Journal of Engineering Physics and Thermophysics, Vol. 69, No. 1, 1996

MECHANISM AND KINETICS OF GRINDING OF ZIRCONIUM DIOXIDE POWDER

S. N. Pashcherenko and I. V. Antsiferova

UDC 539.215.4

A model of grinding for dispersed powders of brittle substances is proposed within the framework of a phenomenological approach. The mechanism is established and the kinetics of grinding of a ZrO_2 powder is described.

The regularities of grinding of coarsely dispersed powders are described by the empirical laws of Kirpichev-Kick, Retinger, and Bond [1], which were found more than a hundred years ago. In finely divided systems, aggregation of powder particles is substantial and is allowed for by the introduction of a limiting particle size a_0 in these laws, modifying them arbitrarily [2]. Since the process of grinding is Markovian, one finds the probability density function of the size distribution of particles by solution of the Fokker-Planck equation, in which the average grinding rate is specified by one of the above laws and the diffusion coefficient is considered constant in the dimension space [3]. Thus, at the present time there is no theory of grinding that is free of arbitrary assumptions (the choice of the grinding law, allowance for aggregation), and, therefore, each investigation of the grinding of a particular powder system rests substantially upon experimental data. The choice of ZrO_2 powder as an object of investigation was determined by its wide use (with an average particle size of ~ 0.1 μm) in modern ceramic materials. This dispersed powder is usually produced by plasma-chemical or sol-gel methods. However, it is not improbable that a substantially cheaper method of grinding can be adopted if the average value of the sizes of particles and their dispersion in the powder that is produced by grinding are at the same level. Therefore, in this work, we propose and validate a model of grinding of dispersed powders based on which a mechanism of fracture of ZrO_2 powder particles is established and demonstrate a procedure for producing dispersed powder mixtures by grinding.

The grinding of ZrO_2 powder was studied in a model experiment on a planetary mill for a rotational velocity of 360 rpm. The grinding time was varied from 0.25 to 5 h. The average size of the powder particles was measured by two methods: a sedimentation method ($\bar{a}_c$) on a HORIBA CAPA-500 unit and measurement of the specific surface of the powder (S): $\bar{a}_s = 6/(\rho S)$, where ρ is the density of the particle material. Experimental data are given in Table 1, from which it can be seen that $\bar{a}_c$ is always larger than $\bar{a}_s$. Consequently, $\bar{a}_c$ is the size of conglomerates that are formed as a result of particle aggregation and $\bar{a}_s$ is of the order of the size of particles that form the conglomerates. In the initial state, the powder consists of weakly bound conglomerates of particles that are fractured during the first 15 min of grinding. The new conglomerates that are formed are then fractured gradually bygrinding.

We analyze the experimental data within the framework of a phenomenological approach. We write the law of grinding of powder particles as a quasilinear Langevin equation

$$\frac{da}{dt} = A(a) + \xi(t), \tag{1}$$

where velocity fluctuations $\xi(t)$ are a random process and δ is a correlated process. We assume that ξ is independent of conglomerate size, i.e., we will consider only the grinding of mixtures of particles that are similar in size, shape, and internal structure. Equation (1) corresponds to the Fokker-Planck equation [4]

Scientific Research Institute of the Problems of Powder Technology and Coatings, Perm'. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 1, pp. 3-8, January 1996. Original article submitted May 27, 1994.

1062-0125/96/6901-0003$15.00

TABLE 1. Granulometric Composition of ZrO_2 Powder Particles as a Function of the Grinding Time

Grinding time, h	Sizes, μm				
	$\bar{a}_c$	$\bar{a}_s$	$\sqrt{D(a_c)}$	$(d\bar{a}_c/dt)_{exp}$	$(d\bar{a}_c/dt)_{calc}$
0	70	0.4	–	–	–
0.25	0.4	0.1	0.3	–	–
0.5	2.3	0.6	1.5	−1.2	−1.0
1	1.8	–	1.5	−0.8	−0.9
5	1.0	–	0.75	−0.02	−0.2

$$\frac{\partial f}{\partial t} = -\frac{\partial (Af)}{\partial a} + B\frac{\partial^2 f}{\partial a^2}, \tag{2}$$

where $f(a, t)$ is the probability density function of the particle size distribution. We determine the initial moments $\overline{a^m}(t)$ as follows:

$$\overline{a^m} = \int_0^\infty a^m f(a, t)\, da. \tag{3}$$

From (3) and (2) upon integrating by parts we obtain

$$\frac{\partial \bar{a}}{\partial t} = \bar{A}, \quad \frac{\partial \overline{a^2}}{\partial t} = 2\overline{aA} + 2B, \tag{4}$$

where account is taken of the fact that $f(a, t)$ and the particle flux in the dimension space $j = -Af + Bdf/da$ are equal to zero for $a = \infty$ and $a = 0$.

