

Chapter 2

High-Energy Milling

2.1 Introduction

Particle size reduction, or comminution is an important step in many technological operations. The process itself is defined as the mechanical breakdown of solids into smaller particles without changing their state of aggregation [Bernotat and Schönert 1998]. It may be used to create particles of a certain size and shape (including nanosize), to increase the surface area and induce defects in solids which is needed for subsequent operations such as chemical reactions, sorption, etc. Milling not only increases the surface area of solids. It is likely to increase the proportion of regions of high activity in the surface. This increase is really dramatic: if a cubic solid is broken down into smaller cubes, each of side $1/n$ of the side of the original cube, the specific surface area is increased n -times, but the broken down mass contains n^2 -times the original length of edge and n^3 -times the number of corners [Welch 1953].

The size reduction of solids is an energy intensive and highly inefficient process: 5% of all electricity generated is used in size reduction [Rhodes 1998].

Conventionally, the term fine milling is used for size range below $100\text{ }\mu\text{m}$ and the ultrafine (or very fine) milling for particles size less than $10\text{ }\mu\text{m}$. In mechanochemistry, the term high-energy milling is frequently used in order to stress the character of applied milling equipments (mills) [Boldyrev 1983; Baláž 2000].

The chapter is intended as an introduction to the topic of high-energy milling and milling equipments used for preparation of micro- and nanosized solids.

2.2 Basic Phenomena

Consider a crystal of sodium chloride NaCl as a simple and convenient model of a brittle material. Such a crystal is composed of a lattice of positively charged sodium ions and negatively charged chloride ions arranged such that each ion is surrounded by six ions of the opposite sign. Between the oppositely charged ions there is an attractive force whose magnitude is inversely proportional to the square

of the separation of the ions. There is also a repulsive force between the negatively charged electron clouds of these ions which becomes important at very small interatomic distances. Therefore two oppositely charged ions have an equilibrium separation such that the attractive and repulsive forces between them are equal and opposite. Figure 2.1 shows how the sum of the attractive and repulsive forces varies with changing separation of the ions. It can be appreciated that if the separation of the ions is increased or decreased by a small amount from the equilibrium separation, there will be a resultant net force restoring the ions to the equilibrium position. The ions in the sodium chloride crystal lattice are held in equilibrium positions governed by the balance between attractive and repulsive forces. Over a small range of interatomic distances the relationship between applied tensile or compressive force and resulting change in ion separation is linear. That is, in this region (AB in Fig. 2.1) Hooke's law applies: strain is directly proportional to applied stress. The Young's modulus of the material (stress/strain) describes this proportionality. In this Hooke's law range the deformation of the crystal is elastic; i.e. the original shape of the crystal is recovered upon removal of the stress [Rhodes 1998].

In order to break the crystal it is necessary to separate adjacent layers of ions in the crystal and this involves increasing the separation of the adjacent ions beyond the region where Hooke's law applies – i.e. beyond point B in Fig. 2.1 into the plastic deformation range. The applied stress required to induce this plastic behaviour is known as the elastic limit or yield stress, and is sometimes defined as the material's strength [Rhodes 1998].

A body under stress stores energy-strain energy. This strain energy is not uniformly distributed throughout the solid but is concentrated around holes, corners and cracks.

The theory of crack formation and propagation has been well demonstrated in literature [Griffith 1920; Smekal 1922, 1936; Rumpf 1962, 1966; Schönert and Weichert 1969; Schönert and Steier 1971; Schönert 1974]. It was postulated that for

