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Mechanoluminescence of quartz particles in the stirred media mill

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The impulses of mechanoluminescence caused by stressing of fine quartz particles in the stirred mill were analysed. An obtained distribution of light impulse can be described by means of the powder function with two different exponents, one for low and other one for high impulse amplitude. The critical amplitude in between remains constant at all investigated process parameters. The observed difference in exponents reflects a different behaviour under applied stress for fine and coarse particles. An intensive production of pores and microcracks occurs during the wet treatment of fine particles. The light emission from stressed particle decreases with growth of pores inside of particles. Consequently, the number of counted stress events at a given impulse amplitude, is reduced. Also, the frequency of impulse decreases with growth of pores. A ratio of current to start impulse frequency reflects the grad of development of pore structure. An intensive particle size reduction occurs when this ratio achieves a critical magnitude. Particle size distribution becomes three-modal instead of bimodal at start of grinding. The third mode with maximum at 100 nm appears due to fracture of porous particles.

1. Introduction

Mechanoluminescence (ML) is a type of luminescence induced by means of any mechanical stress of solids. The study of grinding by use of ML is reviewed in several articles [1–5]. For example, Kürten and Rumpf [1] reported about the use of ML for characterization of grinding in jet mills. A fairly good correlation between power consumption and intensity of ML during the grinding of sugar or ZnS:Mn was observed. Later the same correlation for quartz particles was reviewed [3–5]. In the case of quartz particles the light was radiated from optical active free radicals [2, 6]. These radicals are located within a narrow particle surface layer [3, 6].

The application of ML for studying the processes in grinding machines is often problematic because of a decrease of the total light emission with reduction of particle size. The interpretation of the obtained results is very complex since the ML of single particle with a size of a few microns is not exactly investigated. However, ML reflects the microprocesses on the particle surface and can be very attractive for any applications.

Often the deformation mechanism under applied stress depends on particle size. For example, fine quartz particles tend more to plastics deformation as coarse one. Consequently, the dominant breakage mechanism changes with particle size and the distribution of ML-impulse obtained by grinding of fine quartz particles will reflect this transform. This fact can be used to determine what kind of deformation is dominant in the grinding device—plastics or elastic.

Thus, one may expect that the amplitude of ML-impulse correlates with the particle size and can be used for particle size determination [7]. Furthermore, the primary solid particles and "soft" particles such as hardened aggregates or particles with developed pores structure exhibit different behaviour under applied stress [8]. Mechanical stress applied to bulk primary particles leads to the fracture of the solid matrix and an intensive light emission. In terms of "soft" particles, as agglomerates, the applied stress leads mostly to cracking of the solid bridges between primary particles. As a consequence, ML is not so intensive by breakage of "soft" particle and its contribution to the total ML is not significant. This effect provides a useful way to study the disappearance kinetics of these "soft" particles.

The objective of the research described in this paper is to develop and to test a ML based method for monitoring grinding processes in stirrer media mills.

2. Experimental

ML of quartz particles was studied on the lab-scale stirred media mill produced by Netzsch GmbH. Fig. 1

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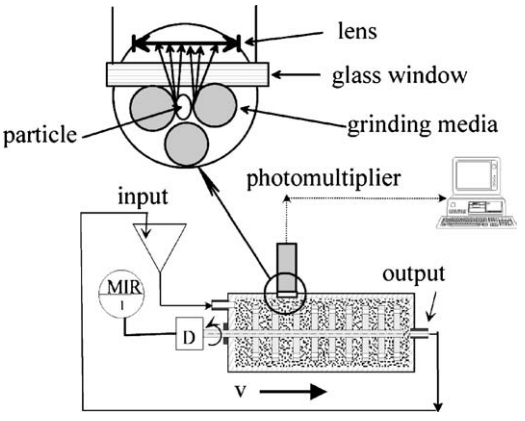

Figure 1 Schematic diagram of test rig and measurement technique.

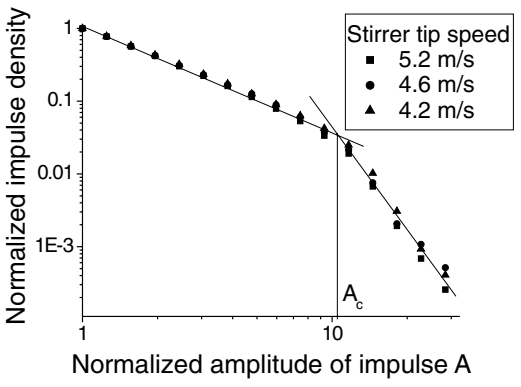

Figure 2 Normalized density of impulse reflects the stressing of solid quartz particles.

shows the schematic diagram of the measurement technique. Grinding chamber was filled with about 2 mm zirconium dioxide ceramic beads. The filling rate of this grinding media (bulk volume related to the net volume of the grinding chamber) was 0.7. The stirrer tip speed was varied from 3.16 to 5.2 m/s.

