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Investigation of the Abrasive-Reaction Interaction of Minerals with the Material of Milling Bodies during Mechanochemical Treatment

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Abstract

The possibility of processing natural and industry-caused materials by carrying out mechanochemical reactions participated by the material of milling bodies is investigated; this possibility is based on the use of abrasive (desirably amorphous) inert additives, such as glass or fused quartz. The essence of the method is the abrasive-reaction wearing of the material of milling bodies of the mechanochemical reactor. Meta-oxide-sulphide composites (during the treatment of tenorite and galena) and composites based on pyrite and quartz (during mechanical activation of a mixture of sulphur and amorphous quartz) were obtained in a planetary AGO-2 mill with steel equipment.

INTRODUCTION

As a rule, researchers studying the effect of the material of milling bodies on the course of mechanochemical processes (for example, [1–3]) only mention the possible contamination. The present work deals with a purposeful investigation of the effect of wearing of milling bodies on the course of MA in the system reagent – abrasive material in a mill with steel equipment.

Treatment, dressing and processing of mineral raw materials, in particular complex oxides and sulphides, by means of mechanochemistry have been widely developed during the recent years [4–12]. First, this is connected with the possibility to obtain, using thermite and mechanothermite methods [6, 7], the metal component and various composite nanocrystalline materials from natural and industry-caused materials, both in the gradual mode [6, 11, 12] and in the explosive regime [7, 10] of exothermal reactions. In connection with sulphur accumulation at the plants of petroleum and gas complex, the problem of sulphur utilization becomes especially urgent. The areas of application of sulphur can be broadened substantially by transforming it into sulphide materials. As a rule, sulphides are obtained from elements by heating; however, homogeneity and morphology of the target products depend on many factors, in particular on the size and surface state of the initial reagents. These shortcomings are absent in the case of treatment in a mechanochemical reactor [11]. Ferrous sulphides, especially nanometer-sized ones [11, 12], are at present used in specific areas: in the batteries with high energy density, photoelectrolysis and solar power engineering, synthesis of superconductors, diagnostic or luminescent materials, and chalcogenide glasses.

On the other hand, the results of modelling of mechanochemical reactions participated by sulphur show [13] that the most important

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process involved in the synthesis of zinc sulphides is plastic yielding of sulphur. The characteristics of this process are defined by the thickness of layers on the surface of zinc particles lined with softer sulphur. Plastic yielding of sulphur causes its amorphization (polymerization with the transformation into the vitreous state); however, one has not succeeded in carrying this process out experimentally. Because of this, in order to confirm the theory, it is necessary to choose such a system for mechanical activation, which contains, along with crystal sulphur, an inert component, desirably amorphous (in order to simplify interpretation of the results of X-ray phase analysis). Amorphous materials are ideally suitable for this purpose: usual glass, which is close in thermal and mechanical properties to zinc, and fused quartz. Using these additives, one will be able not only to carry out amorphization of sulphur but also to process sulphur into the target sulphide materials. In fact, we applied the abrasive-reaction method to modify the surface of quartz particles treated in a mill, with the participation of steel material of milling bodies [14], both for reductive treatment of tenorite (CuO) and galena (PbS), and for the oxidative treatment of sulphur into ferrous sulphides.

EXPERIMENTAL

Mechanochemical reactor used in the present work was a steel two-cylinder ball (the volume of each cylinder: 140 cm^3; 400 balls with the radius of 0.2 cm) water-cooled (water flow rate: 1 cm^3/s, temperature control at the outlet) planetary mill AGO-2. The relative collision velocity of milling bodies was 11 m/s [7]. For more efficient treatment of the samples, four possible orientations of the mill axis were used: vertical, horizontal, and at the angles of ±15° to the horizontal position.

The products of MA were investigated by means of standard X-ray phase analysis (XPA). Mechanically activated samples were annealed isothermally for 2 h at about 700 °C in argon flow (~1 cm^3/s) in alundum crucibles with graphite seals and a titanium sponge placed before the crucibles in the heated region of the quartz tube in order to purify argon from possible oxygen admixture.

