The use of mechano-activation for nanostructuring of quartz materials

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Abstract

The paper presents the results of evaluation of a phase- and nanoscale- heterogeneity of mechano-activated nanostructured quartz (MANS-Q) of different origin: metamorphic (meta-sandstone greenschist facies), magmatic (quartz sand) and hydrothermal genesis and its performance as a pozzolanic component in the portland cement binders.

The mechanical activation of quartz in a planetary mill affects its degree of amorphization. The results of quantitative XRD using the Rietveld method revealed that the concentration of amorphous silica under the same conditions of mechanical activation increases in the order: hydrothermal quartz → magmatic quartz → metamorphic quartz. The BET average particle size and an average thickness of the amorphous layer on the surface of MANS-Q particles was 500 and 100 nm, respectively. Despite of different crystalline structure of investigated MANS-Q at the target surface area of 4.8 m^2/g, for all investigated materials the concentration of amorphous silica reaches the same value of 82%. Therefore, the mechanical activation of quartz of different origin can be used to achieve the desired reactivity for application in blended cements.

The methods of XRD and Raman spectroscopy revealed that the crystalline phase of MANS-Q is composed of α- and β-quartz. Microstructural and quantitative phase analysis using the Rietveld method showed the concentration variations in the range 65-95% α-quartz and 5-35% β-quartz. The maximal concentration of β-quartz is determined in quartz of meta-sandstone greenschist facies. The average crystallite size <D> is 60 and 15 nm for α-quartz and β-quartz, respectively. This crystallite size for β-quartz is consistent with thermodynamic estimates of these values given in [2]. The concentration of high-temperature β-quartz increases monotonically with mechano-activation impact.

Keywords: quartz rocks, mechano-activation, amorphization, high-temperature β-quartz, nano-structured silica.

1. Introduction

Nanosized and nanostructured silica is a widely used material in the construction industry as a reactive powder pozzolanic and filler component of cement and lime-silica binders.
One of the most effective methods to manufacture this material is mehano-activated dispersion of quartz rocks. These may include sedimentary rocks - quartz sand, which is the product of mechanical weathering of primary igneous rocks of "acid" composition, such as granites. Other common raw materials are metamorphic quartzite and low-temperature hydrothermal quartz.

Despite the rather subtle differences in the elemental composition, crystal morphology and structure, these species differ in their thermal history. Quartz based acid magmatic rocks crystallized from the residual silicate melt at temperatures around 900 ºC. Metamorphic

quartz in its geological history has experienced epicrystallization due to thermal effects. Hydrothermal quartz crystallized at relatively low (about 350 ℃) temperatures.

It should be noted that the minerals of the silica is a high-temperature and high-pressure polymorphs; therefore two relaxation processes can be implemented for mechanical activation: through amorphization (nanostructuring) and by the formation of high- temperature polymorphs. It can be proposed that the differences in thermal history of silica materials of different mineralogical and genetic types may affect the final state of these materials after mehano-activated dispersion. In particular, their phase-, nano-size- and micro-size- heterogeneity are affected.

Studies on the mehano-activated dispersion of silica minerals have a history of more than a half century [1-4]. The main prior art findings are related to the observation of amorphous surface on quartz particles and a reduction of crystallite size (Fig. 1). In particular, for non-activated silica the crystallite size is estimated to be > 100 nm (Fig.1, a). Particles of mehano-activated quartz (Fig.1, b) consist of two areas: the central core area of the crystal with a crystallite size ~ 90 nm (I) and surface-amorphized layer with thickness of 20 nm and a crystallite size in the range 1-10 nm (II) [4, 5].
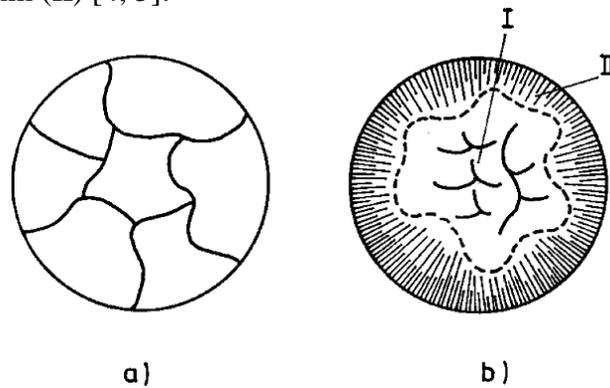
Fig. 1. Quartz particle: (a) non-activated, (b) mechano-activated
(adapted from [4]).

