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Numerical simulation of a new mechanochemical method for the formation of amorphous solids and nanocomposites

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Numerical simulation of the mechanism of amorphous sulfur formation and the chemical interaction of sulfur with abrasives and steel material of milling tools in an AGO-2 mill is carried out.

The modeling of physicochemical phenomena in mechanochemical reactors[1–6] and the processing of geological and human-made materials by mechanical activation methods[7–11] are of considerable interest. As a rule, the role of milling tools in mechanical activation processes reduces to the possibility of contaminating the products of mechanical activation.[5,12–14]

This article is aimed at a complex elucidation of the effect exerted by milling tools materials and abrasives (glass and quartz glass) on the mechanical activation mechanism of α-sulfur in a ball planetary mill with steel accessories. The objects of investigation are chosen based on the unknown mechanism of the participation of crystalline sulfur in mechanical activation reactions[15–18] and the high abrasive ability of glasses. Because of this it was necessary to choose such a system for mechanical activation that would contain, along with sulfur, an inert, desirably amorphous, component in order to simplify the interpretation of the results of X-ray analysis. Glasses, which are fully amorphous materials, are suitable for this purpose. The use of these inert additives can help proving the polymerization of sulfur during mechanical activation. The reaction of sulfur with nano-sized particles of ‘abrasive’ iron[11] can be performed in a mode of combustion.[6]

The accumulation of sulfur at the enterprises of the petroleum and gas complex puts also a problem of recycling. Chalcogenides are synthesised from elements under heating. However, the homogeneity and morphology of the final products are far from being perfect; this depends on many factors, in particular, on the size and surface state of initial reagents. A mechanochemical reactor eliminates these shortcomings. Iron sulfides, especially nanosized ones,[16] are used in various areas.

Studies of the metal–sulfur interaction in various mechanochemical reactors[7,15–18] showed that the process virtually did not begin for a fairly long time τ of mechanical activation. The subsequent reaction developed explosively ($\tau = \tau^*$, τ^* is the induction period) or gradually to produce corresponding metal sulfides. According to the most plausible explanation of the considerable delay before reaction initiation, only sulfur was activated (experienced deep structural and chemical changes) at the first stage of mechanical activation, and the metal–sulfur system underwent a gradual transition to a qualitatively different state caused by sulfur amorphisation (the α-sulfur reflections rapidly disappeared) and then melting and polymerization (Figure 1). The polymerization of sulfur (polymerization onset temperature $T_p = 433$ K) resulted in an anomalous increase in its viscosity.[19–21]

The estimates given below were obtained for abrasive-reactive wear of milling tools and sulfur, *cf.* ref. 11. Mechanical activation was performed in an AGO-2 water-cooled two-drum ball planetary mill with the following parameters: steel ball radius $R = 0.2$ cm; number of balls $N \approx 400$; balls surface area $\Pi_b = 4\pi R^2 N \approx 200$ cm^2; drum cylinder height $h = 4.6$ cm, radius $l_2 = 3.1$ cm, volume $V_d = 140$ cm^3, and ‘active’ surface area $\Pi_d = 2\pi l_2 h \approx 90$ cm^2; $\Pi = \Pi_d + \Pi_b$; centrifugal carrier radius $l_1 = 5.3$ cm, rotation frequency $\omega_1 = 12$ s^{-1}, and opposite drum-rotation number $\omega_2 = 29$ s^{-1}. The mill has the following characteristics:[11] geometrical factor $l = l_1/l_2 = 1.7$; kinematic factor $k = \omega_2/\omega_1 = -2.4$; ball breakaway angle $\cos\varphi = (1 + k)/l = 0.82$. The mechanical activation time τ was 600–10800 s.

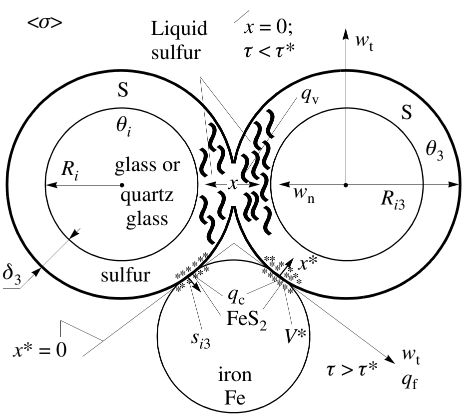

Figure 1 Scheme of mechanical activation stages of the S–abrasive ($i = 1, 2$)–Fe system in the field of dynamic stress $\langle\sigma\rangle$.

Weighed samples ($m_i = 3$ g) of crushed abrasives (glass – microscope slides, $i = 1$; quartz glass – tube, $i = 2$) were mixed with ultra-high-purity α-sulfur ($m_3 = 0.3$–2.5 g, $j = 3$). The samples were ground and homogenised in a Fritsch Pulverisette mill equipped with agate accessories (mortar, 9.2 cm in diameter, and ball, 7.1 cm). The R_{0i} values were obtained from the optical microscopy of the original homogenised samples: $R_{01} \approx 0.020$ and $R_{02} \approx 0.017$ cm. The sample mass m^* required for the formation of a lined monolayer with a thickness equal to a unit diameter of the starting abrasive particles under treatment must amount to $m^* \approx \pi(\rho_3 + \rho_i)R_{0i}(\Pi_d + \Pi_{bi})/6$.[21]

The obtained samples and products of mechanical activation were investigated by standard X-ray powder analysis. Figure 2 shows the results of X-ray analysis of a quartz-containing

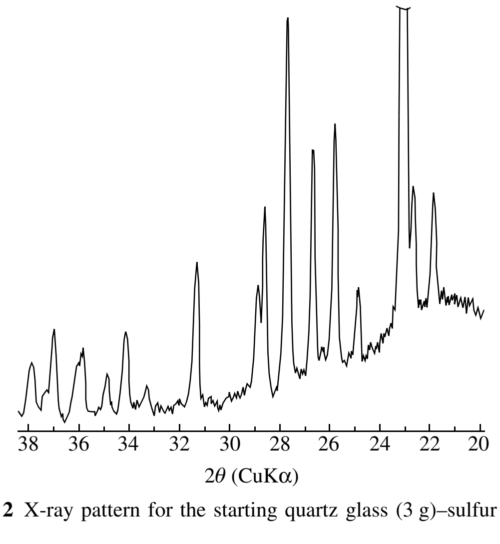

Figure 2 X-ray pattern for the starting quartz glass (3 g)–sulfur (0.53 g) system.