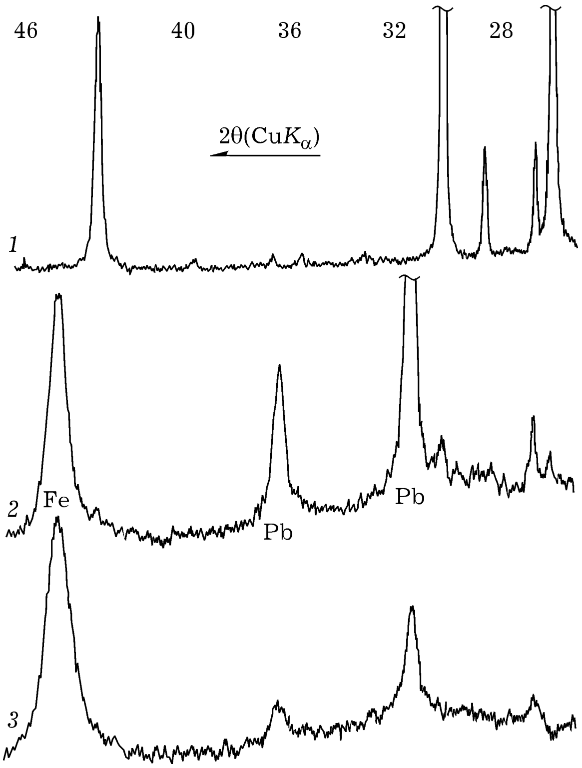

Fig. 1. XPA data for the system: fused quartz (3 g)–galena (1.5 g): *1* – initial mixture (compare with PDF 1-880), *2* – MA time: 1 h (compare with PDF 4-686 and 6-696), *3* – MA time: 3.5 h.

Tenorite, galena or sulphur in the amounts of 0.4–2.5 g were added to the weighed portions (3 g) of crushed fused quartz and usual glass. The samples were preliminarily ground and homogenized together with quartz (glass) for 1 h in a Fritsch Pulverisette mill with the equipment made of agate. According to the results of XPA of one of these samples based on natural galena (Fig. 1, curve *1*), in addition to galena it contains some admixtures (mainly crystal quartz) characteristic of this mineral. The initial tenorite was obtained by thermal decomposition of malachite at ~250 °C for 7 h. The results of XPA of the resulting black powder are shown in Fig. 2, curve *1*.

RESULTS AND DISCUSSION

Preliminary experiments showed both some similarity and essential differences in mechanochemical processes participated by

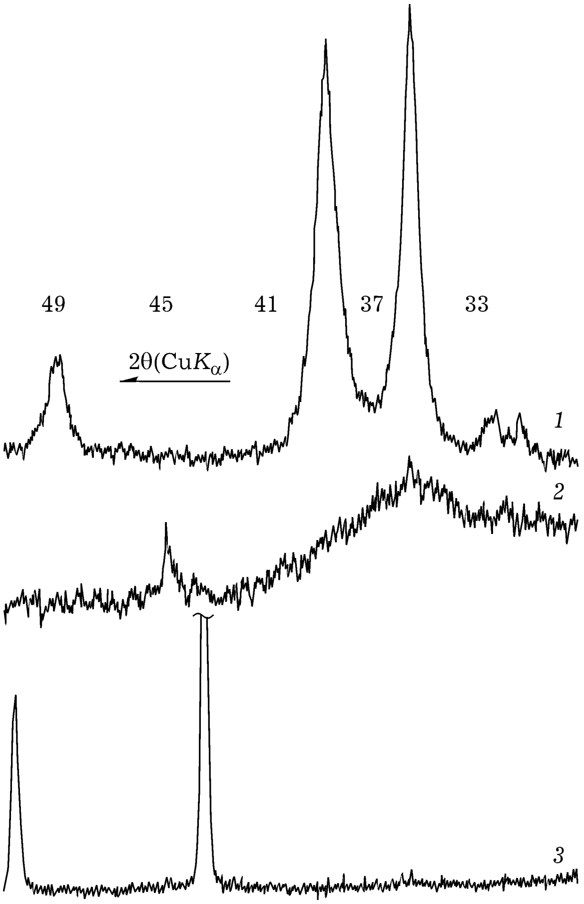

Fig. 2. XPA data for the system: fused quartz (3 g)−tenorite (1.5 g): *1* − initial mixture (PDF 48-1548 and 80-1917), *2* − MA time: 1 h, *3* − MA time: 3.5 g, annealing for 2 h at 700 °C (PDF 4-836).

tenorite and galena. In both systems, abrasive wearing of the steel milling bodies takes place; it is more clearly exhibited in the case of the system with galena. After a short-term (5–15 min) MA of the system with tenorite, self-lining of the milling bodies with the material under treatment occurs [13]. Tenorite starts to change its colour from black to green after treatment for 1 h; this colour gets more intensive in course of further treatment, and self-lining increases. Quite contrary, self-lining is absolutely absent from the system with galena; after MA for a short time, black uniform oily powder is formed.

