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IMPLICATIONS OF FINE GRINDING IN MINERAL PROCESSING

Mechanochemical approach[*]

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Abstract

Fine grinding of minerals may change physical and chemical properties of the material to the extent that has to be considered in laboratory verification work or processing work in the industrial plant. The ground material is mechanically activated by increase of both: specific surface energy and elastic strain energy. The activation energy can then be dissipated through different mechanisms, such as: polymorphic transformation, mechanochemical decomposition or synthesis. The thermodynamical principles and kinetics mechanisms responsible for the relaxation modifications are thoroughly discussed. Important factors such as: Reaction triggering dimension, action of shear stresses, surface groups activity, product reactivity, etc. are described. A short survey on comminution by fine grinding is also presented.

Keywords: activation energy, comminution, mechanochemistry

Introduction

Comminution is highly used in ore dressing and mineral beneficiation. It is associated with techniques such as: crushing, grinding, pulverizing, fragmentation, sawing, cutting, machining, polishing, etc., and applies to different materials, such as: minerals, ceramics, glasses, metals, pigments, polymers, pharmaceutics, cereals, etc.

Comminution may change the physical and chemical properties of the material to the extent that must be accounted for in its verification in the laboratory work, or its processing ability in the industrial plant. Sometimes the changes can be utilized to advantage. Such are: increase of rate and amount of solubility; decrease of processing temperature and reaction time; increase of surface activity and attain better catalytic effects; induce thixotropic properties in slurries; produce new artificial materials; improve sinterability and attain stronger products; use of mechanical alloying for producing new metal alloys and cermets. Acti-

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vated powders have found uses in catalysis, hydrogen storage, plasma coating, energy promotion, etc. Dandurant *et al.* [1] suggested that the knowledge of mechanochemical activities permits better understanding of certain mineral transformations which may have occurred with geological tectonic events, and Kumazawa [2] discussed the application of the theoretical aspects to geological and geophysical problems. In general, same mechanochemical principles apply to shock-induced deformation, or shock compaction of powders. (For information on the dynamical behavior of minerals under shock compression, see Stöffler [3].)

Glasson [4] divided the response of materials to mechanochemical reaction according to their hardness, and have shown that soft minerals (Mohs' scale 1–2) undergo much plastic deformation and strain hardening. Plastic deformation also takes place in harder materials, but under confined conditions. In principle, the energy input in plastic deformation transforms to heat. In cases where grinding conditions become rigorous, also friction transforms to heat. The specific cases where heat is generated during grinding will not be treated here, as heat affects the otherwise non-thermal mechanochemical process. (Albeit the fact that in technology such effects are avoided by cryogenic comminution.) The resent manuscript describes experimental observations and accepted theoretical models by which a self-contained theory on the occurrence of solid-state mechanochemical reaction in materials under comminution is presented.

Comminution and fine grinding

The three main objective of grinding are to provide a material of a size most suitable for subsequent physical or chemical processing, to provide a material with a specific surface, and to liberate the constituent minerals in ores as a preparation for subsequent separation processes, or to promote a greater uniformity of products.

Fine grinding of particulate materials can be achieved in many different ways. Among the most common techniques being used commercially are: tumbling mill grinding (e.g. ball milling), vibratory milling, impact milling, and attrition milling. Particle size range of 10 to 1 microns are usually referred to as fine, and particles predominantly below 1 micron – as ultrafine. The grinding equipment can be defined as low, medium or high-speed mill. The ball mills fall into the first category, medium-speed mills are generally of the roller type, while high-speed mills embrace: pin disc units, hammer mills and disintegrators. Conventional ball milling is the most widely used technique for achieving ground material down to few microns, and for products below 2 micron long retention times and large energy input are necessary. Although impact milling is capable of producing submicron material, unit capacities restrict the application of these devices to small tonnage operation. Vibratory milling has been used to produce tonnage quantities of material in the range of 10–20 microns, but its applicability to fine grinding has not been demonstrated.