sample: only orthorhombic crystals of sulfur were observed (*cf.* with PDF 83-2285). Similar results were obtained for the initial glass-containing samples. Experiments on the mechanical activation of the prepared samples and pure sulfur crystals alone ($m_3 = 2$ g) were performed in an AGO-2 mill. The X-ray analysis of pure sulfur crystals (mechanical activation for a period of time τ up to 10800 s) showed that sulfur did not experience any restructuring (Figure 2): no widening or changes in the relative intensities of the reflexes were observed (except for the absence of the halo associated with the presence of amorphous glass particles).

The situation changes (Figure 3) when sulfur is processed in the presence of inert glass particles. Structural changes in sulfur take place when the required *t–P–T* conditions[2] are attained at the impact-friction contact of the sulfur-lined glass particles. Although the hardness of glass is somewhat higher than that of steel (Table 1), the abrasive wear of the steel fittings is insignificant. In addition, the temperature at the impact-friction contact of the milling bodies and the glass particle cannot exceed the melting (or softening) temperature of sulfur (or glass),[22] a factor unfavourable for the synthesis of iron sulfides during the given time of mechanical activation. Note that the synthesis of iron sulfides through the mechanical alloying of iron and sulfur powders takes tens and hundreds of hours of mechanical activation.[15,16]

Dramatic changes take place during the mechanical activation of the samples containing quartz glass. Figure 4 shows the formation of pyrite (FeS_2, PDF 71-2219). The hardness of quartz glass is much higher than that of steel. The softening temperature of quartz glass is higher than that of glass or steel melting. In this case, the transition of sulfur into the amorphous state and its chemical reaction with iron particles formed in large amounts during the abrasive wear of the steel fittings[11] proceed simultaneously and produce pyrite in the regime of burning (*cf.* refs. 17, 18 and 21).

Absolute (and relative) quantitative characteristics of wear of steel milling tools (drum *d* and balls *b*) after mechanical activation based on the weighing method for the test systems are given below (see also Table 1).

For mechanical activation time of 8100 s and an abrasive (3 g) and sulfur (1.6 g) system:

(*a*) glass abrasive, *d* 0.03 g (0.0037%), *b* 0.043 g (0.046%), and total wear of 0.073 g;

(*b*) quartz glass, *d* 0.21 g (0.028%), *b* 0.47 g (0.49%), and total wear of 0.68 g;

(*c*) quartz glass only (3 g), *d* 0.80 g (0.098%), *b* 0.67 g (0.64%), and total wear of 1.47 g;

(*d*) α-quartz only, *d* 0.36 g (0.044%), *b* 0.41 g (0.42%), and total wear of 0.77 g.

The X-ray data yield the size of crystallites and make it possible to estimate the degree of distortion of the structure of the pyrite (and the iron particles produced).[5,16] The parameters of the fine crystalline structure were calculated from the half-width of the diffraction peaks (220 and 440) for pyrite.[7] The instrumental widening was determined from the line profiles of crystalline pyrite. The mean size of the pyrite crystallites was 24 nm (for iron particles, ~10 nm, see also ref. 11). The degree of distortions was ~1%. Similar results were obtained after a 110 h mechanical activation of Fe and S powders.[16] If we admit that the nanosized particles produced by the abrasive wear of the milling tools are entirely expended in the generation of the pyrite by the reaction $Fe + 2S = FeS_2$, we would have the following composites after the mechanical activation for the mechanical activation quartz glass–sulfur system: FeS_2 (1.46 g)–S (0.82 g)–SiO_2 (3 g). Absence of reflexes of superfluous sulfur (0.82 g) in the described sample (Figure 4) is the unequivocal proof for the formation of amorphous sulfur.

Thus, the mechanical activation of a quartz glass–sulfur mixture (other chalcogens can also be used) in a planetary mill equipped with steel fittings yields nanocomposites composed of pyrite and an inert quartz glass matrix. The process takes a period of time τ one or two orders of magnitude shorter than that required for the traditional mechanical activation of iron and sulfur powders. It is possible to use the scrap of other metals as a material for milling tools in order to obtain the corresponding sulfides. This method may find applications in the production of chalcogenide glasses and in the stripping and processing of various raw materials.

The initial assumptions of the calculation model were as follows (Figure 1 and Table 1):

(*a*) At the initial time moment of treating the mixture, uniform self-lining of milling tools (balls and walls) by a batch mixture layer occurred. The thickness[2,11,21] of the lining was calculated as $\delta_i = (\rho_3 m_i + \rho_i m_3)/\rho_3\rho_i(\Pi_\mathrm{d} + \Pi_{\mathrm{b}i})(1 - p) \approx 4(\rho_3 m_i + \rho_i m_3)/\pi\rho_3\rho_i(\Pi_\mathrm{d} + \Pi_{\mathrm{b}i})$, where $p \approx 1 - \pi/4$ is the porosity of the lining layer set equal to that for a close packing of quasi-spherical particles.

(*b*) At the initial moment of mechanical activation, abrasive particles were ground to some radius[2,23] $R_i(i = 2) \approx 3\times10^{-5}$ cm; the resulting total surface area of the abrasive ($m = 3$ g) was $\Pi_\mathrm{ab} = 3m/\rho_i R_i \approx 9/\rho_i R_i \approx 130000$ cm^2. Sulfur as the most plastic component covered the surface of metal particles by a continuous layer, whose thickness was calculated as $\delta_3 = m_3/\rho_3(\Pi_\mathrm{d} + \Pi_{\mathrm{b}i} + \Pi_\mathrm{ab}) \approx m_3/\rho_3\Pi_\mathrm{ab} \approx 0.6\times10^{-5}$ cm.

