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COMPARATIVE ESTIMATES OF THE STRENGTH OF DRY AND WET QUARTZ IN GRINDING

V. M. Kornev and L. I. Razvorotneva[1]

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A physicochemical description of the fracture process of wet quartz is given for the case where a proton or atomic hydrogen actively interacts with the broken bonds at the tip of a crack, and hydroxyl groups are collected in the crack because of the low reaction rate, thus fixing the opening of the crack. The decrease in the brittle strength of wet quartz compared to dry quartz is estimated quantitatively with allowance for comparative criteria of brittle strength.

"Absorption of surfactants from the surroundings by a deformable solid has been found long ago to affect markedly the deformation and strength properties of a body" [1, p. 652; 2]. "... Chemically assisted fracture is ubiquitous, but there are no systems understood so well that the preceding ideas have been applied in a quantitative way" [3, p. 117].

In the present paper, the effect of water on the process of grinding quartz in a planetary mill is studied. With the Rebinder effect taken into account in adsorption, we construct a model that describes chemically enhanced fracture. To estimate the brittle strength of cracked dry and wet quartz whose crystalline lattice contains no defects, we use Novozhilov's discrete criterion [4, 5] and a discrete-integral criterion that is proposed in this paper. Quantitative estimates of critical loads that were obtained by means of these criteria coincide completely with the observed intensification of wet-quartz grinding.

1. A Physicochemical Description of the Fracture Process. A tendency toward concentration of excess energy in structural defects is a characteristic feature of crystals exposed to mechanical action. In fracture of brittle bodies, a striking example of which is crystalline quartz (SiO_2), incipient cracks are formed and develop. The occurrence of microcracks and submicrocracks is associated with a local break of a superstressed interatomic bond in the vicinity of the tip of a crack [4, 5].

In the process of crack propagation, a break of chemical bonds occurs and valence-nonsaturated radicals appear. This is supported experimentally by the appearance of paramagnetic centers (PMC) in the fracture of quartz in a mill [6, 7]. The existence of PMC in quartz is due to a mechanically initiated break of the Si—O bond. The best examined PMC in quartz are E' centers, recording of which by the method of electron paramagnetic resonance (EPR) is not difficult [8, pp. 121–129]; E' centers that correspond to $\equiv \mathrm{Si}^{\bullet}$ radicals have long been recorded by the EPR method, although these centers are chemically active. The surface of a crack that appears and has nonsaturated valences is energy-unstable and can relax rapidly. Molecules of a gas, liquid, or solid substance that are in close proximity to the surface of a crack in a crystal body react with E' centers.

We chose water as the surfactant. "Surface phenomena in solids are manifested most strikingly and distinctively in deformation and fracture processes in surface-active media, and a distinguishing feature of theirs is the fact that they are observed during the joint action of the medium and a certain stress state" [9, p. 3]. Griscom [10] analyzed in detail various chemical mechanisms of formation of E' centers. "However, a

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Lavrent'ev Institute of Hydrodynamics, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090. [1]Joint Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 39, No. 1, pp. 138–144, January–February, 1998. Original article submitted February 19, 1996; revision submitted May 7, 1996.

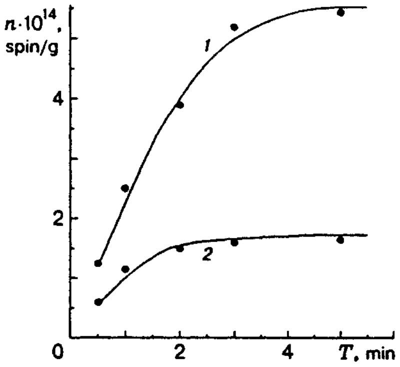

Fig. 1

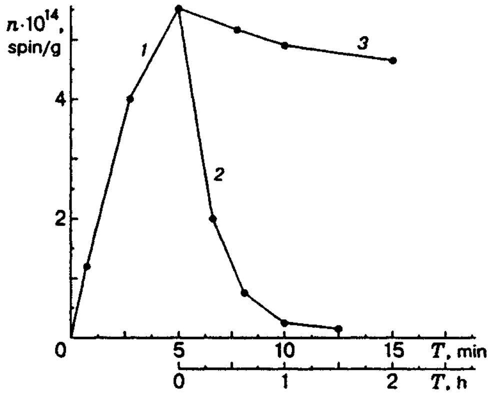

Fig. 2

less exotic mechanism of formation of E' centers, which is not compatible with experiment, can be generated by an instantaneous break of a superstressed Si — O bond" [10, p. 58]:

$$\equiv \mathrm{Si} - - \mathrm{O} - \mathrm{Si} \equiv \longrightarrow \equiv \mathrm{Si} \cdot + \cdot \mathrm{O} - \mathrm{Si} \equiv .$$