The size reduction in comminution process can be considered to be the result of many individual events, e.g. the fragmentation of particles in tumbling mills appear to result from a combination of impact, abrasion (attrition), compression, and chipping. The quantity of mechanical energy expended in present grinding devices is much greater than that actually required to fracture a mineral particle in either dry or wet process. Much of the gross energy input to the crushing media (the mill with its grinding elements), and the material charge, is dissipated through friction, plastic deformation, errosion, and sound generation, mostly as heat losses. The net energy left is directly used for the activation of the individual charge particles which, in principle, can be divided among [5]: surface activation – the increase of specific surface energy by means of the cracking and fracturing, and bulk activation – the increase of elastic strain energy stored in the particles' material. The particle size distribution and the particle shape of a ground product is influenced by the choice of device used, and by the operating conditions. These factors are of prime importance because they affect the physical properties of the finished product, surface area, chemical reactivity, fluid flow through the particulate mass, dispersibility and settling rate, particle strength, consolidation packing density, and sinterability.

As the grinding proceeds into the ultrafine region, conditions which are of little significance during normal operations gradually become controlling the process. These involve increasing resistance to fracture and increasing tendency to aggregate. A growing fraction of the input power is consumed fruitlessly. The reduction of particles terminate at a size called 'grind limit', attributable to the structure of the crystal lattice which prevents the formation of still finer particles. Generally, the limit of comminution is referred to the size distribution to which a comminution process tends as a result of the material properties, the type of device used, and the operating conditions (given sufficient time).

In kinetics sense, the variation of the energy leading to fracture is a decreasing function, since the resistance to fracture is an increasing function, of the particles' fineness. It stems from: (i) increase of the relative strength of the particles as they decrease in size (a statistical outcome, as the probability for crack initiation decrease the smaller the particles are), (ii) the larger particles shielding the smaller particles from impact (screening effect), and (iii) agglomeration of the smaller particles (a mean for reducing the specific surface energy of the particulate system).

The activation free energy of the comminuted material, gained by the increase of specific surface energy and stored elastic strain energy as was described above, can be dissipated by different was of energy transitions. The surface activation can be relaxed as the newly exposed fracture surfaces are becoming active to the extent that agglomeration, or adsorption of environmental gaseous species and moisture, take place. The bulk activation can be relaxed by fracturing of brittle materials, or otherwise by crystallographic lattice rearrangement in polymorphic transformation, mechanical alloying (of solid-solution), mechanochemical decomposition or synthesis (of chemical compound).

Theoretical aspects

The energy dissipation process in the individual particle is mechanical, and not thermal as was thought earlier. Heinicke [6], summarized findings observed during the last century supporting the mechanical approach. For example, Carey-Lea (1892) have shown that mercury chloride can easily be decomposed into components by grinding in a mortar, whereas it melts and sublimes undecomposed by heating. In fact, [5], mechanochemical polymorphic transformation will take place during grinding starting from any one of two related polymorphs, whether it is the high- or the low-temperature polymorph, whether the one with high- or low-density. The second polymorph will always emerge and grow till dynamical equilibrium will develop between the polymorphs while grinding continues. Today multitude of facts prove that the mechanochemical reaction differs from a thermo-chemical one, from both thermodynamical and kinetical aspects. Some scientists opposed the idea suggesting it to be in contrast with the known appearance of 'hot-spot' or 'magma' pockets at contact points of impact and friction [7]. These take place during a period of 10^{-3} seconds at deformation zones of sub-microscopical dimensions. There, high-temperature develops 'adiabatically', believed to be instrumental for the initiation of mechanochemical reaction. However, being important in kinetics sense, the reaction will take place only if the particle is readily available from a thermodynamical sense, by being already properly activated to the required metastable state.