(*c*) The δ_3 value was fairly large, and, in calculating impact interaction parameters for lined milling tools, the compliances of the balls and the wall were set equal[2,24] to the compliance of the lining layer, $\underline{\theta} = (\theta_i + \theta_3)/2$.

(*d*) The $R_i/\delta_3 \approx 5$ value was fairly small. For this reason, the *t* (time)–σ (stress)–*T* (temperature) conditions at the impact-friction contact of sulfur-coated abrasive particles were determined using the normal parameters calculated for collisions between lined abrasive particles with compliance θ_3 of the sulfur film, density $\underline{\rho} = (\rho_i + \rho_3)/2$, and total radius $R_{i3} = R_i + \delta_3 \approx \approx 3.6\times10^{-5}$ cm, and the tangential parameters were determined from the viscous properties of the sulfur film[19] μ_3 with the largest possible thickness $2\delta_3 - \varepsilon_3$, where ε_3 is the summed local deformation of colliding particles.[2]

I also attempted to determine the abrasive and abrasive-reactive wear and, thus, compare the abrasive (glasses, α-SiO_2) and abrasive-reactive (glass + sulfur) characteristics as applied to the wear of the steel milling tools, and the mechanism for the formation amorphous sulfur.

The relative collision velocity[2–4] W of the milling tools in an AGO-2 mill is equal to $|W| = 2\pi\omega_1 l_2[(k + 1)^2 + l^2 - 2l(k - 1)\cos\varphi + + (l + 1)^2]^{0.5} \approx 1100$ cm s^{-1}. The normal component is $W_\mathrm{n} =$

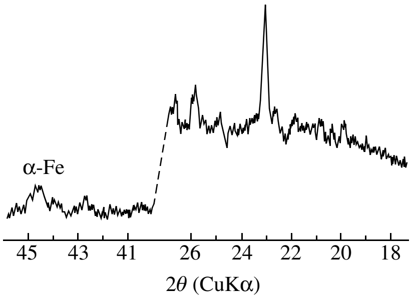

Figure 3 X-ray pattern for the glass (3 g)–sulfur (0.4 g) system mechanical activation for 8100 s.

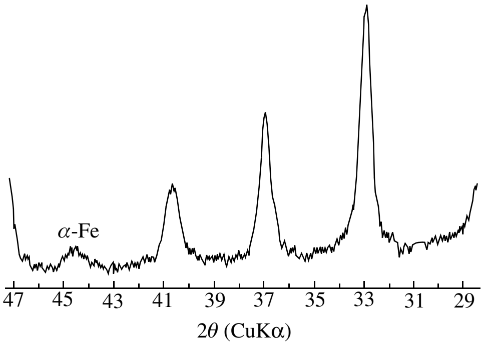

Figure 4 X-ray pattern for the quartz glass (3 g)–sulfur (1.6 g) system mechanical activation for 8100 s.

Table 1 Physicochemical properties[19,24,25] of components for the simulation mechanism of the formation of amorphous sulfur and the results of numerical calculations of the abrasive-reactive wear of the material of steel milling tools.

Properties	Slide glass, $i = 1$	Sulfur, $j = 3$	Quartz glass, $i = 2$	Steel	α-Quartz, $j = 5$	Comments, abrasive alone
Hardness/Mohs	~5	~2	~6	~4.5	7	R_{0j} (SiO$_2$ glass) 0.019 cm;[a]
$E/10^{12}$ dyn cm^{-2}	0.560	0.180	0.732	2.232	0.956	R_{0j}(α-SiO$_2$) 0.022 cm;[b]
ν	0.200	0.342	0.172	0.285	0.073	δ_j $(j = 4, 5) = 4m_j/\pi\rho_j\Pi$;[c]
$\theta/10^{-12}$ cm^2 dyn^{-1}	6.857	19.62	5.303	1.647	4.162	$B_j = \xi_j{<}\sigma_{tj}{>}W_t(c\lambda\rho c_j\lambda_j\rho_j)^{-0.25}$
ρ/g cm^{-3}	2.361	2.070	2.203	7.860	2.650	and $\xi_j = \xi_i$;[d]
$\lambda/10^6$ erg cm^{-1} K^{-1} s^{-1}	0.09^{373}	0.021	0.192^{773}	4.7^{773}	0.365^{673}	
$c/10^6$ erg g^{-1} K^{-1}	6.75^{373}	10^{392}	10.0^{873}	6.6^{773}	16.23^{773}	
$a = \lambda\rho^{-1}c^{-1}$/cm^2 s^{-1}	0.0056	0.001	0.0087	0.091	0.0085	
T_m/K (softening)	(~700)	392.0	(~1900)	1811	1883	
Calculated values for abrasive wear	—	—	—	Quartz glass alone, $j = 4$	—	—
Nm^{-1}/g^{-1}	424/4.6	—	385/4.6	401/3	398/3	$m_4 = m_5 = 3$ g;
m^*/g	9.88	—	7.35	8.83[a]	12.2[b]	$m_j^* \approx \pi\rho_j R_{0j}\Pi/3$ and $R_j = R_i$
$\delta/10^{-4}$ cm	122	0.06	141	86.1[c]	72.1[c]	Hertz's theory
$t_i/10^{-6}$ s	16.9	—	16.6	12.5	11.6	${<}\sigma_{tj}{>} = 2\sigma_{nj}(W_t/W_n)^{0.4}/3$;
$\sigma_n/10^{10}$ dyn cm^{-2}	1.79	—	1.87	3.29	3.80	$(W_t/W_n)^{0.4} = 0.87$;
${<}\sigma_t{>}/10^{10}$ dyn cm^{-2}	1.035	—	1.08	1.90	2.20	ε is only the steel ball local
$B/10^5$ cm^2 K s$^{0.5}$ erg^{-1}	9.6	—	8.8	11.6[d]	6.4[d]	deformation by Hertz's theory;[2]
T/K	2600	—	2400	2700	1600	$t_j = t_i$;
$t_i + t'_{mi} - t_{mi}/10^{-6}$ s	$t_1 = 16.9$	—	26.3	22.9	$t_5 = 12.2$	$M_j > M_i$
$\varepsilon/10^{-4}$ cm	5.44	—	5.62	8.59	9.57	
$s/10^{-4}$ cm^2	30.5	—	29.8	22.5	20.9	
$\exp[1 - (T_m/T^*)]$	0.086		0.33	1	0.87	
$m_i\rho_i RN_i/m_i^*\rho V$	0.0795		0.101	0.0545	0.0471	
τ/s	8100	—	8100	8100	8100	
M/g (theory)	~0.08	—	~0.6	~1.3	~0.6	
M/g (test)	0.073	—	0.68	1.47	0.77	