In addition, it was proved the formation of β-quartz (high-temperature polymorph) at a low-temperature mechanical activation of α-quartz [6]. The possibility of formation of β-quartz at room temperature is justified on the basis of thermodynamic calculations considering the size effect. In particular, β-quartz can exist at low temperatures if the size of its crystallite size does not exceed the range of 20-30 nm [7]. Therefore, based on these experimental results, it was concluded that the mechano-activated quartz is a nano-structured heterogeneous system, or MANS-Q.

2. Experimental Methods

Quartz sand deposits of magma genesis from the Lower Olshansky, Russia; screenings of crushed metamorphic quartzite of greenschist facies from the Kursk Magnetic Anomaly, Russia; and the hydrothermal quartz from the South-Ural province, Russia were used in this research.

All silica materials were milled to the initial values of specific surface area of 100 kg/m^2. Mechano- activated dispersion was carried out in a planetary mill for time periods of 2, 4 and 6 hours. The X-ray diffraction (XRD), Raman spectroscopy, and nitrogen adsorption (BET) methods were used to characterize the allotropical transitions in quartz due to mechano-activation.

Raman spectroscopy (Senterra from Bruker, Germany) was performed using a 523 nm laser as a source of monochromatic exciting light. Each sample of dispersed material was analyzed by 3-5 points and integrated Raman spectrum for each sample was obtained as the arithmetic mean of the local spectra.

The quantitative XRD with an internal calibration of the samples of quartz was used to assess the degree of amorphization. Calculations were performed using the FullProf software [8] (Fig. 2). Well-crystallized natural fluorite sample was used as an internal standard, at a concentration of 20 % by weight. The concentration of the amorphous phase (in %) was calculated by the following equation:

$$C_{amorp.} = \{100 \cdot (C_{starndart.}^{calc.} - C_{standard.}^{real.})\} \frac{100 \cdot (C_{standard.}^{calc.} - C_{standard.}^{real.})}{C_{standard.}^{calc.} \cdot (100 - C_{standard.}^{real.})/100}$$

3. Results and discussion

Graphical representation of the amorphization of investigated silica materials is shown in Fig. 3. The amorphization of MANS-Q vs. the active surface area was investigated using the BET method (Fig. 4). The dependence of the degree of amorphization of MANS-Q vs. the specific surface area is described by a similar function for different forms of quartz minerals. It was observed that metamorphic quartz (3) reached the amorphization limit after 4 hours of activation; which can be explained by an active agglomeration when the particles reach a certain threshold dispersion associated with a high degree of amorphization.
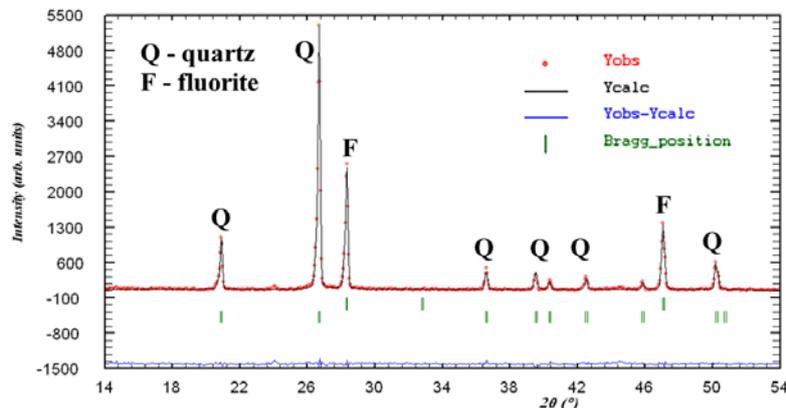
Fig. 2. Diagram of calculation of full X-ray profile of mechano-activated quartz and 20% (by weight) of fluorite; below - the difference between the experimental curve and calculated values of intensities at each point of diffraction spectrum
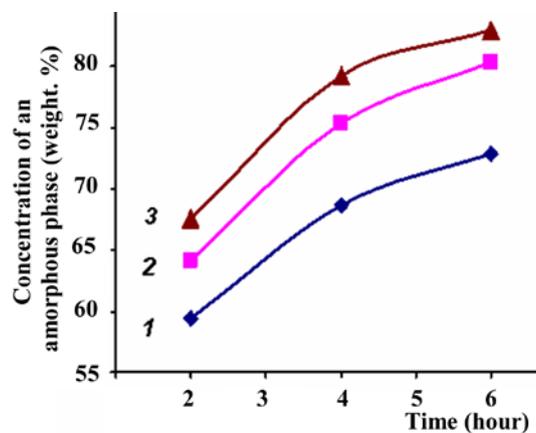
Fig. 3. The degree of amorphization for silica rocks of different genesis vs. activation time
1 - hydrothermal, 2 - magmatic, 3 - metamorphic quartz.