Boldyrev [8] suggested that the excitation of a mechanochemical reaction (termed: 'mechanolysis') differs from thermochemical one (termed: 'thermolysis') by the immediate excitation to the highest available phononic energy level at the very short period of occurrence, leading directly to the formation of vibrational modes which are then followed by gradual bonds rupture. By contrast, in thermolysis phononic energy fluctuations determined by lattice oscillations are sequentially developing along linear, rotational and vibrational modes, the later to be spontaneously followed by bonds rupture. In other words, the model deals with an event that reduces locally to a short-term rise of temperature and pressure, but elsewhere in the particle longer-term irreversible configurational changes must follow before the relaxation may take place. Thus, the increase of configurational rather than thermal entropy controls the mechanochemical process.

There are some fundamental mechanisms important for the solid-state mechanochemical reactions. The first one is related to overcoming of the material's rigidity, as a necessary step in the reaction [9]. It is possible by means of the shear (deviatoric) loading component of the external forces, although the hydrostatic part must also be indicated. Shear is the main mode of stress acting during grinding since only it can produce the significant microstrains observed in the ground powder, and since the crystallographic structural changes observed cannot be accounted for by the contraction of the lattice alone. From thermodynamical point of view all the components of the stress tensor under mechanical loading are legitimate intensive parameters that must be considered in determining the number of degrees of freedom of a system under non-hydrostatic equilibrium conditions. Following Kumazawa [2], a mechanical balance exists between the stress field coordinate system in a given material, and the one-dimensional equilibrium state at the transformation interface within the material (resulting from stress and strain continuity conditions across the interface). This leads to establish the condition for the co-existance of two polymorphs in the non-hydrostatic system, as follows:

$$p_1 - p_o \geq -\frac{\Delta S}{\Delta V}(T - T_o) \geq p_3 - p_o$$

where: p_o, T_o – the hydrostatic pressure and temperature of transformation, respectively. p_1, p_3 – the largest and smallest principal stresses of the non-hydrostatic system. ΔS, ΔV – the entropy and volume of transformation, respectively. At equilibrium, the widest shear interval is $p_1 - p_3 = 2\tau$, and the temperature widest interval then becomes $\Delta T = 2\tau\,\Delta V/\Delta S$. These intervals define a two-phase band about the transformation line between polymorphs in one component $p_o - T_o$ phase diagram. A point of grinding dynamical equilibrium, for a given grinding regime, actually lies within this two phase band.

The second mechanism is related to the role of capillary forces, which manifest the importance of particles size and their free surface curvature on the mechanochemical reactions. Two different solid state spherical particles of two related polymorphs will coexist in a particulate system at a given temperature if [10]:

$$G_L(\infty) + \frac{6\gamma_L}{\rho_l d_L} = G_H(\infty) + \frac{6\gamma_H}{\rho_H d_H}$$

where: $G(\infty)$ is the free-energy of the system with plane surfaces (radius of curvature-infinity), γ, ρ, d – the surface tension, density, and diameter of the particle, respectively. H, L indices stand for the high and low temperature polymorphs, respectively. Particles of the high-temperature polymorph can reappear in low temperature during grinding, if:

$$d_H < \frac{6}{(G_H - G_L)}\left(\frac{\gamma_L}{\rho_L} - \frac{\gamma_H}{\rho_H}\right)$$

provided that $\gamma_M/\rho_M<\gamma_L/\rho_L$. It means that for a particulate system after grinding a two-phase band will appear about the polymorphic transformation line in the one-component p_0 T_0 phase diagram. Each point within the band conforms with some given particle size.

When the particle size becomes very small the capillary forces spread all over the crystallite lattice. This point was demonstrated for ultrafine hematite crystallite (by means of Mössbauer-effect spectroscopy) in which, being affected by the action of adjoining free-surfaces, uniform elastic expansion of the lattice takes place [11] (analogous to the effect of negative hydrostatic pressure), counteracting the surface tension forces (by it actually the particle is 'informed' of its smallness). The fine particle is highly activated, and readily available for a relaxation process. Its smallness also facilitates the shear relaxation mechanism, mentioned above. It, therefore, became evident that the relaxation is associated with a 'reaction triggering dimension' (RTD), which depends much on the crystallographic structure and nature of atomic bonding.