$= W\cos\varphi \approx 900$ cm s^{-1} (determines the conditions for impact interaction abrasive particles in the layer). The tangential component is $W_t = W\sin\varphi \approx 630$ cm s^{-1} (determines the conditions for abrasive wear and mechanochemical processes on the friction surface of contacts of milling tools with abrasive particles).[11] According to $W_n > W_t$, abrasion is less preferable than impact for the mill AGO-2. The values of hardness, density (ρ), Poisson's ratio (ν), Yuong's modulus (E), compliance $\theta = 4(1 - \nu^2)/E$, specific heat capacity (c), heat conductance (λ), temperature conductance $a = \lambda/\rho c$ and melting temperature (T_m) for steel and mechanical activation materials are presented in Table 1.

Let us determine the $t - \sigma - T$ conditions at the impact–friction contact of the milling tools with the lined layer:[2] the interaction time $t_i \approx 3.1R\rho^{0.4}(\theta + \underline{\theta})^{0.4}W_n^{-0.2}$; normal $\sigma_{ni} \approx$ $\approx 1.7\rho^{0.2}(\theta + \underline{\theta})^{-0.8}W_n^{0.4}$, and tangential $\sigma_{ti} = \sigma_{ni}(W_t/W_n)^{0.4}$ stresses; and maximum temperature pulse $\Delta T(0,t_i) = B_i t_i^{0.5}\mathrm{iErfc}[0]$, where $B_i = \xi_i{<}\sigma_{ti}{>}W_t(c\lambda\rho\underline{c}\underline{\lambda}\underline{\rho})^{-0.25}$, ${<}\sigma_{ti}{>} = 2\sigma_{ti}/3$, and $\xi_i \approx$ $\approx (0.8 + 0.3)/2 = 0.55$ is the dynamic friction coefficient.[2,26] Characteristics of steel are given without indexes. The expression for $\Delta T(y,t)$ in the vicinity y of the contact of the milling tools with the lined layer surface will be as follows: $\Delta T(y,t) =$ $= B_i\{t^{0.5}\mathrm{iErfc}[x/2(\underline{a}t)^{0.5}] - (t - t_i)^{0.5}\mathrm{iErfc}[y/2\underline{a}^{0.5}(t - t_i)^{0.5}]\}$; $\mathrm{iErfc}(z)$ is the tabulated integral of errors[27] and $\mathrm{iErfc}(0) = 0.5642$; $\underline{c} =$ $(c_i c_3)^{0.5}$, $\underline{\lambda} = (\lambda_i\lambda_3)^{0.5}$, $\underline{a} = \underline{\lambda}/\underline{c}\underline{\rho}$. Table 1 presents the values $T_i =$ $= T_0 + \Delta T(0,t_i)$ for the systems studied (also at $j = 4, 5$), where $T_0 \approx 350$ K is the background temperature in a water-cooled AGO-2 mill.[11] The T_i value (except for α-quartz, $j = 4$) exceeds the iron melting T_m and slide glass softening T_{m1} temperatures. It is known,[22,28] however, that T cannot exceed the T_m of the most fusible or softening component (steel[11] or slide glass in our case). Using the expression $\Delta T_m = \Delta T(y = 0, t = t_m) =$ $= \Delta T(y = 0, t = t'_m) = T_m - T_0$, one can calculate the lifetime $t'_m - t_m$ of the melted zone on the contact surface of steel milling tools and quartz glass ($i = 2$, $j = 4$), where $t_{mi,j} =$ $= [(T_m - T_0)/B_{i,j}\mathrm{iErfc}(0)]^2$ and $t'_m = (t_{i,j} + t_m)^2/4t_{mi,j}$ are roots in the equation for $\Delta T(0,t_{i,j})$. It is also known[22] that the melted zone thickness $x = x_m$ is close to the deformation zone of the steel milling ball[2] $\varepsilon \approx 1.0R\rho^{0.4}\theta(\theta + \underline{\theta})^{-0.6}W_n^{0.8}$.

In the εs_i volume, where $s_i \approx 3.1R^2\rho^{0.4}(\theta + \underline{\theta})^{0.4}W_n^{0.8}$ is the impact area of the contact between the lined steel milling tools and the lined layer of the mechanical activation particles, the milling tools and treated substance are subjected to various short-term ($t \sim t_i \sim 10^{-5}$ s) physicochemical processes, including melting-crystallization, abrasive wear, and chemical reactions. The ε value can be used to estimate the size of rare split-iron particles, while iron crystallites generated during the rapid quenching (~10^5 K s^{-1}) of the melted zone[22] yield the size of individual iron nanoparticles in the course of the abrasive wear.