It is known [11] that the strength of wet quartz is an order of magnitude less than the strength of dry quartz, and the limiting deformations of wet quartz are larger than those of dry quartz. "Griggs and Blasik postulated that the weakening effect is caused by hydrolysis of high-strength Si — O — Si bonds by water molecules in accordance with the reaction

$$\mathrm{Si} - \mathrm{O} - \mathrm{Si} + \mathrm{H_2O} \longrightarrow \mathrm{Si} - \mathrm{OH} - - - \mathrm{HO} - \mathrm{Si},$$

where the broken line between hydrogen atoms refers to a weakened bond [11, p. 1810].

We performed a comparative study of fracture of dry and wet quartz in a mill [in the latter case, 4–8% (by weight) water was added]. Figure 1 shows the kinetics of PMC accumulation during fracture of quartz $n = n(t)$, where n is the number of PMC per gram of the substance (in spin/g); curves 1 and 2 correspond to grinding of dry quartz and quartz to which 8% water was added. The decrease in the number of PMC in the presence of water can be caused by a chemical interaction of E' centers with water molecules (see the key reaction (19) in [10, p. 61]). When water molecules interact with a "fresh" crack surface, PMC are intensely destroyed (Fig. 2).

Figure 2 shows the change in the number of PMC upon addition of water to freshly ground quartz. Curve 1 illustrates PMC accumulation in dry quartz for the first 5 min, and curves 2 and 3 describe the change in the number of PMC upon addition of 8% water and without water; we note that the time scales for these curves are different: the time is given in minutes for curve 2 and in hours for curve 3. The weak change in the number of PMC in open air is caused by interaction of the freshly formed surface of a crack and the residual amount of water vapor in air.

We analyze the interaction between water molecules and the fractured surface of crystalline quartz using infrared (IR) spectroscopy. The appearance of peaks in the IR spectra corresponds to deformed and dissociated bonds in H_2O molecules adsorbed by the surface of the fractured crystalline quartz. A crucial role in the chemical interactions belongs to hydrogen (see reactions (7)–(10), (12), (13), and (16) in [10, p. 58–61]). In these reactions, atomic hydrogen H^0, which possesses a high reactivity, can appear. The rates of these reactions are much higher than the rates of reactions in which OH^- groups are involved. The remaining OH^- groups fill the crack.

We shall show that OH^- groups are fairly mobile. If freshly ground sample of wet, initial, or dried (dehydrated at 105°C for 4 h) quartz is given an amount of water equal in volume, the acidity pH of the resulting solutions is at the level of 7.7, 6.5, and 5.7 after a transient regime that lasts approximately 1 h. We recall that the solution reaction is neutral at $pH \cong 7$, alkaline (an excess of OH^- ions) at $pH > 7$, and acid (an excess of H^+ ions) at $pH < 7$.

Conclusions: (1) interacting with radicals, the more mobile proton H^+ or atomic hydrogen H^0 hinders relaxation of a broken Si — O bond, thus stabilizing the break;

(2) OH^- groups also interact with radicals; the rate of the latter reaction is lower than in the presence of H^+ or H^0, and, therefore, OH^- groups are accumulated in the vicinity of the tip of a crack and the group nearest to the crack tip serves as a kind of wedge, owing to the dimensional factor.

These conclusions on the action of a surfactant (water) on the fracture process have a probabilistic character from a chemical point of view, because they emphasize the most characteristic features of the reactions, without indicating precisely what chemical reactions occur.

2. Brittle-Fracture Criteria That Take into Account the Effect of a Surfactant at the Tip of a Crack. To obtain comparative estimates of the strength of dry and wet crystalline quartz, we consider two variants of the problem of stretching a plane with a sharp-tipped crack (planar deformation is studied):

(1) in the absence of a surfactant inside the crack,

(2) in the presence of a surfactant (water) inside the crack.