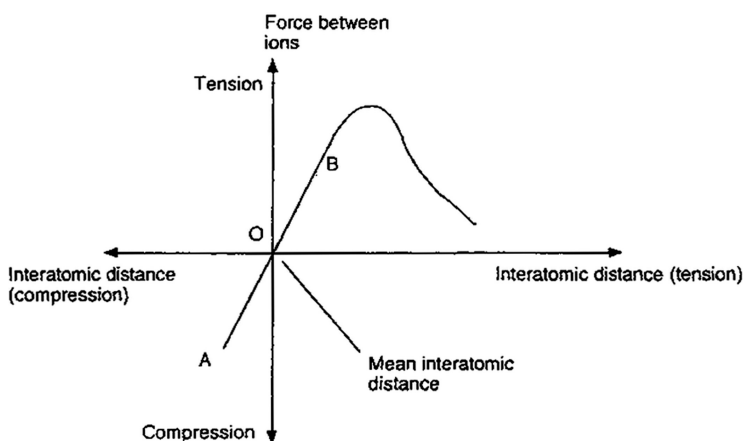
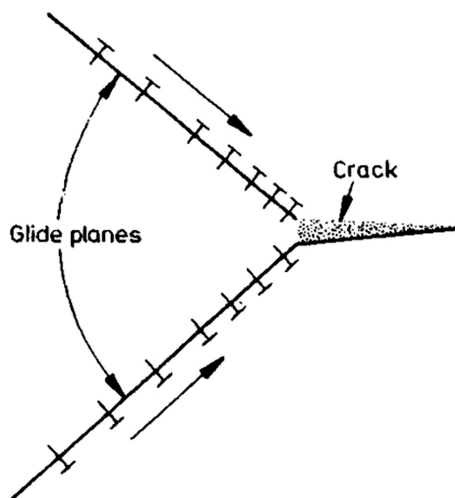


Fig. 2.1 Forces versus distance on an atomic scale [Rhodes 1998]

Fig. 2.2 Formation of a crack along the intersection of glide planes [Cottrell 1958]



fracture to occur the propagation of cracks has to be promoted, and the condition that should lead to a fracture is that a certain minimum length of the microcracks (defect sites) should be formed [Griffith 1920].

This concept was later modified in works of Cottrell who stated that such cracks can also be created by the coalescence of dislocations in solids (Fig. 2.2). According to this model microcracks can develop and dislocations can coalesce at the interfaces of crystals, or at the intersection of two dislocations, or in the case of mosaic structure, at the boundaries of the blocks [Cottrell 1958].

Fracture is a problem of energetics. The propagation of the initially-formed cracks requires that the energy of elastic deformation should be at least as high as the interfacial energy of the system [Griffith 1920]. It was pointed out that fracture energy was much higher than surface free energy [Rumpf 1961, 1966; Schönert and Weichert 1969; Schönert and Steier 1971; Schönert 1974]. Thus, the specific surface energy of solids is about $0.05\text{--}0.5\text{ Jm}^{-2}$, whereas the specific fracture energy for brittle solids is 5 Jm^{-2} , for plastic solids it is 10 Jm^{-2} , and for metals is approximately 500 Jm^{-2} .

2.3 Energy Requirement

In milling practice the quantitative measures of energetics attracted attention for a long time. The literature on the problem is quite extensive and the theories of Rittinger, Kick-Kirpičev and Bond deserve to be mentioned.

Rittiger proposed that the energy required for particle size reduction was directly proportional to the area of new surface created

$$E = C_R \left(\frac{1}{x_2} - \frac{1}{x_1} \right) \quad (2.1)$$

where C_R is constant and x_1 is the starting and x_2 the final particle size [Rittinger 1867].

However, this law ignores the energy absorbed by elastic deformation which is several times greater than that required for creation of new surfaces.

On the basis of stress analysis theory for plastic deformation Kirpičev and independently Kick proposed the energy required for particle size reduction was directly proportional to the ratio of the volume of the feed particle to the product particle [Kirpičev 1874; Kick 1883]

$$E = C_K \ln \left(\frac{x_1}{x_2} \right) \quad (2.2)$$

The main drawback of this theory is that the same energy is required to reduce 10 μm particle to 1 μm as is required to reduce 1 m boulders to 10 cm blocks [Rhodes 1998]. This is a simplification which cannot be accepted especially in the fine and ultrafine milling.

Bond suggested a more useful formula where the total energy that is specific to any size is inversely proportional to the square root of the particle size [Bond 1952]

$$E = C_B \left(\frac{1}{\sqrt{x_2}} - \frac{1}{\sqrt{x_1}} \right) \quad (2.3)$$

In milling practice the formula (2.3) is applied in the modified form which enables determination of the Bond work index W_i . W_i is defined as the energy required to reduce the size of unit mass of material from infinity to 100 μm in size.