The expression for the mass M_i of the abraded steel material of the mechanochemical reactor at the impact-friction contact between the milling tools and the substance under treatment may be derived from the simple physical argument:[2,11]

$$M_i \approx {<}\sigma_{ti}{>}t_i(t_i + t'_{mi} - t_{mi})\varepsilon s_i g\omega_2\tau\exp[1 - (T_m/T^*)](m_i\rho_i RN_i/m_i^*\rho V), \quad (1)$$

where $g \approx 10$ is the coordination number of the balls (the impact-friction interaction also taking place between balls[2]); $\exp[1 - (T_m/T^*)]$ is the relative factor of abrasive wear, $T^* = T_m$ for the quartz glass alone system, $T^* = T_5$ for α-quartz system; $T^* = (T_{mi}T_{m3})^{0.5}$ for the glass-sulfur systems, where $T_{m1} \approx$ ≈ 700 K and $T_{m2} \approx 1900$ K are the slide glass and quartz glass softening temperatures; and the value $(m_i\rho_i RN_i/m_i^*\rho\mathrm{V})^{-1}$ determines the 'effective' wear surface of the material milling tools at mechanical activation and, somewhat, takes into account the entry conditions of mechanical activation by the introduction of the parameter[17,18,21] m/m^*. As can be seen in Table 1, expression (1) adequately reflects the qualitative and quantitative relationships between the abrasive properties of the mechanical activation samples. Note that experiments and calculations give higher abrasive characteristics for quartz glass than for α-quartz.

When metal–sulfur mixtures are mechanical activated, sulfur melting (T_{m3}) allows dry friction heat to be ignored. At the same time, the heat effects of formation of metal sulfides are substantial. For instance, $\Delta_r H^0 = -174$ kJ mol^{-1} for the Fe + 2S = = FeS$_2$ reaction. We selected this reaction as a model reaction for studying the role played by reagent and abrasive (quartz glass only, $i = 2$) properties, and $\Delta_r H$ values in estimating 'hot spot' temperatures[2,28,29] that can initiate explosive combustion or self-propagating high-temperature synthesis (MSR[6]), which accompany mechanical activation of metal–sulfur mixtures.[17,18,21]

Consider the distance x and time t distribution of temperature pulse $\Delta T(x,t)$ in the vicinity of impact-friction contact of an abrasive particles coated by sulfur. Let there be a source of heat with density $2q$, symmetrical with respect to the slip plane, and let this source include heating ($t \leq t^*$) and cooling ($t > t^*$, in the solution to the heat equation,[27] a negative source with density 2q acts) branches.[22] The first component of the total $2q$ density is the $2q_\mathrm{f}$ value, which appears because of dry friction.[2,29] For the first stage of mechanical activation of the S–quartz glass–Fe system, we may write[2]

$$\Delta T(x,t) = 2q_\mathrm{f}(\lambda_3 c_3 \rho_3)^{-0.5}\{t^{0.5}\mathrm{iErfc}[x/2(a_3 t)^{0.5}] - (t - t_3)^{0.5}\mathrm{iErfc}[x/2[a_3(t - t_3)]^{0.5}\}; \quad (2)$$

$$\Delta T(0,t) = 0.5642B_3[t^{0.5} - (t - t_3)^{0.5}], \quad (2a)$$

where $B_3 = \xi_3 {<}\sigma_{\mathrm{t}3}{>} w_\mathrm{t}(\lambda_3 c_3 \rho_3)^{-0.5} \approx 4.1\times10^7$ cm^2 K s$^{0.5}$ erg^{-1} at the temperature $T_{\mathrm{m}3}$ of the sulfur film fusion. The time of impact-friction interaction of particles t_3 and other parameters of mechanical activation of the system (see below) will be estimated using the equations given in Table 4 (ref. 2): $t_3 = 4.6R_{\mathrm{i}3}\rho_\mathrm{i}^{0.5}\theta_3^{0.4}\rho^{-0.1}W_\mathrm{n}^{-0.2} \approx 2.6\times10^{-9}$ s. Consider the density of the heat source, $2q_\mathrm{f}$, in more detail.

For impact-friction interactions of sulfur-coated quartz glass particles ($i = 2$), we have[2]

$$2q_\mathrm{f} = \xi_3 {<}\sigma_{\mathrm{t}3}{>} w_\mathrm{t} \approx 0.18\xi_3\rho_3^{-0.5}\theta_3^{-1.08}\rho^{0.42}W_\mathrm{n}^{0.84} = 2.7\times10^{13}\ \mathrm{erg\ cm^{-2}\ s^{-1}} \quad (3)$$

where $\xi_3 \approx 0.8$ is the dynamic friction coefficient and ${<}\sigma_{\mathrm{t}3}{>} = 0.73\theta_3^{-0.88}\rho^{0.12}W_\mathrm{n}^{0.24} \approx 1.3\times10^{10}$ dyn cm^{-2} and $w_\mathrm{t} = 0.25\rho_3^{-0.5}\theta_3^{-0.2}\rho^{0.3}W_\mathrm{n}^{0.6} \approx 2600$ cm s^{-1} is the mean stress and the tangent velocity at the contact between lined quartz glass particles. The $2q_\mathrm{f}$ value given above has the same order of magnitude as the $2q_\mathrm{f} = 9.1\times10^{13}$ erg cm^{-2} s^{-1} value[2,29] calculated for a similar heat source in describing treatment of NaCl particles in 1.6×10^{-4} cm by steel balls ($R = 0.2$ cm) in an EI2×150 planetary mill ($\omega = 10$ s^{-1}).

Time t_m of attaining the $T_{\mathrm{m}3}$ temperature of sulfur melting on the slip plane $x = 0$ at $\Delta T(0,t_{\mathrm{m}3}) = \Delta T(0,t'_{\mathrm{m}3}) = T_{\mathrm{m}3} - T_0 \approx 50$ K when a heat source with density $2q_\mathrm{f}$ acts, is calculated by (2a), $t_{\mathrm{m}3} \approx (50/0.5642B_3)^2 \approx 4.8\times10^{-12}$ s. As $t_3/t_{\mathrm{m}3} \approx 550$, the sulfur film at the contact[22] is in the molten state during virtually the whole time of impact-friction interaction of particles and $t'_{\mathrm{m}3} - t_{\mathrm{m}3} = (t_3 + t_{\mathrm{m}3})^2/4t_{\mathrm{m}3} - t_{\mathrm{m}3} \approx t_3^2/4t_{\mathrm{m}3} \approx 3.6\times10^{-7}$ s, the dry friction mechanism is inoperative, and $2q_\mathrm{f}(t > t_{\mathrm{m}3}) \equiv 0$. It follows that, at the first stage of mechanical activation of the system, the role played by dry friction reduces to almost instantaneously attaining the temperature of sulfur melting at contacts between particles, which facilitates the formation of a sulfur film of thickness δ_3 on all surfaces within the drum of mill. According to published data,[2,29] source $2q_\mathrm{f}$ is responsible for the temperature of ‘hot spots’ equal to the $T_{\mathrm{m}3}$ temperature of sulfur melting, which is obviously insufficient for the formation of sulfides.[30,31]