Two factors may increase the RTD of a mechanochemical reaction: (the 'mechanochemical reaction availability'): (a) Topotactic relationship – which refers to a solid-state reaction in which the orientation relationship between reactant and product phases is crystallographically correlated, and much of the near-neighbour atomic configurations are conserved. It is mostly observed in coherent shear induced transformation which takes place by cooperative translational movement of atoms (resembling twinning or martensitic trasformation). Topotaxy differs from pseudomorphism – in which the solid-state reaction takes place through a sequence of metastable structures without the change of the crystallite geometrical form, which calls for a thermal long-range diffusion. Comminution, in fact, prevents pseudomorphism. (b) Low crystallographic shear constants (for low rigidity). Anisotropic matrix of elastic constants (following lower point group symmetry), together with relatively high vacancies concentration, may induce shear 'soft-modes' which will facilitate the relaxation process.

If the above factors do not prevail, a state of microcrystallinity (X-ray diffraction – observed amorphous-like state) is necessary for mechanochemical reaction availability in comminution. The same principles are obeyed for mechanochemical decomposition as for polymorphic transformation, as was explained so far. However, for mechanochemical synthesis as for agglomeration, or chemosorption of environmental gaseous species, another mechanism has to be considered.

Medelovici [12] observed that by grinding, lepidocrocite – (γ-FeOOH) decompose directly into fine hematite. The fine particles (superparamagnetic) upon further grinding agglomerate and turn to hematite single crystallites (antiferromagnetic). In the lepidocrocite every iron atom is surrounded by a distorted octahedral group of oxygen atoms, the groups linked together into layers connected through hydrogen bonding to form OH–O directed bonds between the layers. Severing the hydrogen bonds by shearing liberates the intralayer hydroxile ions from adsorbed water (which evaporates), whereas the rearrangement of the octahedra produce the hematite. However, upon further grinding, as shown by IR spectroscopy: (a) Cleavage along the close-packed oxygen framework layers yields surfaces of oxygen ions which with inner iron atoms form passive Fe–O–Fe surface groups. (b) Fracturing on other planes breaks the inner octahedral group structure to form highly active $Fe–O^-$ and $O–Fe^+$ surface groups, which enables the particles cohesion and agglomeration.

It is the active surface groups which have been formed upon particles fracturing which makes it possible to have mechanochemical synthesis taking place during the grinding. For a solid-state reaction like: AB+CD=AD+BC, surface groups such as $B–A^+$ or $A–B^-$ on AB particles, and $C–D^-$ or $D–C^+$ on CD particles, combine on matching surfaces to form AD and BC bonds. Localized short-distance accomodation diffusion (along stress gradients) completes the process.

The products after mechanochemical reaction are always highly reactive and highly loaded with point defects (in the broader sense), and well suitable for sintering and chemical processes. For example [13], the grinding of γ-alumina and active magnesium oxide powders mixture produces spinel of 0.47 degree of inversion, (namely, 47% of magnesium ions are in octahedral positions as was disclosed by neutron diffraction), comparable to 0.1 for thermally obtained spinel. Since all magnesium cations in MgO are in tetrahedral positions, and 62.5% of aluminium cations in γ-alumina are in octahedral positions, it became evident that in mechanochemical spinel 53% of magnesium ions and 14% of aluminium had to change their coordination position, comparable to 90% and 32.5% respectively in thermally-obtained spinel. It manifests the topotactic nature of the mechanochemical reactions. The grinding of thermally obtained spinels proper also increase the degree of inversion – a specific means of activation.