It is worth noting that consideration of planar problems for real "quasiplanar and sharp" cracks in crystalline quartz is a rather rough approximation [12, pp. 23–24 and 406–412]. In what follows, we consider normal-fracture cracks.

In the first case, we use Novozhilov's modified discrete criterion of brittle strength [5, 13]. In the absence of a surfactant in close proximity to the crack tip, interatomic cohesive forces, which are defined by one or another potential, act. The critical lengths of normal-fracture cracks, when interatomic interactions (in a quartz crystal as well) are described by one of the Morse or Lennard-Jones potentials, were calculated by Andreev et al. [13].

In the second case, for normal-fracture cracks we consider the fracture model for crystalline quartz. Figure 3 depicts schematically the left tip of a crack with acting (row 0) and broken (rows 1–3) Si — O bonds; Si and O atoms in the plane of the drawing in rows 1–3 are marked by plus and minus signs, atoms in row 0, which are not seen in the plane of the drawing, are indicated by dashed lines, and a molecule of dissociated water is represented by H^+ and OH^- ions. The small-sized mobile proton H^+ or atomic hydrogen H^0 interacts with radicals (see the corresponding reactions in [10]), while the OH^- ion, which has a finite size relative to the crystal lattice of quartz, is trapped at the crack tip. The OH^- ion does not allow the crack to close after the load is removed. The distance between the nearest atoms in crystalline quartz is $r_{\text{Si–O}} = r_e = 1.84 \cdot 10^{-10}$ m, and the size of the OH^- ion is $r_{OH^-} = 2.16 \cdot 10^{-10}$ m. The size of the H^+ ion is estimated as $r_{H^+} \ll 0.53 \cdot 10^{-10}$ m, since the size of the hydrogen atom is $r_H = 0.53 \cdot 10^{-10}$ m. Most probably, the OH^- ion either is at the site indicated in Fig. 3 or occupies one of the nearest vacancies in the quartz crystal lattice. The size of these vacancies is roughly $2r_e$. The proposed model of the process does not agree with the diagram of chemically assisted fracture given in Fig. 8 in [3, p. 115]. In the second case, we use the discrete-integral criterion of brittle strength [14] for cracks of length $2l$:

$$\frac{1}{r_e} \int_0^{r_e} \sigma_y(x, 0)\, dx \leqslant \sigma_m, \tag{2.1}$$

where σ_y is the normal stresses at the tip of a normal-fracture crack, Oxy is a rectangular coordinate system, r_e is the spacing between the atomic centers, and σ_m is the ideal strength [15]. In relation (2.1), use is made of the classical representation of the solution, in which σ_y has an integrable singularity at zero.

We consider crack propagation in the proposed model in the presence of a surfactant. As the load grows, a successive break of the superstressed bond occurs in row 0 (Fig. 3); after that, the surfactant begins to work: the H^+ ion or the hydrogen atom H^0 blocks the broken bond, and the OH^- ion fixes a new position of the crack tip even after the load is removed, owing to the dimensional factor. During the next loading, the process repeats, but for the next row of atoms with number −1.

We shall use the solution for stresses in extension of a sharp-tipped crack $y = 0$ in the form of a sum of regular and singular constituents, the latter containing the stress-intensity coefficient as a factor. After straightforward manipulations, we obtain the critical stress-intensity coefficient K_I^* and the critical length $2l^*$

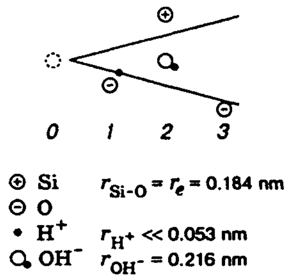

Fig. 3

TABLE 1

σ_m/σ_∞	$2l^*/r_e$		
10	81	530	680
20	361	2120	2700
100	9801	53110	67600

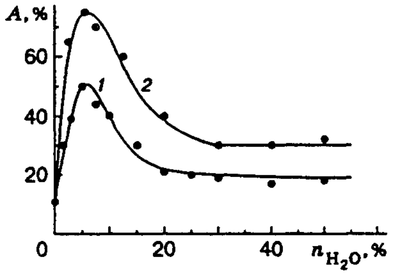

Fig. 4

TABLE 2

σ_m/σ_∞	$\sigma_\infty/\sigma_\infty^*$	
10	2.40	2.70
20	2.35	2.65
100	2.31	2.61

of a sharp crack, which depend on the given level of loading at infinity σ_∞^*:

$$\frac{K_I^*}{\sigma_\infty^*} = \left(\frac{\sigma_m}{\sigma_\infty^*} - 1\right)\left(\frac{\pi r_e}{2}\right)^{1/2}, \quad \frac{2l^*}{r_e} = \left(\frac{\sigma_m}{\sigma_\infty^*} - 1\right)^2. \tag{2.2}$$

