond (≈2.8 g) was spent for the coating on the surface of milling bodies. This explains so insignificant decrease in the mass of milling bodies (0.253 g).

Graphite. Graphite of Alfa Aesar Co. was used; the weighted portion was 5.090 g. The characteristics of copper milling bodies are: m_{Cu} = 128.953 g, N = 144, R = 0.288 cm. After MA, the mass of milling bodies was 128.591 g. The initial mass of the side wall (the sheet 1 mm thick) was 119.892 g, after MA it was 119.169 g; the masses of caps were 142.577 and 134.659 g before experiment, 142.440 and 134.574 g after MA, respectively. A decrease in the mass of copper milling bodies after experiment was equal to 1.307 g. After MA, 6.237 g of copper-graphite composite was taken out, and a copper-graphite oily-black coating was obtained in the copper sidewall surface. After the treatment of XPA data, we obtained: D_{gr} = 380 Å ≈ 38 nm, ε_{gr} = 0.0008 (0.08 %), D_{Cu} (111) ≈ 20 nm. Copper content of the composite was 32.5 mass %. The missing amount of graphite (≈0.9 g) was spent for coating on the surface of milling bodies.

Silicon. The weighted portion of the material was 3.100 g. The characteristics of copper milling bodies: m_{Cu} = 77.565 g, N = 99, R = 0.275 cm. After MA, the difference between the masses was 0.090 g for caps, for the side wall 0.103 g, for milling bodies 0.060 g; total decrease was equal to 0.133 g. A very high ability to face the surface of milling bodies is characteristic of silicon, so only 2.667 g of copper-silicon composite was taken out; a strong coating was obtained on the surface of copper sidewall. This coating looked very similar to the copper-diamond coating. Copper content in the composite was determined to be 47.5 mass %; the missing amount of silicon (≈1.7 g) was spent for coating on the surface of milling bodies. The following results were obtained by processing the XPA data: D_{Si} = 462 Å ≈ 46 nm, ε_{Si} = 0.0020 (0.2 %), D_{Cu}(111) ≈ 34 nm.

It should be noted that, in spite of the incommensurable value of graphite hardness in comparison with those of diamond and silicon, their abrasive properties are alike. This similarity is due to the high ability of solid particles for surface hardening, which determines their stability to wear.

Diamond (2.833 g)–graphite (2.902 g) system. Graphite of Alfa Aestar Co. was used. The characteristics of copper milling bodies were: m_{Cu} = 166.155 g, N = 193, R = 0.284 cm. After MA, the mass of milling bodies was 135.903 g

(mass difference was 30.252 g). The mass of the sheet side wall 1 mm thick was 109.288 g before the experiment and 89.403 g after MA (the difference was 19.885 g); initial masses of caps were 142.440 and 134.575 g. After MA their masses were 141.857 and 133.879 g, respectively (mass difference was 1.279 g). Total decrease in the mass of copper milling bodies in this experiment turned out to be maximal and equal to 51.416 g. The mass of the copper-diamond-graphite composite taken out was 56.933 g (a heavy powder with copper tint). Copper content in the composite determined gravimetrically was 0.899, or 89.9 %. Copper content determined by means of pyrolysis was 92.4 %. So, the missing amount of the diamond-graphite mixture (≈1.4 g) was spent to coat the surface of milling bodies. The results obtained by processing the XPA data are: D_{Cu} = 352 Å ≈ 35 nm, ε_{Cu} = 0.0022 (0.22 %), D_{gr} ≈ 26 nm.

This experiment showed that the addition of graphite causes substantial changes of the abrasive properties of diamond (by more than an order of magnitude in comparison with the experiment on MA of diamond alone). In th is connection, the quantitative studies of the acceleration of wear of copper material of milling bodies was continued with two more abrasive systems but this time with graphite of the MG-OSCh grade (Russia). Unlike for previous experiments in which the coatings on removable shell side walls 1 mm thick were obtained, in this case we used cylinders with stationary side walls made of copper sheet 3 mm thick. The quantitative wear degree was determined from the measurements of the mass of milling bodies, caps and the formed composite.

Diamond (10.244 g)–graphite (10.128 g) system. The characteristics of copper milling bodies were: m_{Cu} = 251.704 g, N = 393, R = 0.257 cm. The mass of milling bodies after MA was 204.302 g. The wear of copper mobile milling bodies alone reached 47.402 g, the mass of copper-diamond-graphite composite taken out was 98.488 g, the wear of copper caps and side wall was at least 30.714 g. The composition of the composite was determined by means of gravimetry (mass %): diamond 10.4, graphite 10.3, copper 79.3. Copper content determined by means of pyrolysis was 80.5 mass %. The missing amount of the diamond-graphite mixture (≈1.2 g) was spent to coat the surface of milling bodies. The treatment of XPA data gave: D_{Cu} = 243 Å ≈ 24 nm, ε_{Cu} = 0.0011 (0.11 %), D_{gr} (111) ≈ 34 nm.