Fig. 4 shows the diameters of silica particles (with the assumption of spherical particles) for the respective values of the active surface area. Assuming the density of the amorphous layer to be equal to the density of crystalline quartz (which could still introduce some errors), the estimated thickness of the amorphous layer is in the range of 100 - 130 nm. These estimates are considerably higher than those reported in [4,5].
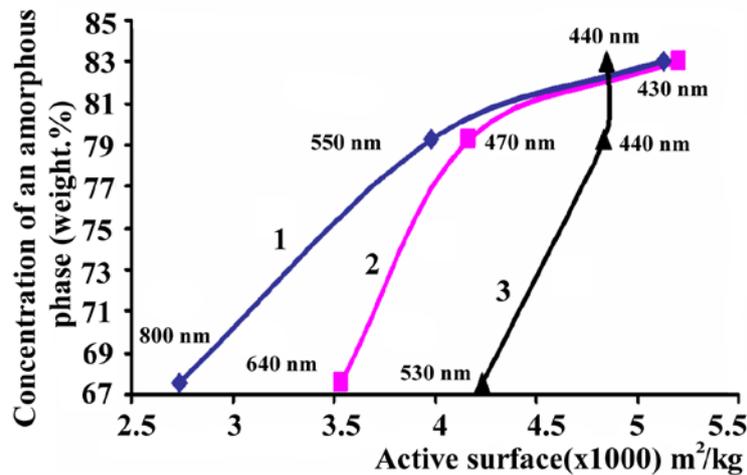
Fig. 4. Changing the phase-dimensional heterogeneity of quartz rocks during mechanical activation: 1 - hydrothermal, 2 - magmatic, 3 - metamorphic quartz

A graphical comparison of the Raman spectra of magmatic and metamorphic quartz, mechanically activated in a planetary mill for 6 and 10 hours vs. reference quartz R050125 (Linopolis, Minas Gerais, Brazil) from the RRUFF-database of the Raman spectra [9] in the region of small wave numbers is shown in Figs. 5, 6. The impact of mechano-activation resulted in a shift of the A1mode (207 cm^{-1}) of quartz in the long wavelength region and also in a shift of the E- mode (127 cm^{-1}). Previously, this phenomenon was observed in the study of α → β transition of quartz. In particular, a comparative analysis of experimentally obtained and theoretically calculated Raman spectra of α-and β-quartz, showed that the position of the maxima of the intensity of Raman scattering in α → β transition tend to shift toward lower wave numbers [10].
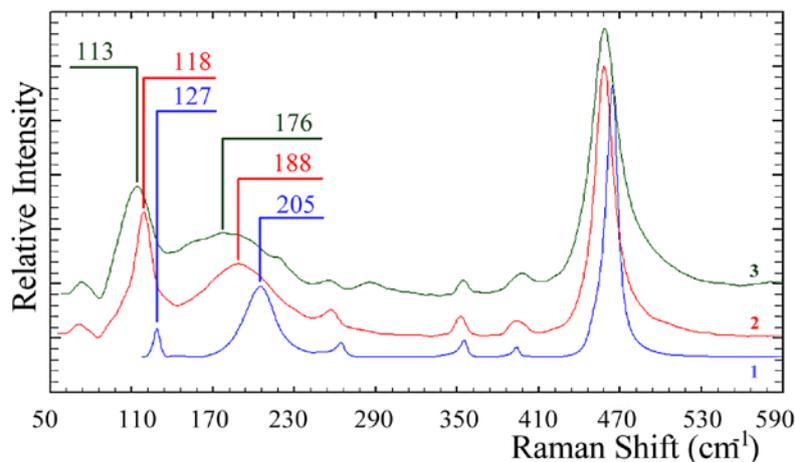
Fig. 5. The long-wavelength parts of the Raman spectra of quartz:
1 - the reference quartz, 2-3 - spectra of magma - quartz, mechanically activated for 6 and 10 hours respectively.
Note: the change of the wave numbers of modes A1 (207 cm^{-1}) and E (127 cm^{-1}).