It is clear that another heat source, potentially capable of initiating and developing sulfur polymerization and subsequent mechanochemical formation of FeS_2, can only be the viscous flow[28] of the molten sulfur film. This heat source has density $q_\mathrm{v}(t > t_{\mathrm{m}3}) = \mu_3 w_\mathrm{t}^2/\delta(t)$. Consider its limiting characteristics. Clearly,[22,28] temperature at interparticle contacts can only exceed $T_{\mathrm{m}3}$ when the thickness of the molten film $\delta(t)$ attains its maximum value $\delta^* = 2\delta_3 - \varepsilon_3 \approx 2\delta_3 \approx 7.2\times10^{-5}$ cm, where $\varepsilon_3 = 0.66R_{\mathrm{i}3}\theta_3^{0.4}\rho^{0.4}W_\mathrm{n}^{0.8} \approx 6.5\times10^{-7}$ cm. The $2\delta_3 >> \varepsilon_3$ value is also evidence of the validity of initial assumption (*d*). The viscosity of α–S at $T_{\mathrm{m}3}$ is $\mu_{3\mathrm{m}} \approx 0.1$ dyn s cm^{-2}, and polymerised sulfur attains a maximum viscosity[19] at $T_{\mathrm{p}*} = 473$ K, $\mu_{3\mathrm{p}*} \approx 215$ dyn s cm^{-2}. It follows that, during mechanical activation of the system, the density of the ‘viscous’ heat source can change by several orders of magnitude as a result of polymerization, from the lowest $2q_\mathrm{v}(\mathrm{min}) = 2\mu_{3\mathrm{m}}w_\mathrm{t}^2/\delta_3 \approx 2.0\times10^{10}$ erg cm^{-2} s^{-1} value to a maximum of

$$2q_\mathrm{v}(\mathrm{max}) = \mu_{3\mathrm{p}*}w_\mathrm{t}^2/\delta_3 \approx 4.2\times10^{13}\ \mathrm{erg\ cm^{-2}\ s^{-1}} \quad (4)$$

It follows that an anomalous increase in molten sulfur viscosity caused by the unique ability of sulfur to polymerise[19] is capable of continuously increasing the viscous heat source density at impact contacts between particles to a value exceeding heat source density $2q_\mathrm{f}$ of dry friction. This leads us to suggest that, upon attaining some critical sulfur viscosity density ($\mu_3 = \mu_{3*}$), mechanical activation characteristics qualitatively change, and shear at the glass-sulfur interface by the dry friction mechanism becomes more favourable that viscous sulfur flow. This results in local failures of the sulfur film caused by its embrittlement (vitrification,[19], and in the further calculations it is accepted $\theta_3 = \theta_1$) even to its complete separation from the surface of glass particles. The corresponding mechanical activation time τ^* (Figure 1) signifies the end of sulfur activation or the beginning of the second stage of mechanical activation of the quartz glass–sulfur–iron system. At this stage, sulfur no longer possesses the property of crystalline substances to have a certain melting temperature and participates in the process as an amorphous compound. An increase in temperature at x^* close to the Fe–S contact then is not limited by the $T_{\mathrm{m}3}$ value.[22,28] Taking into account the heat effect of the reaction, this increase can be written[2] as

$$\Delta T(x^*,t) = 2B^*\{qt^{0.5}\mathrm{iErfc}[x^*/2(a^*t)^{0.5}] - q^*(t - t^*)^{0.5}\mathrm{iErfc}[x^*/2[a^*(t - t^*)]^{0.5}\}; \quad (5)$$

$$\Delta T(0,t) = 2B^*0.5642[qt^{0.5} - q^*(t - t^*)^{0.5}], \quad (5a)$$

where $B^* = \xi^* {<}\sigma_\mathrm{t}^*{>} w_\mathrm{t}^* (\lambda c\rho\lambda_3 c_3\rho_3)^{-0.25} \approx 2.25\times10^7$ cm^2 K s$^{0.5}$ erg^{-1} at $2q = 2q_\mathrm{f}^* = 7.2\times10^{13}$ erg cm^{-2} s^{-1}, $a^* = (aa_3)^{0.5} \approx 0.019$ cm^2 s^{-1} at $T = T_{\mathrm{p}*} \approx 470$ K;[19] q-values are calculated at $\xi^* \approx \xi_3$; and (see also Table 3 in ref. 2): $t^* \approx 4.6\theta^{*0.4}\rho^{-0.1}W_\mathrm{n}^{-0.2}[\rho\rho_3 r^2 R_3^2 \times (R_3 + r)/(\rho_3 R_3^3 + \rho r^3)]^{0.5} \approx 22.5\times10^{-12}$ s, where $\theta^* = (\theta_2 + \theta + \theta_1)/3 \approx 4.6\times10^{-12}$ cm^2 dyn^{-1},[24] $r \approx 0.5\times10^{-6}$ cm is a radius of the ‘abrasive iron’ particles, $R_3 \approx \delta_3/2 \approx 3.0\times10^{-6}$ cm; $w_\mathrm{t}^* = 0.25\theta^{*-0.2}\rho^{0.3}W_\mathrm{n}^{0.6}[(\rho_3 R_3^3 + \rho r^3)/\rho\rho_3(R_3 + r)^3]^{0.5} \approx 1450$ cm s^{-1}; ${<}\sigma_\mathrm{t}^*{>} = 1.0\theta^{*-0.88}\rho^{0.12}W_\mathrm{n}^{0.24} \approx 6.2\times10^{10}$ dyn cm^{-2}. As distinguished from (2), the heat source densities in (5) at $\Delta T(x^*,t)$ rise and fall branches are different and equal $q(t \le t^*) = q_\mathrm{f}^* + q_\mathrm{c}(t \le t^*)$ and $q^*(t > t^*) = q_\mathrm{f}^* - q_\mathrm{c}(t > t^*)$, where q_c is the chemical heat source density. This is caused by the properties of q_c.

