

Abrasive-reaction Interactions for Nano-composite Structures

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Abstract New methods of nano sized material and composite coating preparations have been considered on the base of mathematical model of abrasion reaction interaction of milling and grinding bodies in planetary centrifugal mill. The essence of the method is the abrasive and oxidative wear of the milling bodies and amorphous (better inert) additives. Interactions between them has been supplied the necessary impulse of pressure and temperature on the impact frictional contacts and promoted chemical processes. The offered method can find application for such processing as sintering and geological minerals opening.

Introduction

One of the most effective methods for intensification of heterogeneous solid phase processes is a mechanical activation of initial mixtures resulting in a structural homogeneity of reagents, modifications of physical and chemical properties and reactivity of solid substances. The paper reports on the concepts developed in the field of mechano-chemistry and the mechanical activation of inorganic solids, revealing the dynamic character of mechanical activation as a process

determining the state of the reagent at different moments during the a reaction.

In addition to attrition and agglomeration, high energy milling can induce chemical reactions, which can be used to influence the milling process and the properties of the product. This fact was utilized to prepare magnetic oxide-metal nano-composites via mechanically induced displacement reactions between a metal oxide and a more reactive metal. High energy ball milling can also induce chemical changes in non-metallurgical systems, including silicates, minerals,

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ferrites, ceramics, and organic compounds. The research area of mechano-chemistry developed to study and utilizes these processes. As many mechanical alloying processes involve chemical changes, the distinction between mechanical alloying and mechano-chemistry is often arbitrary. Mechanical energy can set off chemical changes in many different situations. For example, wear of a material involves chemical processes; corrosion is influenced by lattice defects created by plastic deformation, etc. We are primarily interested in mechano-chemical reactions induced by high energy ball milling. The processes taking place in a ball mill are very complex. One of our primary goals is to understand their mechanism by separating and modeling their individual components.

Therefore, in this paper, we applied the abrasion-reaction method of modifying the surface of treated quartz particles by the steel milling body material for reducing the opening of tenorite and galenite by iron.

Experimental part

a) Mechanical activation of SiO_2 particles and their reaction with FeO

For mechanical treatment we used three-drum steel planetary-centrifugal ball mill designed in the Scientific Industrial University. The mill had the following parameters: the ratio of the ball charge mass M to the quartz mass M_1 was assumed to equal 4 at $M+M_1=480+120=600\text{g}$. The parameters of the balls were the radius $R=0.5\text{ cm}$, the density $\rho = 7.8\text{ kg/m}^3$, the number $N=120$, and the total surface $\Pi b=4\pi R^2N\approx 370\text{ cm}^2$.

b) Treatment of minerals

The procedure was realized by means of tenorite and galenite processing in mixtures with crushed quartz in planetary mill with steel fittings. Crushed amorphous melted quartz 3 g in mass was added with 15 g of tenorite or galenite. Initial tenorite was obtained by thermal decomposition of malachite under the temperature of about 250° within 7 hours. The samples were preliminary ground and homogenized together with quartz in the Fintsch Pulvensette mill equipped with agate fittings during 1 hour.

Results and Discussion

Ball milling can be used to induce solid state reactions in a variety of technologies, including the activation of silicates, inorganic synthesis, and mechanical alloying. Some data on iron content were obtained by the Nuclear Gamma-Resonance Spectroscopy (NGRS). As gamma-quantum source, we used ^{57}Co in radium matrix 60 mCi in activity.

The gamma-radiation was recorded by scintillation counter with the NaI(Te) crystal. Table 2 presents the NGRS parameters of two quartz samples differing in activation time.

The Mössbauer spectra of iron atoms in Fe_2O_4 and Fe_3O_4 represent the characteristic sextets of the magnetic splitting of nucleus levels. In the samples considered, the additional lines are observed; they indicate the change in connection of iron atoms

with environment. The internal part of the spectrum is described by quadruple doublet with ultra-fine interaction parameters showing that iron takes two non-equivalent positions D_1 and D_2 in quartz lattice. According to the parameters of isomeric shear (δ -0.648 mm/s) and quadrupole splitting ($\epsilon \sim 1.054$ mm/s), the Fe^{+2} iron ions are better than ever in form typical to oxides in super-paramagnetic state. The values of ultra-fine parameters of the second doublet (δ -0.835 mm/s and $\epsilon \sim 2.8$ mm/s) can be referred to the Fe^{+2} ions in high-spin state.

