

REACTION OF THE MATERIAL OF MILLING TOOLS WITH TREATED NATIVE QUARTZ IN A MILL WITH STEEL FURNITURE

Urakaev F.Kh.

(United Institute of Geology, Geophysics and Mineralogy SB RAS, Novosibirsk State University
Novosibirsk, Russia)

urakaev@uiggm.nsc.ru

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Numerical modeling of the mechanism and kinetics of the chemical interaction between the material of milling tools and the substance under treatment is performed for the case of the treatment of quartz in steel ball planetary-centrifugal mill under the conditions when air is admitted into mechanochemical reactor. It is demonstrated that along with grinding and amorphization of the quartz surface, mechanical treatment of quartz involves mechanochemical synthesis of iron silicates from silicon and iron oxides. Submicron particles of iron and iron oxide are formed as a result of abrasive and oxidative wear of the steel furniture of the mill by quartz particles. Estimated thickness of the formed layer of iron silicates on the surface of quartz particles is ~2 nm.

In the recent years, we evidence a rapid increase in the number of investigations into the modeling of mechanical activation (MA) phenomena [1-3] and into the processing of geological and technogeneous materials by MA methods [3,4]. Ingenuous role of milling tools in MA processes is usually limited only by verification of the possibility of contamination of the final products of mechanical activation by the material of milling tools [3]. The goal of the present work is study of the influence of the material of milling tools on the progress of MA of quartz as an abrasive in planetary mill with steel furniture. Mechanical activation (MA) was performed with a steel planetary mill made in the NPO "Mekhanobr" [5]. The ratio of the mass of ball load M to the mass of quartz M_1 was 4 for $M + M_1 = 480 + 120 = 600$ g. AGO-2 planetary mill [2,4] was used in some reference experiments. In order to determine possible forms of iron presence in quartz particles, the MA material was subjected to acid etching; MA samples after washing from elemental iron were investigated by usual analysis methods (X-ray, Electron microscopy, Mössbauer and infrared (IR) spectroscopy).

A reference experiment (Fig. 1) provides confirmation of the abrasive wear of iron. It follows from the data of Table 1 that ~90% of iron is present in MA quartz samples in acid-soluble metal phase. One also can see that the total wear of the steel furniture of the mill can reach ~5% (~7 g), while the dependence of the amount of abradant iron on MA time is not linear. The deviation from linearity is connected with self-lining of the milling tools [1,5], the degree of which increases with an increase in $S(\tau)$ of MA material (Fig. 2), which provides partial protection of milling tools from wear.

Table 1.
Iron content in MA quartz samples

Activation time τ , minutes	Specific surface $S(\tau)$, m^2/g	Iron content m and $m^\#$, mass %		
		gravimetric, after activation	after etching	
			spectrography	microprobe [#]
0	(~0.01)	(0.06)	-	-
5	1*/1	1.43	0.10	-
10	5.3*/4.6	2.68	0.18	0.16
15	6.8*/2.7	3.74	0.24	0.23
30	7.2*/2.7	3.90	0.41	0.35
60	7.2*/2.7	4.50	0.52	-
90	7.2*/2.7	5.14	0.64	0.40

^{*)} specific surface after disaggregation; ^{#)} the data of microprobe.

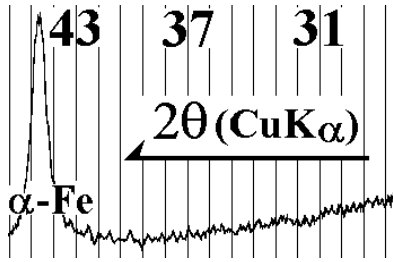


Fig. 1. X-ray data of mechanically activated (MA) fused quartz for MA time $\tau = 12$ min in AGO-2 mill.

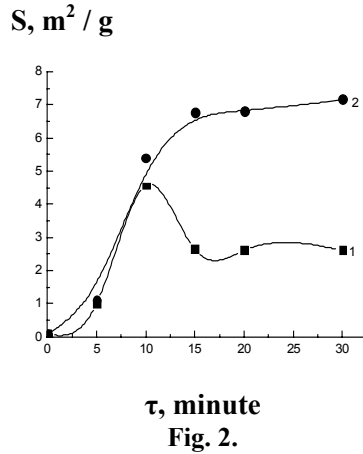


Fig. 2.

