Bull. Nov. Comp. Center, Math. Model. in Geoph., 4 (1998), 121–126

The influence of vibroaction on the structure and activation of substances

V.S. Krivoputsky

Differences and regularities of the behavior of quartz under the action of the both methods make it possible to conclude that vibroaction is a promising and highly effective method of activation of substances. It allows (given the deformation of the structure is small without reconstruction) a considerable increase of the patchiness of samples without rendering them amorphous or contaminating them. This unveils the potential for application of this method.

Activation of substances by hyperfine grinding (in addition to the action of high temperature, pressure, catalysts) is used to initiate chemical reactions and ensure full course of technological processes. Sometimes vibroaction is applied for activation of substances and technological processes.

However, there are no data for changes in the structure of substances and their chemical activity during vibroaction and comparison of these characteristics in the technologies with the both initiating factors (vibration and hyperfine grinding).

Hyperfine grinding is known to be a complex process. It is accompanied, along with dispersion (up to the micron size and less), by deep physicochemical and structural transformations of substances. They lead to destruction of molecules, deformation of structural polyhedrons, angles between planes, changes or breakage of intermolecular and interatomic bonds, resulting appearance of excess surface energy and free uncompensated bonds on newly formed surfaces.

It has been established [1, 2] that changes in the structure of a substance and its activity are correlated with the size of mosaic blocks and the extent of microdistortions of the structure. For example, in accordance with the data of T.A. Andreeva et al. [3], hyperfine grinding of quartz accompanied by a considerable reduction in the size of mosaic blocks and an increase of microdistortions in the structure causes an increase in the chemical activity of its finely divided particles to such an extent that they dissolve even in water and water solutions of acids and alkalis.

It is shown in [2] that hyperfine grinding of apatite in water and a weak solution of an alkali induces a considerable deterioration of the efficiency of the structure, namely, intensive development of microdistortions and considerable diminution of the mosaic blocks. This is the determining factor of active destruction of the mineral and transition of fluorine, calcium, and phosphorus ions which constitute it into water solutions of alkalis and acids.

It was established by T.S. Yusupov et al. in [4] that natural inert cassiterite transforms to a soluble form after mechanical activation which leads to an increase in the lattice distortions and a considerable reduction of mosaic block sizes.

It should be noted that activation of substances by hyperfine grinding is accompanied in the majority of cases by:

- local pressures of short duration and temperatures reaching high values in the area of contact of rubbing bodies. Sometimes this leads to structural reconstruction of substances, in addition to the activation of molecules and appearance of defects, the relaxation of which is difficult;
- contamination of substances being activated by the material of which the grinding balls, rods and cylinder walls are made;
- aggregation of particles, which causes nonreproducibility of the process and distortion of the results of determination of the specific surface. This makes understanding of the technology of activation of substances difficult;
- formation of an amorphous layer and the next quasiamorphous layer on the surface of substances. The micropores and cracks of the quasiamorphous layer are filled with the amorphous component, ions of the medium, and the substance of the walls and balls of the grinding apparatus. The thickness of these layers is determined mostly not by the size of the particles being activated, but by the power strength of the grinding apparatus, the time of dispersion and the quality of the sample.

The method of vibroaction is free from these shortcomings, because it makes it possible to activate substance without contaminating it, rendering it amorphous, or causing its structural reconstruction. This is important, for example, in identification of the structure and composition of substances, their refining. It is expedient to subject substances to vibroaction in such areas as powder metallurgy, food, pharmaceutical industries, etc.

We have performed a series of experimental investigations to study the reaction of the substance structure to vibroaction, choose the criteria for estimation of the efficiency and applicability of this method in design of technological processes. Quartz was chosen for these investigations, because it is polygeneous and one of the basic rock-forming minerals. Besides, quartz samples of various efficiency of structure have been examined to analyze the influence of the initial structure on the final characteristics.

The sizes of mosaic blocks and the degree of microdistortions of the structure (in accordance with the above and the data presented in [5–7] and others) are universal indicators of structural inefficiency resulting from various

The results of investigations of the quartz samples activated by hyperfine grinding (I) and vibroaction (V)

Sample, №	Å,%	L,Å	$D \cdot 10^{-2}$	$C \cdot 10^{-3}$
№ 1 init.	0	960	0.1	0.1
№ 1 I	3	830	17.2	20.7
	10	640	42.0	65.6
	23	420	56.8	135.2
№ 1 V	0	740	0.9	1.2
	0.1	430	13.2	30.7
	0.4	90	31.6	35.1
№ 2 init.	0	890	0.7	0.8
№ 2 I	5	770	25.6	33.2
	14	680	57.2	84.1
	42	370	74.0	200.4
№ 2 V	0.1	740	0.9	1.3
	0.4	400	20.1	51.1
	0.7	75	38.6	51.6
№ 3 init.	0	810	0.7	0.9
№ 3 I	5	720	28.1	38.8
	15	550	64.6	116.3
	42	340	80.2	235.2
№ 3 V	0.1	650	10.9	16.7
	0.7	360	21.9	60.6
	1.1	65	41.7	64.0
№ 4 init.	0	730	0.9	1.2
№ 4 I	6	630	37.6	59.6
	17	470	76.0	161.7
	56	280	96.8	345.7
№ 4 V	0.3	590	11.8	20.0
	0.8	340	22.2	65.1
	1.9	60	42.1	70.2
№ 5 init.	0	270	1.8	6.7
№ 5 I	7	210	48.4	230.4
	20	170	90.8	534.1
	81	120	110.4	920.0
№ 5 V	0.4	195	16.0	82.1
	1.2	100	23.9	239.1
	2.8	55	44.2	803.6