The particle size distribution for large grinding times $f_\infty(a)$ is independent of the initial distribution and is governed only by the law of grinding. We find it from (2) by assuming $\partial f/\partial t = 0$:

$$f_\infty(a) \sim \frac{1}{B}\exp\left\{\frac{1}{B}\int_0^a A(x)\, dx\right\}. \tag{5}$$

It would appear resonable that $\partial \bar{a}/\partial t|_{t=\infty} = 0$; then, (4) and (5) yield

$$\bar{A} \sim \int_0^\infty da\, \frac{A(a)}{B}\exp\left\{\int_0^a \frac{A(x)}{B}\, dx\right\} = \exp(F(\infty) - F(0)) - 1 = 0, \tag{6}$$

from which $F(\infty) = F(0)$, where $dF/da = A/B$. Consequently,

$$\frac{1}{B}\int_0^\infty A(a)\, da = F(\infty) - F(0) = 0, \tag{7}$$

The latter expression, in combination with the above statement of the existence of a size a_0 such that $A(a_0) = 0$, imposes restrictions on the form of the function $A(a)$.

We find the dependence $A(a)$ by comparing (5) with the expression obtained by the method of the most probable distribution from the condition of maximum information enthropy [5]

$$I = -\int_0^\infty f_\infty(a) \ln f_\infty(a)\, da = -\overline{\ln f_\infty} \tag{8}$$

under the additional conditions: normalization $f_\infty(a)$ and the law of conservation of energy $\overline{\varepsilon(a)p(a)} = E$, where E is the energy dissipated, on the average, by one powder particle; $p(a)$ is the probability of this mechanism of energy dissipation by a particle of size a; $\varepsilon(a)$ is the energy dissipated by the particle in fracture. Having applied the method of Lagrangian multipliers, we find the stationary size distribution of the particles:

$$f_\infty(a) = N \exp\left\{ -\beta p(a)\, \varepsilon(a) \right\}, \tag{9}$$

where N and β are constants. By comparing the expressions obtained for $f_\infty(a)$ we find

$$A(a) = -\beta \frac{d}{da}\left\{ p(a)\, \varepsilon(a) \right\}. \tag{10}$$

The value of $\varepsilon(a)$ is proportional to the surface area of the cracks formed in brittle fracture of a powder particle of size a, i.e., $\varepsilon(a) \sim a^{d_f}$, where d_f is the fractal dimensionality of the cluster of microcracks formed in the particle prior to its fracture.

If we ignore conglomeration processes (i.e., the condition $\Delta(a_0 = 0)$) and condition (7), from (10) we obtain the basic empirical laws of grinding. Thus, we obtain the Kirpichev-Kick law if we consider the probability of fracture of all particles the same, i.e., $p(a) = \text{const}$ and the fracture is brittle: $d_f \approx 2$; then $A \sim a$. If the energy supplied is dissipated in the entire volume of particles, for example, in the process of their plastic deformation ($d_f \approx 3$), we obtain the Bond law: $A \sim a^2$. If the probability of particle fracture is proportional to the breaking stress $p(a) \sim \sigma_p$, then, since $\sigma_p \sim K_c/\sqrt{l}$ and the crack length is proportional to the particle size, $p \sim a^{-1/2}$. Then if the supplied energy dissipates in the entire volume via multiple nucleation of microcracks ($d_f \approx 3$), we obtain the Retinger law: $A \sim a^{3/2}$.