The results of investigation of the products of MA by means of XPA and isothermal annealing showed that abrasive wearing of the steel milling bodies, amorphization, recovery of copper from tenorite and lead from galena occur; crystal phases of oxides and sulphides of iron (other products of reduction, for example $CuO + Fe = Cu + FeO$ ($\Delta_r G^o = -28.0$ kcal/mol) were not discovered.

One can see in Fig. 2, curve *2* that an X-ray amorphous product is formed in the system with tenorite and wearing of iron occurs (see a peak within the angle range 44–45°). The degree of amorphization increases with an increase in treatment time; the iron peak becomes broader and its shape becomes less distinct. Only metal copper is the product formed after annealing of this sample in argon at ~700 °C (which corresponds to the maximal temperature of crystallization of MA products [6]); there are no reflections of other possible products of the exchange reaction (see Fig. 2, curve *3*).

A similar phenomenon of iron wear and reduction of galena with iron resulting in the formation of the metal phase (lead) but directly during MA of the system with galena is shown in Fig. 1, curve *2*. Attention should be paid to the absence of reflections of other possible products of exchange reaction, namely, sulphides of iron. An increase in the time of MA to 2 h does not cause changes in the spectra, except for the disappearance (amorphization) of the reflections of the admixture of crystal quartz in natural galena. After annealing of these products, only insignificant changes of relative intensities and substantial narrowing of the corresponding reflections are observed. A further increase in MA duration results in predominance of the abrasive wearing of iron over all the other processes (see Fig. 1, curve *3*).

The XPA data of the samples prepared on the basis of glass and quartz with sulphur point to the presence of orthorhombic crystals of the initial sulphur only (see PDF 83-2285). The results of XPA on MA of sulphur crystals (with the weighed portion of 2 g, activation time up to 3 h) without an abrasive added show that sulphur does not undergo structural rearrangements. All the reflections are conserved without broadening or changes in their relative intensities, except for the absence of a halo, which was due to the presence of amorphous abrasive particles.

The situation changes (Fig. 3, *a*) in the case when sulphur is treated in mixture with glass. The structural changes occurring with sulphur in this case are due to the achievement of the

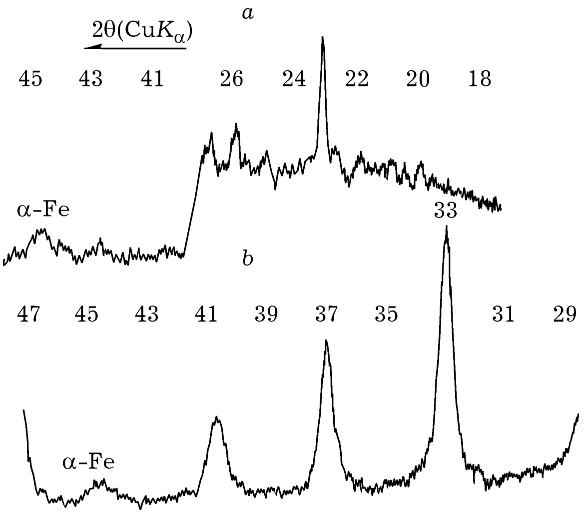

Fig. 3. XPA data for the systems: *a* – glass (3 g) – sulphur (0.4 g), MA for 135 min; *b* – fused quartz (3 g) – sulphur (1.6 g), MA for 135 min.

necessary *t–P–T* (time – pressure – temperature) conditions in the site of a shock-friction contact of glass particles lined with sulphur, in agreement with the results of modelling [13]. Though the hardness of glass particles is only slightly larger than that of steel, abrasive wear of steel equipment is insignificant. In addition, temperature pulse in the point of a shock-friction contact of the milling bodies and glass particles under treatment cannot exceed glass softening temperature (~500 °C), so the sulphides of iron are not formed within the indicated activation time. It should be noted that the synthesis of iron sulphides during mechanical alloying of iron and sulphur powders [11] is carried out within hundreds hours of mechanical treatment.