postcrystalline actions and the chemical activity of substances. Therefore, the reactivity and the change of the quartz structure initiated by vibroaction and hyperfine grinding were estimated from these characteristics.

The microdistortions of the lattice and the size of mosaic blocks were calculated by the harmonic analysis method [8]. The efficiency of the structure was estimated from the relation between the values of microdistortions and mosaic blocks. The size of the amorphous layer was determined from the difference between the sizes of mosaic blocks obtained in the process of vibroaction and hyperfine grinding and the same blocks treated for 3 minutes in a water solution of hydrofluoric acid in order to remove the amorphous layer.

The experimental investigations were carried out on samples of the 1.0–0.5 mm fraction. The samples had been preliminarily treated in water solutions of the hydrochloric acid to dissolve admixtures of the mechanical character and hydrofluoric acid to eliminate the layer damaged in the process of the fraction preparation from the surface of particles [9]. Smaller particles were sifted from the samples to obtain a clear picture at vibroaction and avoid an effect, when the radius of particle capture is inside a larger radius of an oscillating liquid bubble.

One part of the samples was subjected to hyperfine grinding in a centrifugal planetary grinder, and the other to Tvibroaction by magnetostrictive UZG-4 generator with an oscillation frequency of 18.5 kHz in 10% water solution of alkali during 5, 15 and 30 minutes.

It is seen from the table that α and β-quartz are the extremes in the series of structure efficiency of the samples. α-quartz formed in the low-temperature range (<150°C) has the most efficient structure: the largest mosaic blocks (960Å), the smallest value of lattice microdistortions ($0.1 \cdot 10^{-2}$), its efficiency is $0.1 \cdot 10^{-3}$. β-quartz formed in the high temperature range is characterized by the lowest efficiency of structure ($6.7 \cdot 10^{-3}$), small size of blocks (270Å), and a large value of microdistortions ($1.8 \cdot 10^{-2}$).

The data for the samples № 2–4 are as follows: the efficiency of the structure is $0.8 \cdot 10^{-3}$; $0.9 \cdot 10^{-3}$; $1.2 \cdot 10^{-3}$; the sizes of blocks are 890; 810; 730Å; the values of microdistortions are $0.7 \cdot 10^{-2}$; $0.7 \cdot 10^{-2}$; $0.9 \cdot 10^{-2}$, respectively.

An analysis of the data obtained as a result of initiation of the initial samples shows that the both methods of quartz activation are effective. All the characteristics of the quarts structure change with increasing time of treatment. The character of these changes, however, depends on the method of activation.

First, grinding is accompanied by intensive amorphization of the samples. The increase of the amorphous and quasiamorphous components naturally depends both on the time of grinding and on the initial efficiency of the sample structure. Thus, 30-minute grinding renders α-quartz with the most efficient structure amorphous up to 23%, and β-quartz with the least efficient structure – up to 81%.

Vibroaction practically does not lead to amorphization of the samples. For β-quartz its maximal value reaches only 2.8% with the time of treatment.

Second, changes in the sizes of mosaic blocks and the values of microdistortions of the structure depend on the method of activation of the samples. Intensive development of microdistortions takes place during grinding; especially in the first minutes of treatment. After 15-minute grinding the process of accumulation of microdistortions is slower.

Activation of samples by vibration also deforms their structure, but formation of microdistortions is less intensive. In this method of treatment, their value is on the average by a factor of 2 less than at grinding. Under vibroaction the value of microdistortions is $0.9 \cdot 10^{-2} - 44.2 \cdot 10^{-2}$, and at grinding it naturally increases from $17.2 \cdot 10^{-2}$ to $110.4 \cdot 10^{-2}$.

It should be noted that within this time interval microdistortions under vibration increase, in contrast to grinding, at a constant rate, slightly slowing down towards the end of 30-minute action.

The efficiency of the structure of the initial samples influences the development of microdistortions for the both methods. Thus, after 30-minute grinding the values of microdistortions are $56.8 \cdot 10^{-2}$ for sample № 1 (α-quartz), $74.0 \cdot 10^{-2}$ for sample № 2, $80.0 \cdot 10^{-2}$ for sample № 3, $96.8 \cdot 10^{-2}$ for sample № 4. The value of microdistortions for sample № 5 (β-quartz) is by a factor of two more than that for sample № 1, and constitutes $110.4 \cdot 10^{-2}$. After 30-minute vibroaction microdistortions increase proportionally to the initial efficiency of the structure and are, respectively, $38.6 \cdot 10^{-2}$; $42.1 \cdot 10^{-2}$; $44.2 \cdot 10^{-2}$.

