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Preparation of nanoscale particles and coatings on the basis of copper, carbon and silicon by the abrasive-reactive wear method

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An abrasive-reactive wear technology has been developed that utilizes wear debris as an integral component of the reaction system rather than treating it as a harmful impurity; this technology is applied to the processing of low-grade diamond and silicon by cupric milling tools, and an abnormal influence of graphite on wear degree is established.

The mechanical activation (MA) of powders, usually carried out in ball mills that are considered mechanochemical reactors (MRs), essentially consists of the repeated mechanical loading of powders trapped between the colliding surfaces of the milling tools. The local compressive and shear events create hot spots and induce plastic deformation and fracturing of the particles.[1,2] Under such circumstances, powder particles undergo continuous comminution associated with interface renewal processes. These promote the occurrence of physicochemical transformations including the microstructural refinement down to nanometer size.[3] Besides these processes, contamination due to the abrasion of milling tools is also inherent to conventional MA in MR; the level of contamination can reach several percent, and it can rarely be kept below a few tenths of a percent.[3] Sometimes, it is possible to select the material of the milling tools in such a way that the wear debris becomes a beneficial component of the intended product. We developed a technique called abrasive-reactive wear (ARW) that uses the material of the milling tools as a reactant that becomes a major component of the product, not just a tolerable impurity.[4]

From the point of view of enhancing the possibilities of the ARW method, the use of diamond and silicon is of special interest owing to their unique physicochemical and abrasive properties and ability to interact with transition metals and alloys, *i.e.*, a combination of properties of both abrasives and reagents.[5]

A property of technological relevance that characterizes materials prepared in this work is heat conductivity. The problem of heat removal is very important for the semiconductor industry. For this reason, the improvement of thermal properties of materials used for manufacturing microelectronics components becomes crucial.[6–9] The ADS company offered nanocomposite materials on a copper and diamond basis that have higher heat conductivity in comparison with traditionally used materials on a Cu or Al basis.[10] Moreover, diamond particles in copper–diamond composites show a high degree of stability to graphitization under sintering at temperatures up to 1150–1250 K. Thus, this composite material can be used for the creation of contacts and high-current electric contacts in the low-voltage equipment.[11]

The nanoscale ARW of the diamond–graphite–silicon system and copper milling tools of MR was applied to the preparation of composites and coatings.[†]

The experimental results demonstrated both similarities and dissimilarities of MA only for diamond [sample 1, S1, Figure 1(*a*)], graphite [S2, Figure 1(*b*)], silicon [S3, Figure 1(*c*)] and a mixture of diamond and silicon powders (S4), and the diamond–graphite [S5, Figure 1(*d*)], silicon–graphite (S6), diamond–silicon–graphite [S7, Figure 1(*e*)] mixtures. In all cases, the movable copper milling tools were subject to rolling and transformed into ellipsoids. However, unexpectedly, the wear of copper milling tools after the MA of samples 1–4 appeared nearly one order of magnitude lower than that of samples 5–7 (abnormal influence of graphite-containing systems on abrasive wear degree is established). Examination of working surfaces of milling tools with optical microscopy showed that the change in mass of the copper inserts is related to the phenomenon of cold hardening, *i.e.*, uniform penetration of diamond particles (S1) or the diamond–graphite mixture (S5) into the working layer of inserts with formation of the coatings. This phenomenon hampered the determination of the exact composition of the newly formed composites by gravimetric analysis. For example,[14] based on the masses of milling tools weighed before and after the MA of S1, the composite corresponds to a diamond content (wt%) of 75.8% (the Cu content is 24.2%). After the MA of S5, the content of carbon (diamond and graphite) in the composite was 22.6% and the Cu content was 77.4%. We could solve this problem by XRD analysis, Raman spectroscopy and differential thermal analysis.[14]

[†] AGO-2 (water-cooled two-vial planetary mill[12]), EI-2×150 (two-vial planetary mill[13]) and planetary mono mill pulverisette-6 were used to carry out the MA. We constructed duralumin vials adapted for use in all mills. The vials were equipped with cylindrical inserts made of copper rod and plate. The movable milling tools were prepared from copper rod and 3 mm thick sheet. The vials can also be adapted to the preparation of coatings: copper plate (1 mm thick) is attached to the wall of the inserts; the impacts by the copper milling tools activate the surface of the plate, deliver particles from the powder charge and pound them onto or into the surface.

Natural diamond (> 99% purity; 1.5–0.5 μm; 1.5–10 g) was used to prepare the copper–diamond composites and coatings, while graphite powder (Alfa Aesar, 99.9995%; 1.5–10 g) and a mixture of diamond and graphite powders (3–20 g) were applied to prepare the copper–graphite and copper–diamond–graphite composites and coatings. Silicon powder was made from a single crystal by the ARW technique (preliminary grinding of the crystals using copper milling tools). The silicon powder was used to obtain the copper–silicon, copper–silicon–diamond, copper–silicon–graphite and copper–silicon–diamond–graphite composites and coatings.