Zinc ferrite (normal spinel) can be synthesized [14] by prolonged grinding of α-Fe_2O_3 and ZnO powders. When the first traces of ferrite were detected the average ZnO crystallite size was 70Å, and Fe_2O_3 size 125Å. Use of $ZnCO_3$ instead of ZnO makes for faster reaction, as upon the mechanical decomposition of the carbonate the ZnO crystallites emerge in microcrystalline size. Topotaxy is obeyed since Zn^{2+} is in a tetrahedral positions in ZnO, and $Fe_2O_3–Fe^{3+}$ in octahedral positions, as in the normal spinel. The cation-anion distances are also conserved. Mechanical attempts to produce nickel ferrite from a mixture of α-Fe_2O_3 and NiO failed. Although Ni^{2+} ions conserve octahedral sites, half of the Fe^{3+} have to change positions and move into tetrahedral sites against the stress-relief tendency. When Fe_2O_3 crystallite size upon grinding reaches 125Å, NiO crystallites are still 200Å.

Magnetic effects

Differences in magnetic ordering temperatures may reflect the MC stability of ferrites. Fine particles should become superparamagnetic, and in fact zinc-ferrite is paramagnetic at room temperature. But nickel ferrite, being ferrimagnetic at room temperature, cannot be obtained from superparamagnetic hematite particles unless it loses its coericivity, which is possible below 130Å crystallite size. In fact, nickel ferrite can be obtained by grinding a mixture of γ-FeOOH and $Ni(OH)_2$, when after decomposition microcrystalline particles are formed.

In ground nickel ferrite powder, Mossbauer effect spectroscopy shows [15] that the hfs spectrum changes. Instead of two superimposed equal sextets of Fe^{3+} ions of both the octahedral and tetrahedral sites, that of the octahedral sites becomes pronounced. Also, a symmetrical doublet appears in the center. However, with equal quadropole splitting and an equal number of iron ions in both sites, while the isomer shifts differ, one should expect a non-symmetrical doublet. It was therefore inferred that during grinding tetrahedral cations move into unoccupied octahedral sites, whose space is larger. Under prolonged grinding the superparamagnetic doublets at room temperature of both ferrites become equal, as the iron cations occupy practically the same positions. Drastic magnetic changes are observed [16]. The magnetic transition temperature of $NiFe_2O_4$ drops from 858 to 260 K, whereas that of $ZnFe_2O_4$ rises from 9 to 210 K. During grinding, plastic deformation of the particles takes place – in parallel with fragmentation – by motion of partial dislocations forming CPH stacking faults in the oxygen CCP framework [17]. The magnetic coupling exchange interaction [18] between octa- and tetra-cations is much stronger in ordered spinel that between the octa-cations themselves. As the cations move into octahedral positions in a disordered distribution, and changes occur in cation-anion-cation bond angles-new exchange bond pairs form, responsible for the observed magnetic changes.

Mechanical-alloying

Coarse powdered material of different metal species are mixed and ground [19]. During grinding the particles are repeatedly flattened plastically, cold-welded, strain-hardened, and fractured. With time the particles become harder and fracture more frequent, the tendency to reweld decreases. The end particles have a layered, optically unresolvable, structure of both species, which converts readily into homogeneous solid solution upon sintering. The process is advantageous when: (a) one of the metallic elements is highly reactive or has a high vapour pressure, (b) the constituent metals differ widely by their melting points, (c) the cast alloy has a high microsegregation tendency. At first the process was used mostly for nickel-base alloys, but recently became important in production of light-element alloys based on aluminium, magnesium, lithium, and titanium, and compete economically with the atomization and rapid-solidification process. For example: an aluminium–lithium–magnesium alloy was obtained [20] by a sequence of processes as follows: aluminium–lithium master alloy powder was first obtained by thermal decomposition of $AlLiH_4$ source material under vacuum. Next it was mixed with magnesium powder and ground to form a master alloy powder of hard and brittle particles. This powder was then diluted by gradual addition of pure deoxidized aluminium powder, so as to prevent sticking of its particles to the grinding elements, and avoid agglomeration. The whole process took place under vacuum in a vibratory mill. The powder obtained is free from oxide and nitride inclusions. The technology is simple since being carried out at room temperature.

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