Put $q_\mathrm{c} = 0$ or $q = q^* \approx q_\mathrm{f}^*$ in (5) as a first approximation, see also (2). Let us determine the largest temperature increase at the contact surface between iron and sulfur, $\Delta T(0,t^*) \approx 0.5642B^*t^{*0.5} \approx 60$ K or $T = T(0,t^*) = T_0 + \Delta T(0,t^*) \approx 410$ K. It is not enough for the temperature of formation of pyrite,[32] and insufficiently for initiating the synthesis of iron sulfides.[7,15,16,30–32] This is shown in (5) by the introduction of source q_c, which arises because of the occurrence of this exothermic reaction, *cf.* ref. 29. It follows that the $2q_\mathrm{v}$ viscous flow heat source is responsible for the transition of the iron–sulfur system into a qualitatively new state, in which the synthesis of metal sulfides is made possible again by the dry friction mechanism at the second stage of mechanical activation.

Let us accept that parameters for the thermal synthesis of pyrite are identical to synthesis of zinc sulfide. According to Sirota and Koren’,[31] thermal synthesis of ZnS is provided by reactive diffusion of the elements with the diffusion coefficient $D_\mathrm{ZnS} = D_0\exp(-U/kT)$, where $D_0 = 0.012$ cm^2 s^{-1} and $U \approx 2.2\times10^{-12}$ erg. On the other hand,[22,29,33] the distinguishing feature of mechanical activation is a decrease in the activation energy of the thermal process as a result of the action of contact stresses σ. This decrease amounts to $\chi\sigma$, where χ is the structure factor.[33] We used $\chi\sigma^* = 1.9\times10^{-12}$ erg in calculating $U(\sigma) = U - \chi\sigma^* \approx 3.0\times10^{-13}$ erg. This $\chi\sigma^*$ value was measured at the largest applied mechanical load $\sigma^* = 20$ kg mm$^{-2} \approx 2.0\times10^9$ dyn cm^{-2} in fracture of polycrystalline zinc samples.[33] The σ^* value was smaller than the ${<}\sigma{>}$ mean contact stress in collisions of sulfur-coated iron (zinc) particles in the AGO-2 mill, which showed that the estimate made above was fairly correct. The final expression for the mechanical activation reactive diffusion coefficient in vicinity x^* of interparticle contacts takes the form (cm^2 s^{-1})

$$D_\mathrm{ZnS}(x^*,t) = D_0\exp\{[-U(\sigma)/k[T_0 + \Delta T(x',t)]]\}; \quad (6)$$

$$D_\mathrm{ZnS}(0,t) \approx 0.012\exp\{-2200\ \mathrm{K}/[330\ \mathrm{K} + \Delta T(0,t)]\}. \quad (6a)$$

Calculations at $T = T_0 + \Delta T(0,t^*) \approx 350 + 60 = 410$ K give $D_\mathrm{ZnS}(t = t^*) \approx 7.8\times10^{-5}$ cm^2 s^{-1} at the impact-friction surface of the zinc (iron)–sulfur contact.

Such a high D_ZnS value ensures a fairly high rate of ZnS (and pyrite) formation and, as a consequence, additional heat evolution in vicinity x^* of interparticle contacts, whose value is determined by the $\Delta_r H$ chemical reaction enthalpy value. It follows that, simultaneously with heat source $2q_f^*$, a heat source with density $2q_c$ begins to act at the impact-friction contact[29]

$$2q_c(x^*,t) = H_r\Phi^*V^*(x^*,t)/ts^* = \rho^*H_r d(x^*,t)/t = 2\rho^*H_r[D(x^*,t)/t]^{0.5}; \quad (7)$$

$$2q_c(0,t) = \rho^*H_r D_0^{0.5}|\{\exp[-U(\sigma)/k(T_0 + \Delta T(0,t)]\}/t|^{0.5}, \quad (7a)$$

where number 2 shows that $2q_c$ is symmetrical with respect to the $x^* = 0$ glide plane; $H_r = \Delta_r H^0/M \approx 145\times10^8$ erg g^{-1} is the specific heat effect of formation of FeS_2; $M = 119.98$ is the molecular weight of FeS_2; Φ^* is the degree of completion of the synthesis of FeS_2 in the $V^*(x^*,t) = s^*d(x^*,t)$ reaction volume;[2,22] $d(x^*,t)$ and $\rho^* = (\rho + \rho_3)/2 = 5.0$ g cm^{-3} are the linear size of V^* and the mean density in the reaction volume; and s^* is the impact contact area of the particles (Figure 1). It is shown[22] that $\Phi^* \equiv 1$ for diffusion-controlled chemical reactions. Clearly, by its physical meaning, $d(x^*,t)$ equals the diffusion zone thickness or twice the depth of reactive diffusion of the elements, $d_D(x^*,t)$, with respect to the glide plane under the $\Delta T(x^*,t)$ conditions, $d(x^*,t) = 2d_D(x^*,t) = 2[tD(x^*,t)]^{0.5}$.