The MA was performed both in air [Figure 1(*a*)] and under air-proof conditions [Figure 1(*b*)–(*e*)] for 120 min. The surfaces of the milling tools were coated with the MA powder. Compositions and structures of samples were studied by gravimetry, Raman spectroscopy (Dilor/OMARS), X-ray diffraction (XRD) analysis (DRON-3), differential thermal analysis (Q-1000), optical microscopy (NU-2E) and scanning electron microscopy (JSM-6380 and LEO-1550).

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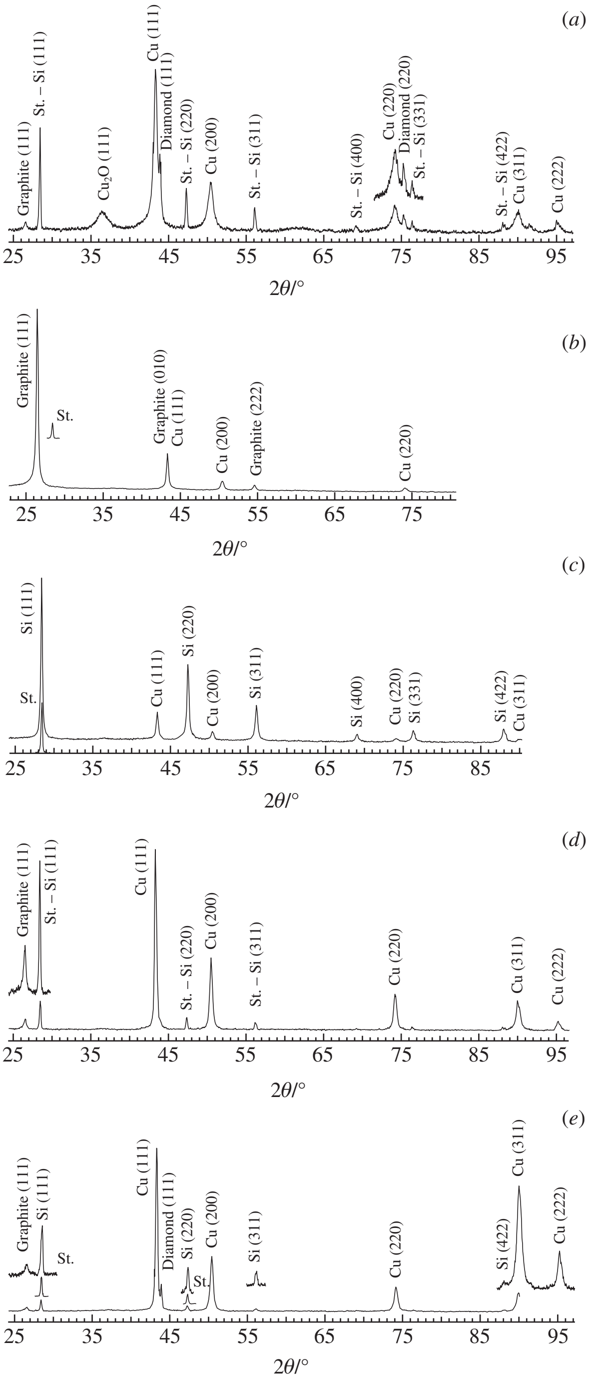

Figure 1 XRD patterns of the products of MA for 120 min: (*a*) 4.192 g of diamond (sample S1, St. are lines of standard); (*b*) 5.090 g of graphite (S2); (*c*) 3.100 g of silicon (S3); (*d*) diamond (10.244 g)–graphite (10.128 g) mixture (S5); (*e*) diamond (4.197 g)–graphite (5.418 g)–silicon (5.715 g) mixture (S7).

The powder XRD data on diamond, graphite, silicon and their mixtures were identical to PDF 79-1467 for diamond, PDF 75-2078 for R-3m graphite, PDF 27-1402 for silicon, PDF 3-1018 for copper and the superposition of all patterns for the mixtures. After the MA of samples, the XRD data virtually did not differ under identical measurement conditions (Figure 1): diamond crystals remain in the crystalline state, but the reflections are strongly masked by reflections of nanowear particles of the copper furniture of milling tools [Figure 1(*a*)]; hence, the MA of all samples does not produce carbon (or silicon) and copper compounds (it is well known that copper does not react with carbon) and the newly formed composites have a copper–carbon–silicon composition. Raman spectrometric data on the starting diamond (or silicon) and its MA product[14] indicate that MA does not create chemical bonds between copper and carbon (or silicon) atoms. Analysis of samples, as well as the control sample of powder mixture of diamond, graphite, silicon and copper, in air by the thermogravimetry (TGA, heating rate of 10 K min^{-1}) yielded important information.[14] The results show that a significant variation in the sample mass begins at $T > 700$ °C (burning of diamond) for S1, at $T > 100$ °C (burning of MA graphite) for S2, and at $T > 400$ °C (oxidation of silicon) for S3. Based on a TGA pattern similar to that in ref. 14, the mass of the control mixture also increases markedly due to oxidation at $T \sim 1000$ °C (the presence of carbon creates a reducing environment in the crucible and hampers the oxidation of copper). Therefore, the TGA data can be used to analyse the constituents of composites. For example, based on the TGA data,[14] the composite in S5 includes 24% carbon (7.3% graphite and 16.7% diamond). Hence, the Cu content should be 76%, which is very close to the weight analysis data. For comparison, the TGA data indicate that the MA product in S1 contains 77% diamond and 23% Cu.