Dramatic changes occur during the activation of samples based on amorphous quartz. Figure 3, *b* shows the formation of pyrite (FeS_2, PDF 71-2219). The hardness of quartz particles is much larger than that of steel, while its melting point is much higher than temperature of glass melting. In this case, the processes of sulphur amorphization and its chemical interaction with the particles of iron which is formed in substantial amounts as a result of abrasive wearing of steel equipment [14] take place simultaneously and result in the synthesis of pyrite FeS_2 in combustion regime (compare with [6, 7, 10]). As a rule, crystallized final products are formed in the combustion regime [7], while the gradual regime results in the formation of amorphous ones.

Passing to discussion, let us once more mention the effect of self-lining on the course of mechanochemical processes. The data obtained provide unambiguous confirmation of the fact that self-lining of milling bodies prevents their abrasive wearing and, as a consequence, hinders reductive reaction of tenorite with the material of milling bodies during MA. Quite contrary, a complete absence of self-lining in the system with galena leads to rapid treatment of galena by the steel material of milling bodies.

It would be difficult to provide an unambiguous explanation of the disappearance of the reflections of oxides (sulphides) of iron after reductive treatment of tenorite (galena) without complex investigation of the MA of natural quartz in a planetary mill with steel equipment. However, we may state on the basis of the results obtained in the present investigation that the surface of quartz particles can be modified not only as a result of the formation of amorphous silicates of iron (which occurs after annealing of the mechanically activated tenorite samples) but also sulphides of iron after MA of galena together with the amorphous quartz particles. In the case of galena, the nanometer-sized surface layer on quartz particles is likely to correspond in its composition to some amorphous compound in the system Fe_xS_y–SiO_2. Even more complicated compound which is formed after MA of tenorite and contains nanometer-sized particles of the abrasive wear of steel equipment of the mill (see Fig. 2, curve *2*) is likely to correspond to the amorphous product known to be formed on the quartz surface in the system $Cu_xFe_yO_z$–SiO_2.

The next aspect is connected with the dimensional effects. With the traditional methods of mechanochemical reduction, for example, of copper sulphides [12] with the application of metal iron powder with the initial particle size of about ~50 μm, the duration of MA is several ten hours. In the new abrasive-reaction method of treatment proposed by us, for example for galena, the size of the initial particles of abrasive wear of iron is about 10 nm, that is, several orders of magnitude less than for the traditional method to perform the exchange mechanochemical reaction. So, the rate of treatment according to the abrasive reaction procedure with the participation of the material of steel milling bodies is higher; as a consequence, the time of MA treatment of minerals decreases by 1–2 orders of magnitude.

On the basis of XPA data, we used a known procedure [2, 4, 11, 12] to calculate the size of crystal blocks in the structure of the resulting metal particles formed during MA of the system with galena. The parameters of fine crystal structure were calculated basing on the half-width of the profile of diffraction peak intensities (see Fig. 1, curves *2* and *3*) for MA time equal to 1, 3.5 and 2 h (the XPA spectrum for the latter case is not shown). In order to determine the instrumental broadening, of lines, we used the profile of the corresponding reflections after annealing these samples. The resulting dimensions of lead blocks depending on MA time were 83 (1 h), 61 (2 h), and 46 nm (3.5 h). The corresponding data for iron wear particles are: 24, 19 and 12 nm. We also calculated crystal blocks and distortions in the structure of the resulting pyrite composite (see Fig. 3, *b*). The parameters of fine crystal structure were calculated on the basis of half-width of the intensity profile for diffraction peaks (220) and (440) accepted for pyrite [4]. In order to determine the instrumental broadening, we used the profile of lines of crystal pyrite. The resulting size of blocks in pyrite was ~24 nm (for iron particles, about 10 nm), distortions accounted for about 1 %. Similar results were obtained also in [11], but in that work the mechanical treatment of a mixture of Fe + 2S lasted for more than 110 h.

CONCLUSION

Thus, MA of natural (tenorite and galena) and industry-related (sulphur) minerals in mixture with an abrasive agent (amorphous quartz) in AGO-2 mill with steel equipment resulted in the formation of the metal-oxide-sulphide nanocomposite powders based on a quartz matrix within the time which was 1–2 orders of magnitude shorter than that for the traditional mechanical alloying of the initial powders of iron and the corresponding substances. It should also be noted that scrap of any other metals could be used as filler (milling bodies) to obtain nanocomposites based on their oxides and/or sulphides.

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