Analysis of the Raman spectra of metamorphic quartz was complicated due to the presence of impurities of feldspar, mainly anorthoclase. However, the appearance of a new Raman band at 147 cm^{-1} in the mechano-activated material was observed, which, according to the authors of [11], is a fundamental measure of $\alpha \rightarrow \beta$ transition in quartz.
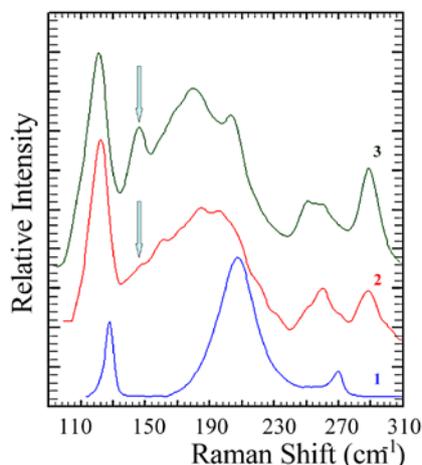
Fig. 6. The long-wavelength parts of the Raman spectra for metamorphic quartz:
1 - the reference quartz, 2, 3 - spectra of quartz mechanically activated for 6 and 10 hours respectively.
Note: the arrows show the scatter mode 147 cm^{-1}.

Thus, based on an analysis of the spectra of Raman scattering it can be concluded that the mechanical activation of quartz minerals results in formation of the nano-clusters of high-temperature β-quartz within the crystalline matrix of low-temperature α-quartz. In addition, the observed broadening of the Raman profiles with mechanical activation is associated with a decrease in the size of the clusters. This indirectly confirms the results obtained in [7].

The presence of β-quartz in the studied materials was also confirmed by the X-ray diffraction methods. Because of only slight difference in elementary cell parameters of α- and β-quartz of less than 30 nm [7], the diffractograms of mechanically activated quartz materials must have the asymmetry of diffraction profiles towards a low-angle region. However, such asymmetry of diffraction profiles may be caused by the divergence of the X-rays in the plane of the beam. To minimize this effect, the investigation was conducted using Soller slits with an angular divergence of 1.5 °. The X-ray phase analysis was performed to clarify the microstructural parameters using the software FullProf [8] which demonstrated a good agreement between the experimental and calculated diffraction spectra (Fig. 7).

The microstructural analysis included the determination of crystallite size in isotropic approximation with macrocrystalline silica as a reference for the profile function. X-ray studies have shown the variation of the phase parameters and dimensional heterogeneity of mechano-activated quartz material of various origin. In the initial (non-activated) state, only magmatic and metamorphic quartz forms contain about 5 and 10 % of β-quartz, respectively. In the initial hydrothermal materials β quartz was not present. This is consistent with the thermal trends in the geologic history of investigated quartz rocks.
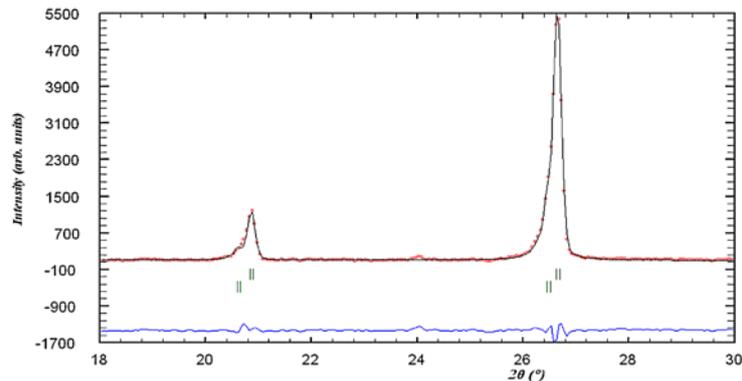
Fig. 7. The fragment of small-angle Rietveld diagrams for mechano-activated composition of α- and β-quartz.