Diamond (4.917 g)–graphite (5.418 g)–silicon (5.715 g) system. The characteristics of copper milling bodies were: m_{Cu} = 191.869 g, N = 299, R = 0.258 cm. The mass of milling bodies after MA was 154.862 g. The wear of mobile milling bodies was 37.007 g. The mass of the composite taken out was 99.111 g (oily powder with brown tint). Therefore, the wear of copper caps and side wall was at least 46.044 g. The composition of the composite determined by means of gravimetry was (mass %): diamond 4.96, graphite 5.47, silicon 5.77, copper 83.8. Copper content determined by means of pyrolysis was 84.7 mass %. The missing amount of the diamond-graphite-silicon mixture (≈0.9 g) was spent to coat the surface of milling bodies.

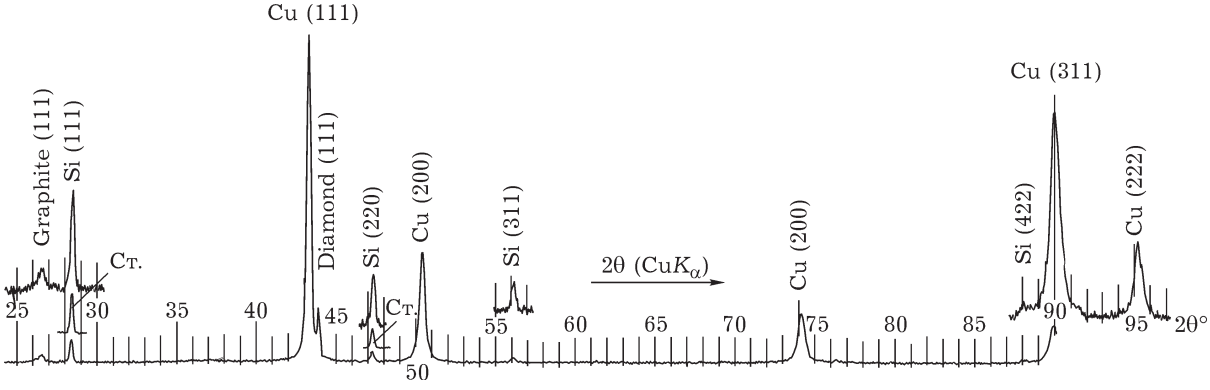

Fig. 2. XPA reflections of the copper-diamond-graphite-silicon composite within the range 25–97° of reflection angles 2θ(CuK_α) and the lines of reference (Re). Within angle ranges 25–30, 47–48, 55–57 and 87–97°, the lines obtained by signal amplification are shown.

TABLE 1

Quantitative data on material wear during MA of the studied systems, g

Exp. No.	System	Wear				Composite mass*	Spent for coating**
		milling bodies	caps	side wall	total		
1	Diamond	0.244	−0.315	0.324	0.253	3.794	2.8
2	Graphite	0.362	0.222	0.723	1.307	6.237	0.9
3	Silicon	−0.060	0.090	0.103	0.133	2.667	1.7
4	Diamond–graphite	30.252	1.279	19.885	51.416	56.933	1.4
5	The same	47.402	1.536	29.178	78.116	98.488	1.2
6	Diamond–graphite–silicon	37.007	3.223	42.821	83.051	99.111	0.9

* Mass of intermediate product taken out (powdered copper-containing nanocomposite).

** Total mass of the components of MA system spent for the formation of coating on the surface of milling bodies.

After processing the data shown in Fig. 2, we obtained: $D_{Cu} = 440$ Å ≈ 44 nm, $\varepsilon_{Cu} = 0.0025$ (0.25 %), and on the basis of separate reflections $D_{gr}(111) \approx 24$ nm, $D_{Si}(111) \approx 56$ nm, $D_{Si}(220) \approx 52$ nm.

It should be stressed that the wear of milling bodies (37.007 g) in case of MA of this system is smaller than the total wear of caps and side wall (46.044 g). Quite contrary, for the diamond–graphite system the wear of milling bodies exceeds the total wear of caps and side wall. The data on the wear of material during MA of the studied systems are generalized in Table 1. One can see that the mass of milling bodies may even increase as a result of MA (exp. No. 1 – caps, No. 3 – mobile bodies), the wear of side wall is substantially higher than the wear of caps, the addition of graphite (exp. Nos. 4–6) provides anomalous increase in wear.

CONCLUSION

It has been discovered that the wear of copper milling bodies accelerates by almost two orders of magnitude in the presence of graphite. This opens good outlooks for the development of a small-scale technology of the production of nanocomposites and functional ware based on them, for example coolers with a high heat conductivity, substrates for electronics, friction units and sleeve bearings. This fact is of scientific and practical interest requiring further studies; thus obtained results will allow the purposeful design and application of mechanochemical reactors and industrial grinding devices.

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