Table 1 lists critical lengths according to relations (2.2) and Novozhilov's modified discrete criterion. The first column refers to values of the level of loading σ_m/σ_∞, the second indicates critical lengths of cracks according to the discrete-integral criterion of brittle strength [14], and the third and forth columns refer to corresponding values obtained according to Novozhilov's modified discrete criterion [13] for the Morse and Lennard-Jones potentials, respectively. The critical lengths of cracks for wet and dry quartz (the second, third, and fourth columns) differ by a factor of 5–8, depending on the level of loading σ_m/σ_∞ and the choice of the potential. The results obtained for the discrete-integral criterion of brittle strength are not connected with a concrete form of the potential of interatomic interaction if the ideal strength σ_m is considered to be prescribed.

We compare the critical stresses σ_∞ and σ_∞^* according to Novozhilov's modified discrete criterion of brittle strength and the discrete-integral criterion, respectively, for fixed lengths of the cracks. We take the lengths of these cracks from Table 1 (third and fourth columns).

Calculation results are given in Table 2, where the second and third columns correspond to the Morse and Lennard-Jones potentials. The critical load $\sigma_\infty/\sigma_\infty^*$ of wet quartz decreases 2.5-fold on average compared with dry quartz. The surfactant "works" more efficiently the shorter the crack. Thus, introduction of a small amount of water into crystalline quartz intensifies the grinding process.

Remark 1. We note that the discussion was devoted to fairly coarse particles whose linear dimensions differ by one or two orders of magnitude from the critical lengths of the cracks in Table 1.

Remark 2. The critical load $\sigma_\infty/\sigma_\infty^*$ of wet quartz decreases 4–5-fold compared with dry quartz if there is a cluster of 3–4 vacancies in front of the crack and only one interatomic bond acts at the crack tip [14] Formation of such clusters is possible in dynamic grinding of quartz that initially has an ideal crystal structure.

3. Discussion of Results. A new free surface is formed in grinding dry or wet quarts. This is the case at the crack sides as well. The surface layers of a crystalline substance are chemically active and intense sorption of surfactant particles (water in our case) is possible on these layers. Water molecules come to a crack tip in the neighborhood of which there are superstressed interatomic bonds (Novozhilov's model [4]). After that, dissociated molecules react with the corresponding ions (see Sec. 1 and Fig. 3). As a result of this adsorption reaction, superstressed bonds at the crack tip break; thus, we obtain a different loading pattern for a sharp crack and now it is reasonable to use the discrete-integral criterion of brittle strength [14].

We note that, usually, the OH^- ion hinders restoration of broken bonds at the crack tip. If the load on a crystalline-quartz particle with a surface crack did not decrease significantly during grinding, the crack enlarges owing to its propagation. A stopped crack has superstressed interatomic bonds at the tip. These bonds "await" the next surfactant molecules, and after they arrive, the process repeats.

Thus, when a surfactant (water) is added, grinding of crystalline quartz intensifies. Experimental data show that the amount of quartz that fractures for the same time is much larger in grinding with small additions of water than the amount of dry quartz in dry air or very wet quartz. Figure 4 shows experimental dependences of the degree of structural fracture in quartz A on the content of water in the sample n (n in percent of the weight of the sample). Curves 1 and 2 correspond to grinding for 5 and 10 min. For a perfect crystal, $A = 0$. The initial quartz had $A = 10\%$ before grinding. Maximum intensification of the fracture process is observed for low surfactant (water) concentrations; we note that $n = 5$–6%. For high concentrations of water ($n \geqslant 10\%$), the surfaces of the particles being ground are covered by several monolayers of water molecules. These interlayers serve as a kind of buffer weakening impacts in particle collisions. Even for excess water ($n \geqslant 20\%$), accumulation of structural fractures intensifies somewhat compared with the same process for dry quartz.

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