In finely divided grinding (see, for example, Table 1), conglomeration processes are considerable; therefore, the probability of fracture $p(a)$ can be approximated, as is usually done in statistical description of the reliability of complex systems (in this case, the conglomerate of particles is dealt with as such a system), by the Weibull distribution [6]: $p(a) \sim a^{\alpha-1}\exp(-\lambda a^\alpha)$. Then, in view of conditions (7) and $A(a_0) = 0$, we find the law of grinding:

$$A(x) = q a_0^{\alpha+d_f-2}(\alpha + d_f - 1)\, x^{\alpha+d_f-2}(1 - x^\alpha)\exp(-bx^\alpha), \tag{11}$$

where $x = a/a_0$, $q = \text{const}$, $b = (\alpha + d_f - 1)/\alpha$. From (11), it can be seen that $A(0) = 0$ and grows as the particle size increases, reaching its maximum at $x = x_1$. With a further increase in particle size, A becomes negative and decreases, reaching its minimum at $x = x_2$, where $x_{1,2} = ((3 + d_f/(1 - \alpha - d_f) \pm \sqrt{(3 + d_f(1 - \alpha - d_f)^2 - 4(1 + 1/(1 - \alpha - d_f))}/2)^{1/\alpha}$. Then $A(x)$ grows asymptotically up to zero, remaining negative. Particles of size a_0x_2 are fractured at the maximum rate, and those of a_0x_1 conglomerate at the maximum rate. The areas between the curve at $A(x)$ and the axis of abscissas are equal in the interval of from 0 to a_0 and of from a_0 to ∞.

Since the sizes of the particle conglomerates had a narrow spread ($\sim 1\ \mu$m), in what follows we will ignore their size distribution. Then, the first equation of (4) yields a differential equation for a_0:

$$\frac{d\bar{a}}{dt} = \overline{A(a)} = A(\bar{a}). \tag{12}$$

According to the table, the grinding rate decreases with decreasing $\bar{a}_c$. The function $A(\bar{a})$ satisfies this condition for $\bar{a}/a_0 \in [1, x_2]$. The maximum value of x_2, which is equal to 2.718, is attained as $\alpha \to 0$. Consequently, $a_0 \geq \bar{a}/2.718$, i.e., $a_0 \geq 2.3/2.718 \approx 0.9\ \mu$m.

From the condition of the best approximation of the experimental data by Eq. (12), we found the following values of its parameters: $\alpha = 0.1$, $a_0 = 0.9\ \mu$m, $q a_0^{\alpha+d_f-2}(\alpha + d_f - 1) \sim 10^2\ \mu$m/sec. The fractal dimensionality of the fracture surface d_f is equal to 2, i.e., the fracture was brittle. The results of approximation of the experimental data are also given in the table. The Weibull function describes the probability of fracture of complex systems [6],

in the life of which we recognize three periods: alignment ($\alpha < 1$), when objects with internal defects are fractured; normal operation ($\alpha = 1$); and aging ($\alpha > 1$). Consequently, the ZrO_2 powder particles are crushed due to defects in the particle material structure.

According to these data, $x_1 a_0 \approx 0$; $x_2 \sim 2.5\,\mu$m. Since most of the powder particles have sizes in the interval $(a_0 x_1, a_0 x_2)$ we can approximately describe the obtained experimental data by simple dependences, substituting the linear function $A = -k(x - 1)$ for $A(x)$ in the interval (x_1, x_2). This dependence yields a realistic description of conglomeration processes; however, it is agreed [7] that conglomeration processes proceed more actively than grinding processes. Analysis of the proposed dependence $A(x)$ showed that $A(x_1) > |A(x_2)|$ for $\alpha < 3.1$; it is only then that conglomeration is more active than grinding.

The table shows that $x >> 1$ virtually over the entire range of grinding times, therefore, to approximate the results of this experiment we resort to the approximation $A = -ka$. Then the solution of the first equation of (4) appears as: $\bar{a} = a_0 + a(0) \exp(-kt)$. The constants were found by comparison with the experimental data:

$$\bar{a}_c = 0.98 + 2.12 \exp(-0.954t), \quad t \geq 0.5 \text{ h}, \tag{13}$$

where the length is measured in μm and the time in hours. From (5), we obtain

$$f_\infty(a) \sim \exp\left\{ -\frac{k}{2B}(a - a_0)^2 \right\}. \tag{14}$$

Consequently, the dispersion of the particle size distribution is $D = B/k$ and the average $\bar{a} = a_0$. Since, according to the experimental data (see Table 1), $\bar{a} \approx \sqrt{D}$, then $B \sim a_0^2 k \sim 2 \cdot 10^{-4}\,\mu\text{m}^2/\text{sec}$. Then the spread of conglomerate size due to random processes in grinding is equal to $\sim\sqrt{Bt} \sim 1\,\mu$m, which is in agreement with experiment.