Data on the microanalysis of different points of samples confirmed qualitatively the XRD data. In terms of quantitative assessment, the images obtained indicate the presence of some heterogeneity in the distribution of carbon and silicon. Light-coloured areas correspond to C-rich zones, while dark areas indicate C-poor zones. The images also show areas with an intermediate composition. SEM images of the samples show that the copper–carbon composites mainly include agglomerates 5–10 μm in size. Higher resolution images show that the agglomerates can be composed of particles much smaller than 1 μm. In order to determine the crystallite size and microstrain of copper in the MA powder samples, we processed the XRD data using the Williamson–Hall plot:[15,16]

$$\beta^2\cos^2\theta = (\lambda/D)^2 + 16\varepsilon^2\sin^2\theta,$$

where β is the broadening of reflections after the subtraction of the individual broadening of reflections of the standard (carbonyl silicon powder was used as a standard sample for instrumental broadening), $(\lambda/D)^2$ is the Y intercept, $\lambda = 0.15418$ nm is the CuKα radiation wavelength, and D is the size of crystallites; $16\varepsilon^2$ is the slope of a line on a $\sin^2\theta - \beta^2\cos^2\theta$ plot; it yields the microstrain ε of crystallites. Analytical data and microstructural characteristics of composites obtained from XRD are given in Table 1. For example, processing of data in Figure 1(*a*) and materials pertaining to the analogous (in terms of MA) S1 and S5 (see ref. 14) yielded the following results (Table 1): S1 (copper–

Table 1 MA products and coatings.

Sample	Powder charge/g	Mass, spent on a covering of the surface of milling tools	Cu content in composite (wt%)	Crystallite size D/nm	Microstrain ε (%)
S1 [Figure 1(*a*)]	4.192	2.8 g of diamond	63.3	$D_{\text{Cu}} = 25$	$\varepsilon_{\text{Cu}} = 0.21$
S2 [Figure 1(*b*)]	5.090	0.9 g of graphite	32.5	$D_{\text{Gr}} = 38$ $D_{\text{Cu}} = 20$	$\varepsilon_{\text{Gr}} = 0.08$
S3 [Figure 1(*c*)]	3.100	1.7 g of silicon	47.5	$D_{\text{Si}} = 46$ $D_{\text{Cu}} = 34$	$\varepsilon_{\text{Si}} = 0.2$
S5 [Figure 1(*d*)]	20.372	1.2 g of diamond–graphite mixture	80.5	$D_{\text{Cu}} = 24$ $D_{\text{Gr}} \approx 34$	$\varepsilon_{\text{Cu}} = 0.11$
S7 [Figure 1(*e*)]	16.060	0.9 g of diamond–graphite–silicon mixture	84.7	$D_{\text{Cu}} = 44$ $D_{\text{Gr}} = 24$ $D_{\text{Si}} = 54$	$\varepsilon_{\text{Cu}} = 0.25$

diamond system): $D_{\text{Cu}} = 25$ nm, $\varepsilon_{\text{Cu}} = 0.21\%$; the composite in S1 includes 63.3% Cu (the missing mass 2.8 g of diamond was spent on a covering of a surface of milling tools).

Based on the high-resolution SEM data, the relatively large agglomerates of particles have a cauliflower-type internal structure with a block dimension similar to certain dimensions of crystallites. The results for the MA of graphite-containing mixtures suggest that graphite can be used to produce a nonautonomous phase[17] on the surface of other composite particles. The nonautonomous phase has a significant influence on the process of MA. In particular, the formation of amorphous carbon enhances the degree of nanowear of the copper material of milling tools.

ARW can also be adapted to the preparation of coatings.[18] For example, if a copper plate is attached to the wall of the milling container, the impacts by the copper milling tools activate the surface of the plate, deliver particles from the powder charge and pound them onto or into the surface. The structure and properties of the coating depend on the MA conditions.

We have substantiated a new field of low-grade materials (diamond, silicon, *etc.*) utilization, namely, an abrasive-reactive synthesis based on the copper material of the milling tools of a planetary mill. A scrap of any metal and ceramic products can be used as milling tools, which makes it possible to considerably extend the potential of the abrasive-reactive wear method and the range of treated compounds.

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