The properties of the $2q_c$ chemical heat source qualitatively differ from those of the $2q_f$ dry friction source, which acts only during time t^* of interaction of particles on the ascending temperature pulse branch $\Delta T(x^*, t \leq t^*)$ and only on the impact surface area between particles $s^* = 1.0(\theta^*\rho W_n^2)^{0.4}[rR_3/(r + R_3)]^2 \approx \approx 28.2\times10^{-12}$ cm^2. The $2q_c$ volume-point chemical source acts during reactive diffusion of the elements on both ascending $\Delta T(x^*, t \leq t^*)$ and descending $\Delta T(x^*, t > t^*)$ branches with equal activation energy $U(\sigma)$ values, because the collision time between a lined milling tools t_i during which stress σ acts is $\sim 2R/(r + R_3) \sim \sim 10^5$ times longer than time t^*.[2]

Consider the applicability range of (6) and (7) and their particular forms (6a) and (7a). When I use more general equations (6) and (7), we assume that a film of the FeS_2 reaction product of a certain thickness already exists on the abrasive particles prior to their impact-fiction interaction. We do not consider the possibility of reaction product formation and evolution. Conversely, equations (6a) and (7a) describe diffusion only at the glide surface ($x^* = 0$). As the distance from the glide surface increases ($x^* > 0$), temperature decreases, and, therefore, the equality $D(x^*,t) < D(0,t)$ always holds. This assumption would be valid if only the $2q_f^*$ heat source acted. As soon as the $2q_c$ heat source appears, it becomes reasonable to assume that, in the vicinity of the impact-friction contact and during interaction time t^*, the equality $D(x^*; t \sim t^*) \approx D(0; t \sim t^*)$ may hold. In other words, some increase in $D(x^*,t)$ estimated by (6) is to a certain degree balanced by a decrease in $D(x^*,t)$ caused by ignoring the heat effect of the reaction in the approximation $q_c = 0$ and $q = q^* = q_f^*$, because the $2q_c$ value necessary for calculating ΔT by (5), where $q = q_f^* + q_c$, still remains undefined. Thanks to this balancing, we obtain a fairly correct $2q_c$ value even in the first approximation, see (6a) and (7a),

$$<2q_c> \approx 2\rho^*H_r D_0^{0.5}(1/t^*)\{\int_0^{t^*}\mathrm{d}t[D(t)/t]^{0.5} + \\ + [1/(n-1)]\int_{t^*}^{nt^*}\mathrm{d}t[D(t)/t]^{0.5}\} \quad (8)$$

where $n > 1$ fairly accurately determines the second integral value and $t^* \approx 28.2\times10^{-12}$ s. The mean first term value (ascending ΔT branch) is $2q_c(t \leq t^*) \approx 13.6\times10^{13}$ erg cm^{-2} s^{-1}, and the second term $2q_c(t > t^*; n)\times10^{-13}$ (in erg cm^{-2} s^{-1}), averages ~5.9 at $n = 2$, ~4.9 at $n = 3$, ~4.2 at $n = 4$, *etc.* The $<2q_c(t > t^*)>$ value smoothly decreases as n increases.

In subsequent applications, I can use the following heat source densities in (5): $2q(t \leq t^*) = 2q_f^* + 2q_c(t \leq t') \approx 20.8\times10^{13}$ erg cm^{-2} s^{-1}, and the negative source $2q^*(t^* > t') = 2q(t \leq t^*) - 2q_c(t > t^*) \approx \approx 15\times10^{13}$ erg cm^{-2} s^{-1}. For correctness of calculations, $\Delta T(x^*; t > t^*)$ should be given in an analytic form by substituting the second integral from (7). Calculations by (5a) with these sources give the $T(0,t^*) \approx 520$ K. This is already close to the temperature of formation of pyrite, and sufficient for initiating the synthesis of iron sulfides.[32] It follows[22] that the temperature at the impact-friction contact between iron and sulfur particles is bounded from above by the temperature (~800 K) of sulfur softening[19] at the second stage of mechanical activation, and the presence of the $2q_c(t > t^*)$ chemical source substantially decreases the rate of $\Delta T(x^*; t > t^*)$ pulse weakening. In simulations,[22,34] this increases the size of the reaction volume V^* and can change the kinetic parameters of the mechanosynthesis.

In the future, the suggested model and equations (1)–(8) can be used to estimate both the rate constant[2,22] for the gradual mechanochemical reaction in the metal–sulfur system[5,15,16,35] and the induction period of ignition of explosive synthesis of metal sulfides in ball mills.[6,17,18,21]

In summary, the heat source densities of viscous flow ($2q_v$) and of the chemical reaction of pyrite formation ($2q_c$) are comparable in the order of magnitude with the density of the heat source formed by the mechanism of dry friction ($2q_f$). This is related to essential changes in the physicochemical properties of sulfur during mechanical activation, in particular, to the propensity of sulfur to polymerise and turn amorphous. The results should be taken into account in simulating the mechano-chemical processes with the participation of elemental sulfur and similar substances that are characterised by substantial heat effects.

We have experimentally and theoretically shown for the first time the possibility of participation of the abrasive-reactive properties of glass–sulfur systems coupled with the steel material of milling tools in the mechanochemical production of pyrite-based composites. We carried out measurements and numerical simulation of the mechanism of abrasive wear of the steel milling tools of an AGO-2 planetary mill under fixed mechanical activation conditions. However, the structure of the composites can be significantly more complex.[34,35] In particular, the issues of the localization of the mechanical activation product phases and their possible impact on the modification of the surfaces of the mechanical activation abrasive particles by iron and pyrite to be solved. Results of the modeling of mechanochemical reactions involving sulfur show that the most important process in the synthesis of sulfides (*e.g.*, of pyrite) is the plastic flow of sulfur that yields amorphous sulfur (polymerization and vitrification). The parameters of this process depend on the thickness of the sulfur layers on the surface of abrasive particles. Thus, the mechanical activation of a glass–sulfur mixture (other chalcogens can be used) in a planetary mill equipped with steel fittings yields nanocomposites composed of pyrite, iron and an inert glass matrix. The process takes a period of time one or two orders of magnitude shorter than that required for the traditional mechanical alloying of iron and sulfur powders. It is possible to use other metals in order to obtain the corresponding sulfides (let us note that scraps of any metallic or ceramic article can be used as the milling tools). The proposed method can also find a broad application both for obtaining new nanocomposite powders[11,34] and for the processing of various materials.[35]

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