We obtain from (4) an equation for the dispersion of the size distribution of particles $D = \overline{a^2} - \bar{a}^2$. For $A = -ka$ we have

$$\frac{dD}{dt} = -2kD + 2B, \tag{15}$$

hence $D = B/k + \text{const} \cdot \exp(-2kt)$. Since $B/k = a_0^2$:

$$D = 0.96 + 0.29 \exp(-1.91t). \tag{16}$$

After grinding, the ZrO_2 powder particles had a fragmentary shape; consequently, fracture was preceded by microcracking. It is agreed [6] that a microcrack at the instant it nucleates, whether the fracture mechanism is viscous or brittle, has a length of $\sim 1\,\mu$m, which coincides in our case with a_0 in order of magnitude. Therefore, the finite dispersion of the ZrO_2 powder is determined by a_0 and hence the properties of the particle material and the medium in which the grinding occurs. The duration of grinding and its intensity have a little effect on $f_\infty(a)$ and mainly increase the number of particles of a size smaller than $x_1 a_0$. As long as $\bar{a} > a_0$, it is predominantly particles of large fractions ($a > a_0$) that break down, since small particles, by being in the interparticle space of large ones, are protected by them from impacts of the grinding bodies. When $\bar{a}$ becomes of the order of a_0, the process of grinding enters stationary stage. A fundamental decrease in powder dispersion can be attained by altering the fracture mechanism so that the lattice loses its stability uniformly over the entire volume of the particle rather than in the region of microcrack nucleation. These are apparently the conditions of failure of a conducting wire in its electrodynamic explosion by a supercritical pulse of electric current.

By selecting a small fraction with $a < x_1 a_0$ we could decrease the average size of the powder particles, since the conglomeration of particles of size $a < x_1 a_0$, according to (11), is small. However, for a given powder, this is impossible, since $x_1 \approx 0$ and the interval $[0, x_1 a_0]$ is so narrow that its corresponding portion of particles is negligibly small. Therefore, an increase in dispersion for ZrO_2 powder is possible only at the expense of a decrease in a_0 with a change in the grinding medium. Since the basic process that retards the grinding of dispersed powders is conglomeration, which is realized by forces of an electrostatic nature, media with high dielectric permittivity should be used.

According to the above results, dispersed ZrO_2 powders are highly prone to conglomeration, and, since they are virtually not used as a single-component mixture, mixtures of components of the required chemical composition must be ground.

CONCLUSIONS

1. A phenomenological model of the kinetics of powder grinding is proposed and the required conditions that the coefficient $A(a)$ of the Fokker-Planck equation should satisfy are found.

2. All basic empirical laws of grinding and the law of grinding of finely divided powders are derived.

3. It is established that particles of a ZrO_2 powder are fractured by microcracking at defects of the material structure and conglomerate for $a \leq a_0$ ($a_0 \sim 1$ μm). For larger grinding times, the average particle size is $\sim a_0$, the dispersion is $\sim a_0^2$, and the law of size distribution is normal.

NOTATION

$\bar{a}_c$, $\bar{a}_s$, average size of particles measured by a sedimentation method and calculated based on measuring the specific surface; ρ, density; a, size of powder particles; $A(a)$, average grinding rate; a_0, minimum size of the conglomerate is determined from the condition $A(A_0) = 0$; x_1, x_2, points of the extremum of the function $A(x)$, $x = a/a_0$; $f(a, t)$, probability density function of the size distribution of particles; B, diffusion coefficient in the dimension space; $p(a)$, probability of fracture for a particle of size a; $e(a)$, energy dissipated by a particle of size a in grinding; I, information entropy; d_f, fractal dimensionality of cluster of microcracks; D, dispersion of particle size distribution.

REFERENCES

1. V. I. Renivtsev (ed.), Selective Failure [in Russian], Moscow (1988).
2. E. N. Nepomnyashchii, Teor. Osn. Khim. Tekhnol., **11**, No. 3, 477-480 (1977).
3. I. O. Protod'akonov and S.R.Bogdanov, Statistical Theory of Transfer Phenomena in the Processes of Chemical Engineering [in Russian], Leningrad (1983).
4. N. G. Van Kampen, Stochastic Processes in Physics and Chemistry [Russian translation], Moscow (1990).
5. G. Haken, Information and Self-Organization [Russian translation], Moscow (1991).
6. S. A. Aivazyan, I. S. Enyukov, et al., Applied Statistics. Fundamentals of Modeling and Primary Processing of Data [in Russian], Moscow (1983).
7. Ya. D. Vishnyakov, Modern Methods for Investigating the Structure of Deformed Metals [in Russian], Moscow (1975).