The window in the grinding chamber was made from silica glass. The number of light impulses $N(A_k)$ with amplitude larger than A_k was counted in the time interval $\Delta t = 0.333$ s. The lowest applied amplitude A_0 was 28.7 mV. The density of impulse n_I and frequency of impulses F_I were calculated by following expressions

$$n_I(A_k) = \frac{\Delta N}{\Delta A} = \frac{N(A_{k+1}) - N(A_k)}{(A_{k+1} - A_k)} \quad (1)$$

$$F_I(A_k) = \frac{N(A_{k+1}) - N(A_k)}{\Delta t} \quad (2)$$

To achieve statistical validation of measured data the count of impulse was repeated one hundred times at each fixed grinding time. A test count of noise impulses (without particles in the mill) was carried out to enhance the precision of counting.

3. Results and discussions

3.1. Impulse distribution and breakage of particles

The density of impulses n_I was found to be uniform for different stirrer tip speeds. The normalized density of impulses varies versus amplitude from 1 to 2×10^{-4} (Fig. 2). A grinding time of 9 min was chosen for this distribution. One can assume that the obtained function $n(A)$ reflects a different breakage behaviour of particles under applied mechanical stressing:

(a) the first part reflects the mechanical stressing of fine particles. In this case the impulse amplitude is lower than the critical amplitude $A_c = 10$.

(b) the second part with amplitude higher than the critical amplitude $A_c = 10$ corresponds to the breakage of coarse particles [3, 5].

The line $n(A)$ on the Fig. 2 can be fitted with:

$$\ln(n(A)) = \alpha \cdot \ln(A) + C \quad (3)$$

with an exponent $\alpha_1 = -(2.5 \pm 0.04)$ for low amplitude

$$A < A_c \quad (4)$$

and an exponent $\alpha_2 = -(6 \pm 0.2)$ for larger amplitude

$$A > A_c \quad (5)$$

The exponent α_1 is equal to that one found in terms of grinding quartz particles in the jet mill [4, 5] where an intensive development of pores took place.

Fig. 3 represents the size volume fraction measured by the Mastersizer (Malvern Instruments). The bimodal size distribution with split size d_c about 2 μm between fine and coarse modes was observed at start of grinding. Such bimodal distribution with large difference between "child" (fine) and "parent" (coarse) particles is typically for disintegration of aggregates.

Therefore, the observed size distribution is a superposition of two sub-collectives, i.e., primary particles and aggregates. Both the split size d_c and the critical amplitude A_c do not depend on the grinding time. It makes sense to conclude, that the critical amplitude $A_c = 10$ (Fig. 2) corresponds to a split size d_c between fine and coarse modes. The resulting fine particles have almost uniform size distribution and only the fraction of these particles is increasing with time. The sub-collective of primary fine particles already exists in aggregates as bonded constituents. During the wet

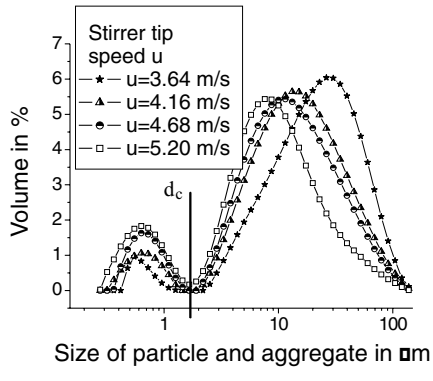

Figure 3 The variation in particle/aggregate volume fraction caused by the disintegration of aggregates during 1 min treatment in the stirred media mill.

treatment in the stirrer media mill the primary particles are so to say "liberated" from that parent aggregates. The mechanical properties of fine primary particles are different from those ones of primary coarse particles. Consequently, fine primary and coarse particles exhibit a different deformation or breakage behaviour under applied stress in the stirrer media mill. Hogg and Cho reported about the similar difference in breakage behaviour for fine and coarse particles [9]. The distribution of ML-impulse with amplitude reflects this different deformation behaviour. This leads to the difference between exponents in observed distribution of impulse.

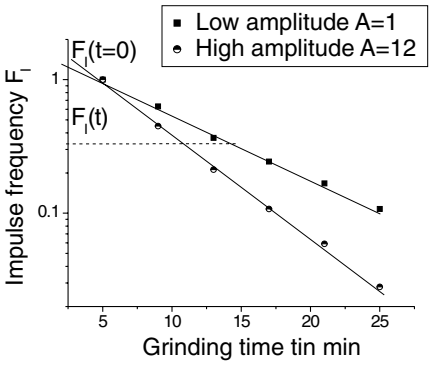

Figure 5 Normalized impulse frequency decreases with time.

3.2. Disappearance kinetics of aggregates

As mentioned above, ML cannot be as intensive by stressing of "soft" particles. This fact provides a useful way to study the breakage of aggregates and development of particle pore structure. Fig. 3 represents the size distribution at the different stirrer tip speeds. The feed material is always the same. However, a large difference in size distribution was observed just after 1 min of grinding.

The observed characteristic time of size reduction is estimated to be about a few minutes. This time is too short for effective grinding of the primary particles. Therefore, the size reduction due to breakage of aggregates is dominant in this time interval.