It is common fault of all three theories that they do not take account of particle size distribution of the feed and the product, nor do they take account of particle interactions and the energy consumed by plastic deformation [Juhász and Opoczky 1990].

Attempts have been made [Holmes 1957; Charles 1957; Hukki 1961] to find the general formula for which proposals of Rittinger, Kick-Kirpičev and Bond are special cases. These attempts concluded that these three proposals can be considered as being the integrals of the same differential equation

$$\frac{dE}{dx} = -C \frac{1}{x^N} \quad (2.4)$$

with

$N = 2$, $C = C_R$ for Rittinger

$N = 1$, $C = C_K$ for Kick-Kirpičev

$N = 1.5$, $C = C_B$ for Bond

2.4 Milling Equipments

Besides of energy considerations, especially for the energy consumed by plastic deformation, the form of mechanical activation in high-energy milling is important. The main stress types applied are compression, shear (attrition), impact (stroke) and impact (collision), Fig. 2.3.

The multi-stage character of mechanical activation requires the application of high-energy mills with different working regimes.

The principles of most frequently mills applied in high-energy milling are shown in Fig. 2.4.

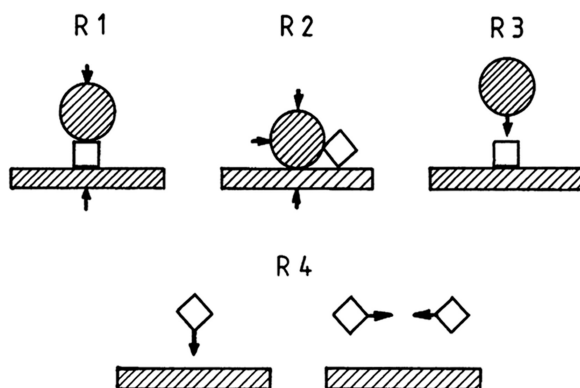


Fig. 2.3 Main stress types in mills, R1 – compression, R2 – shear (attrition), R3 – impact (stroke), R4 – impact (collision), *circle* – mass of milling media, *square* – mass of material charge, *rectangle* – mass of mill wall [Heinicke 1984]

When using mills with application of balls as milling media, different motion of the balls can be observed (Fig. 2.5). The motion can be described as cascading (A), falling or cataracting (B) or centrifugal (C).

2.4.1 Vibration Mills

A vibration mill is an reservoir or tank-like type of mill containing material and milling media, either wet or dry. The milling chamber is set in motion along a circular or elliptic trajectory by the rotation of out-of-balance weights. The three dimensional motion involves four factors: the speed of the vibration, the horizontal amplitude, the vertical amplitude and the phase angle [Klimpel 1997]. The acceleration of the vibration motion is specified by its frequency and amplitude.

The performance of a laboratory mill (Fig. 2.6) is characterized by high frequencies (usually up to 25 rev s^{-1}) but low amplitudes (2–4 mm).

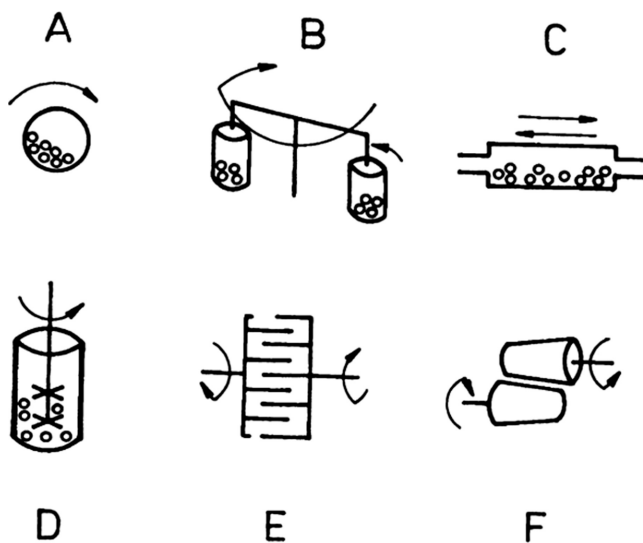


Fig. 2.4 Types of mills for high-energy milling (the stress type is given in parenthesis): (A) ball mill (R1–R4), (B) planetary mill (R1–R4), (C) vibration mill (R1–R4), (D) attritor – stirring ball mill (R1–R4), (E) pin mill (R4), (F) rolling mill (R1–R2) [BOLDYREV 1986]