The average crystallite size <D> was found to be 60 nm for α-quartz and 15 nm for β quartz. The crystallite size obtained for β-quartz corresponds to the thermodynamic estimates of the values obtained in [7]. It was observed that the concentration of β-quartz monotonically increases with mechano-activation (Fig. 8) [12]. The obtained mechano-activated nanostructured quartz, MANS-Q can be used as a component of the composite binders. It was demonstrated that the strength of binders with MANS-Q depends on the concentration of high-temperature nano-sized β-quartz [13, 14].
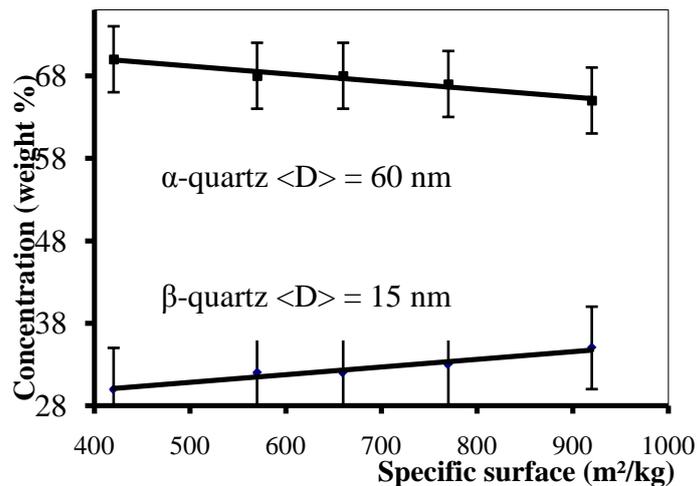
Fig. 8. Changing the mineral composition of quartz sand (magma genesis) for mechanical activation in the vibratory mill.

4. Conclusions

The results the research demonstrated the phase- and nanoscale- heterogeneity of mechano-activated nanostructured quartz (MANS-Q) of different origin: metamorphic (meta-sandstone greenschist facies), magmatic (quartz sand) and hydrothermal genesis.

In the process of mechanical activation of rocks, consisting of low-temperature α-quartz crystallites of high-temperature β-quartz are formed and the concentration of this phase depends on the degree of activation.The formation of agglomerates - the opposite process to the dispersion - is associated with achieving a certain level of amorphization of silica material. The mechanical activation of quartz in a planetary mill affects its degree of amorphization. The results of quantitative XRD using the Rietveld method revealed that the concentration of amorphous silica under the same conditions of mechanical activation increases in the order:

hydrothermal quartz → magmatic quartz → metamorphic quartz. The mechanical activation of quartz can be used to achieve the desired reactivity for application in blended cements.

The results of reported investigation on phase and dimensional heterogeneity of mechanically activated silica materials may need additional clarification, which will be the subject of further research.

Acknowledgement

References

1. Khodakov G.S. Fine grinding of construction materials. 1972, 239 p.
2. Avakumov E.G. Mechanical methods of activation of chemical processes. Novosibirsk. 1980, 297 p.
3. Khodakov G.S. Physics of grinding. 1985, 307 p.
4. Baláž P. Mechanochemistry in Nanoscience and Minerals Engineering. Springer-Verlag Berlin Heidelberg. 2008, 413 p.
5. Heinicke, G. Tribochemistry. Akademie Verlag, Berlin. 1984, 495p.
6. Archipenko D.C. A new phase of quartz, stable at room temperature encountered during tribo-treatment (the study using X-ray diffraction). / D.K. Archipenko, G.B. Boki, T.N. Grigoriev, S.M. Koroleva, T.S. Felix, Reports of the USSR Academy of Science; Vol. 296, № 6, 1987, pp. 1370-1374.
7. Dubrovinsky L.S., Piloyan G.O. Reports of the USSR Academy of Science; Vol. 286, 1986, pp. 958-961.
8. Rodriguez-Carvajal J. *An introduction to the program FullProf 2000.* Saclay, 91191 Cif sur Yvette, Cedex, France, 2000.
9. RRUFF database of Raman spectra, X-ray diffraction and chemistry data for minerals http://rruff.info/about/about_general.php.
10. Iishi K., Yamaguhi H. Study of the Force Field and the Vibrational Normal Modes in the α-β Quartz Phase Transition. The American Mineralogist, Vol. 60, 1975, 907-912.
11. Shapiro S.M., D.C. O'Shea and H.Z. Cummins. Raman Scattering Study of the Alpha-Beta Phase Transition in Quartz Phys. Rev. Lett. 19, 1967, 361–364.
12. Zhernovsky I.V., Strokova V.V., Lesovik V.S. In 2nd Central-European Mineralogical Conference 2008 (CEMC), edited by Mineralogia Polonica – Special Papers, 32, 2008, 175.
13. Strokova V.V., Zhernovsky I.V., Fomenko J.V. Bulletin of the Belgorod State Technological University named after V.G. Shukhov, 2007, 4, 48–49.
14. Lesovik V.S., Zhernovsky I.V., Building materials , 2008, 8, 78-79.