On the other hand, the breakage of aggregates leads to increasing number of "liberated" particles that are not bound in "soft" aggregates. Also, the number of particles subjected to effective stressing to provide ML-impulse should be increased. In Fig. 4 the frequency of impulse F_I is plotted versus time at fixed normalized amplitude $A = 1$. The impulse number reaches its maximum at short operating time (<10 min) and then decreases exponentially. This is typically for impulse frequency F_I at all investigated amplitudes. Therefore, the observed increase of impulse frequency is caused by breakage of aggregates.

3.3. Development of the pore structure and acceleration of size reduction

Figs 4 and 5 show that the logarithm of impulse frequency $\ln(F_I)$ decreases linearly with operation time. This is valid only for larger operation times. However, the number of "liberated" fine primary particles, that seems to be able to produce the significant ML-impulse, increases with time. There are two reasons that can cause this decreasing impulse frequency. The first one is hydrolysis of the optical active radicals in the aqueous solution. That leads to reduction of total light emission from particles being stressed. Consequently, the number of light impulse that can be counted at fixed impulse amplitude becomes lower. The second reason of decreasing of impulse frequency is the building of microcracks and pores of particle surface and within the particle. The particles become "softer" with process time. This may happen without an effective reduction of measured particle size. However, the number of microcracks and pores increases.

If the second microprocess of particle structure modification is dominant, the critical number of microcracks needed to break particles can be reached at any treatment time. An intensive reduction of particle size can be observed after this time. Both size reduction and surface modification occur simultaneously. Consequently, the obtained size distribution correlates with the number of microcracks. In terms of bimodal size distribution the degree of size reduction can be characterised by the ratio R of the fine mode peak V_f to the coarse mode peak V_c (see Fig. 6).

Fig. 6 shows a typical development of multi-modal size distribution versus time. The mode of fine particles increases with time a compared to coarse one. When a fixed for all investigated operating parameters ratio $R = 1.3 \pm 0.1$ is exceeded, an intensive size reduction occurs. The total size distribution becomes three-modal

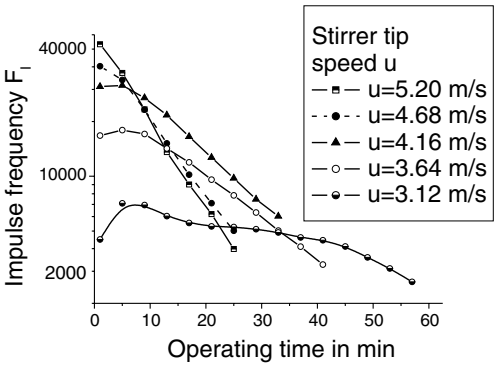

Figure 4 Impulse frequency versus grinding time.

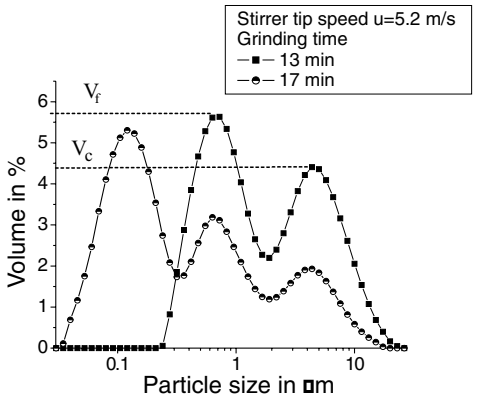

Figure 6 Typical evolution of size distribution with time.

with a third maximum at 100 nm. The ratio R between two previously observed peaks increases up to 1.8. The increasing of fine particle sub-collective indicates the fracture of coarse particles. On the other hand, it can be very useful to compare the kinetics of size distribution and those of impulse frequency. The frequency of impulses is proportional to stress number per unit time. However, "soft" particles do not contribute to the count of impulses. Fig. 5 shows a dependence of normalized impulse frequency on the time. The total size distribution becomes three-modal in the time interval between 13 and 17 min (see Fig. 6). However, the kinetic of impulse frequency has no breaking point at this time. Therefore, the intensive size reduction occurs by grinding of "soft" particles only. The beginning of the intensive size reduction corresponds to the decreasing current impulse frequency $F_1(t)$ about of 4.8 ± 0.2 times compared with those $F_1(t = 0)$ extrapolated back to the start of grinding (see Fig. 5 at $A = 1$). This ratio of frequencies depends on material properties only and does not vary with operating parameters.

The frequency of impulses with low amplitude that corresponds to stressing of fine particle decreases slowly as compared with those for coarse particle. This dependence of the frequency kinetic on the amplitude can be used to determinate the size distribution of primary particles.

4. Conclusions

Two different stressing mechanisms of particles in a stirred media mill were observed. The mechanoluminescence (ML) based method can be used to study the kinetic of size reduction in stirred media mills. Generally, the size distribution of primary particles in a collective, which consists of aggregates and primary particles, can be calculated from impulse amplitude distribution. This allows the on-line monitoring of size reduction of primary particles in such collectives. Another application of ML is to study particle surface modification during grinding. For example, the intensive size reduction can be predicted using time analysis of the impulse frequency.

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