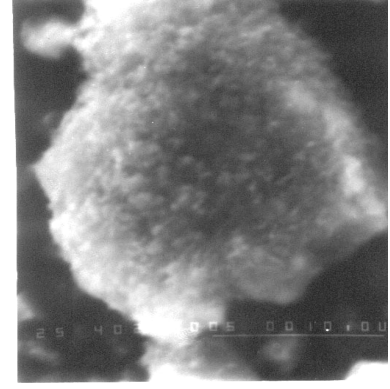


Fig. 3. E/m of quartz particle, MA 10 min, 25 kV/x4800.

As a result of abradant-oxidative wear, the formed particles of Fe and FeO (oxidation by air) are nanosized; they should be adsorbed on much larger quartz particles. On the other hand, it is known [6] that some surface layer of quartz particles is amorphized during MA. Both the amorphization mechanism and the thickness of the amorphized layer have been a subject of discussion [6-8].

One can see in Table 1 that the samples washed from elemental iron are represented only by quartz particles (Fig. 3) with the content of acid-insoluble form of iron up to $\sim 0.6\%$ or up to ~ 0.75 g calculated for Fe. Some data on the form in which iron is present in the system have been obtained by means of **Mössbauer** and **IR** spectroscopy. The Mössbauer spectra were performed with MC1104EM instrument at room temperature in the constant acceleration mode. The internal part of the spectrum is described by a quadrupole doublet; its hyperfine splitting constants indicate that iron occupies two unequivalent positions in the quartz lattice - D1 and D2: the parameters for the isomeric shift ($\delta \sim 0.648$ mm/s) and quadrupole splitting ($\varepsilon \sim 1.054$ mm/s) for the first doublet indicate that iron ions Fe^{2+} occur in super-paramagnetic state; the hyperfine parameters of the second doublet ($\delta \sim 0.835$ mm/s and $\varepsilon \sim 2.8$ mm/s) can be related to Fe^{2+} ions that are in high-spin state. The population of these two positions by iron ions depends on the time of MA. According to [8-10], such a position of iron ions in quartz can be explained only by the formation of iron silicates.

Confirmation of the formation of iron silicates is also the **IRS** data for the initial quartz samples and those MA. Measurements were performed with the IR spectrometer «Satellite FTIR» of «Mattson» company (USA). No differences in the bands related to Si-O-Si and O-Si-O bonds were detected for the samples under comparison. However, a band at ~ 833 cm^{-1} appears in the activated sample; it is assigned to the Si-O-Me bond [11].

From the thermodynamic and kinetic viewpoints in the system $\text{FeO} - \text{SiO}_2$ the formation of meta-silicate is preferable ($\text{FeO} + \text{SiO}_2 = \text{FeSiO}_3$), rather than ortho-silicate ($2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$), since the process occurs under the excess of quartz. Since no separate phase of iron silicates is detected, they can be present only in the amorphized surface layer of the quartz particles. Using the data of Table 1 one can easily estimate the empirical mean thickness $\langle \delta \rangle$ of the layer of iron silicates on the surface of quartz particles for the case of their uniform distribution: $\langle \delta \rangle = a_m / \rho S(\tau) \approx m / S(\tau)$, where m is relative (in %) iron content in washed samples, $a/\rho \approx 1$, where $a \approx 2.5$ is the ratio of the molecular mass of silicates to that of iron, $\rho \approx 2.5$ is the density of iron silicates, $S(\tau = 1800 \text{ s}) = 7.2 \cdot 10^4 \text{ cm}^2/\text{g}$, see Fig. 2. It is clear that this is a lower estimation of δ , since the additional amount of FeO during the oxidation of iron adsorbed on the surface of quartz particles cannot be estimated and it should be taken into account that the values of $\langle \delta \rangle$ can only be underestimated, because the solubility of amorphized layers of the activated quartz particles, and thus iron silicates, in acids is rather high, compared to the initial quartz particles [6,7].

The established mean $\langle \delta \rangle$ do not exceed the thickness of the amorphized layer of MA quartz particles determined by other methods ~ 2 nm [6]. This gives us reasons to state that the amorphized layer on the surface of quartz particles is to a great extent composed of iron silicates and it obtained, unlike from [8], by the abradant-oxidative wear of steel milling tools. Moreover, the synthesis of iron silicates that occurs at the impact-friction contact of the treated quartz particles according to the model mechanism [5] most probably leads to the formation of the amorphized layer; its thickness is in agreement with the results of the performed modeling [5].

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