Changes of the mosaic block sizes of the samples depending on the method of their activation are as follows. Under grinding decrease in the block sizes is less than development of microdistortions. Under vibroaction, on the contrary, decrease in the block sizes is larger than deformation of the structure.

The patchiness of the samples is larger under vibroaction, i. e., blocks decrease to a greater extent than under grinding. Thus, after 30-minute treatment their sizes decrease under vibroaction and grinding, respectively, from 960 to 90 and 420Å for sample № 1 (α -quartz), from 890 to 75 and 370 Å for sample № 2, from 810 to 65 and 340 Å for sample № 3, from 730 to 60 and 280Å for sample № 4, from 270 to 55 and 120Å for sample № 5 (β -quartz).

The efficiency of structure under grinding increases with time from $0.1 \cdot 10^{-3}$ to $135.2 \cdot 10^{-3}$ for sample № 1, from $0.8 \cdot 10^{-3}$ to $200.0 \cdot 10^{-3}$ for sample № 2, from $0.9 \cdot 10^{-3}$ to $235.2 \cdot 10^{-3}$ for sample № 3, from $1.2 \cdot 10^{-3}$ to $920 \cdot 10^{-3}$ for sample № 4.

Under vibroaction this characteristic increases with time, but to a lesser degree. Thus, it increases after a 30-minute action only to $35.1 \cdot 10^{-3}$ for sample № 1 , to $51.5 \cdot 10^{-3}$ for sample № 2, to $64.0 \cdot 10^{-3}$ for sample № 3, to $70.2 \cdot 10^{-3}$ for sample № 4. Its value is equal to $803.6 \cdot 10^{-3}$ for sample № 5, i. e., it approaches the efficiency obtained for this sample under grinding.

The efficiency of these samples deserves consideration: activation by grinding causes a several fold (by a factor of 2–4 on the average) increase of this parameter in comparison to vibration. Sample № 5 which was activated for 30 minutes is an exception. For sample № 1 this difference increases by a factor of 20, for sample № 2 it decreases by a factor of 1.1.

Hence, when efficient samples are activated, in the first minutes of action the efficiency increases considerably under grinding, and increase in the time of action of the both methods on samples with low efficiency leads to closer values of this parameter.

In summary it should be noted that the revealed peculiarities, differences and regularities of the behavior of quartz under the action of the both methods make it possible to conclude that vibroaction is a promising and highly effective method of activation of substances. It allows (given the deformation of the structure is small without reconstruction) a considerable increase of the patchiness of samples without rendering them amorphous or contaminating them. This unveils the potential for application of this method.

References

[1] Mirtov Yu.V. et al. Ultramicrostructures of Phosphorites. – Novosibirsk: Nauka, 1987 (in Russian).

[2] Krivoputskaya L.M., Lemina N.M., Gusev G.M. Change in the structure and chemical composition of activated apatite under leaching in various media // Izv. Sib. Otd. AN SSSR. Ser. Khim. Nauk. – 1978. – Vol. 2, № 4. – P. 65–71 (in Russian).

[3] Andreyeva T.A. et al. The influence of a medium and mechanical actions on the destruction of low-temperature quartz // Geochemistry of Pre-Cambrian and Palaeozoic Sediments of Siberia. – Novosibirsk, 1973. – P. 144–160 (in Russian).

[4] Yusupov T.S., Krivoputskaya L.M., Kirillova E.A. On the interrelation between structural changes and solubility of mechanically activated minerals using cassiterite as an example // Physicochemical Investigations of Mechanically Activated Minerals. – ?, 1975. – P. 37–45 (in Russian).

[5] Stokes A.R. A numerical Fourier-analysis method for the corrections of widths and shares of lines on X-ray powder photography // Proc. Phys. Soc. – 1978. – Vol. 61. – P. 384–387.

[6] Zanin Yu.N., Krasilnikova N.A., Mirtov Yu.V. The ultramicrostructure of phosphorites and their genetic interpretation. – Sophija, 1982.

[7] Schoening E.R. Strain and particle size from X-ray line breadth // Acta Crystallogr. – 1965. – Vol. 18, № 5. – P. 975–979.

[8] Warren B.E. X-ray studies of deformed metals // Progress in Metal Physics. – 1957. – 1957. – Vol. 8. – P. 147–200.

[9] Krivoputskaya L.M., Urosov I.I., Kondratskii V.L. Methods of preparation of quartz specimens to obtain reproducible radiospectroscopic and roentgen characteristics // Geologiya i Geofizika. – 1988. – № 8. – P. 72–77 (in Russian).