The formation of iron silicates is indirectly confirmed by the data of the IS carried out for original quartz samples and those treated mechanically within 10 min (Fig. 2). The measurements were conducted on the infrared "Satellite FTIR" spectrometer. There were no differences in bands of the Si-O-Si and O-Si-O bonds for

Table 2. Parameters on NGRS of Washed Quartz Samples

τ , min	1st doublet				2nd doublet			
	δ , mm/s	ϵ , m/s	Γ , mm/s	D %	Δ , m/s	ϵ , mm/s	Γ , mm/s	D %
30	0.648	1.054	1.165	68.66	0.835	2.812	1.23	31.34
90	0.708	1.058	1.21	82.0	1.098	1.416	0.6	18.0

samples compared. However, the band of approximately 833 cm^{-1} referred to the Si-O-Me bond appears in activated sample, and the band of approximately 881 cm^{-1} corresponding to the Si-OH bond disappears in original quartz.

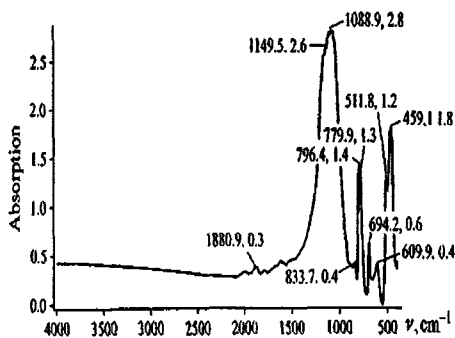


Fig.2. IR spectroscopy of quartz activated within 10 min.

From thermodynamic and kinetic viewpoints, at high temperatures of 1500-1700 K ($\sim T_m \sim T_{ml}$), meta-silicate ($\text{Fe} + \text{SiO}_2 = \text{FeSiO}_3$) and not ortho-silicate ($2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$) is more preferable to be formed in the FeO-SiO₂ system, since the process proceeds under conditions of quartz excess.

Figure 3b demonstrates the analogous phenomenon of iron abrasion and galenite recovery, but in mechanical activation of the system with galenite directly. In this case, we should also note the absence of

the reflexes of other possible reduction-exchange reaction products, i.e., iron sulfides. The increase in duration of mechanical activation up to 2 h does not lead to the change in the spectrum, except that reflexes of crystal quartz admixture in natural galenite disappear (amorphism phenomenon). The annealing of these products does not affect the situation; it results in insignificant variations in relative intensities and considerable smoothing of corresponding reflexes. The further increase in time of mechanical activation leads to prevail of iron abrasion over other processes (Fig. 3c).

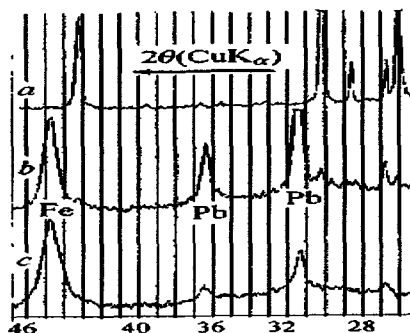


Fig.3. X ray phase analysis data for the sintered quartz - galenite, a) initial mixture, b) mechanical activation time is 1h, c) mechanical activation time is 3.5h.

Proceeding to the discussion, we again apply to the role of self-lining phenomenon in mechano-chemical processes. The data

obtained confirm unambiguously that the self-lining of milling bodies prevent their abrasion and the reduction reaction of tenorite with the milling body material during mechanical activation. The absence of self-lining in the system with galenite causes the rapid opening of galenite by steel substance of the milling bodies.

Conclusion

We proposed mechanism of the iron silicates formation via intermediate of nano-sized iron oxides as a result of abrasive-oxidative wear of the steel milling tools, followed by the mechanical reaction of these iron oxides with quartz surface. This provides evidence that at present the numerical modeling of mechano-chemical processes is of independent interest; important problems for experimental investigation can be formulated on this basis.

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