Industrial mills operate at frequencies $16\text{--}19\text{ rev s}^{-1}$ and amplitudes below 6 mm. The acceleration scarcely exceeds 10-times the gravitational acceleration (10 g). There is a tendency in the design of vibration mills in an increase the amplitude to 7–10 mm at frequencies sufficient to transport the charge. This will allow acceleration of the vibration motion to the values 12–20 g [TKÁČOVÁ 1989].

Milling media are usually balls, cylpebs or rods with degree of filling 70–80%. The application of balls predominates, rods are preferred for coarse milling, cylpebs are preferred for pulverizing [SCHUBERT 1989].

The theory of vibration mills was elaborated [BACHMANN 1940]. According to ROSE high frequency vibration is to be preferred and it is essential that the

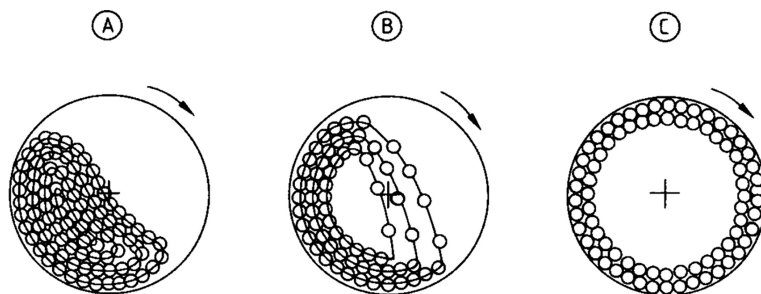


Fig. 2.5 Types of motion in a ball mill: (A) cascading, (B) falling or cataracting, (C) centrifugal [BERNOTAT and SCHÖNERT 1998]



Fig. 2.6 Laboratory vibration mill

dimensions of the milling bodies should be adjusted to the strength and particle size of the feed [Rose and Sullivan 1961; Rose 1962]. In the opinion of Bernhardt and Heegn the amplitude of the vibration mill and the quantity of the feed is prime importance in mechanical and mechanochemical activation [Bernhardt and Heegn 1976a, b; Heegn 1989].

Vibration mills are frequently applied for the preparation of very fine products and in case of induced mechanical activation the nanosized particles have been prepared [Baláž 1981]. Mechanical activation of solid, if performed in this type of mill, usually requires long milling times and is often carried out as a batch process. However, the residence time can be reduced to less than 30 minutes and mechanical activation is in principle possible also in continuously operation vibration mills [Husemann et al. 1976; Tkáčová et al. 1993].

An important disadvantage of vibration mills is their low output. Because of the high-input of energy and the low throughput of material, the high temperatures are developing in the mill. The high temperature is caused by the fact that the mill is almost completely filled and by the complex trajectory of the grinding bodies within the mill [Schubert 1989].

The new concept of vibration mills working in “eccentric” mode has been introduced by Gock et al. [Beenken et al. 1996; Gock and Kurrer 1996, 1998, 1999; Kurrer and Gock 1997] and applied in milling practice (Fig. 2.8).

Unlike conventional vibratory mills with circular vibrations, this machine performs elliptical, circular and linear vibrations (Fig. 2.7). As a result of dismissing the homogeneous circular vibrations, the motion process drastically changes: the amplitude of the vibrations of the individual milling media increases, the rotation speed of the grinding media filling increases and the direction of motion is irreversibly set. Apart from the surface area enlargement, eccentric vibratory milling with 30 mm diameter balls have led to a mechanical activation of the material.

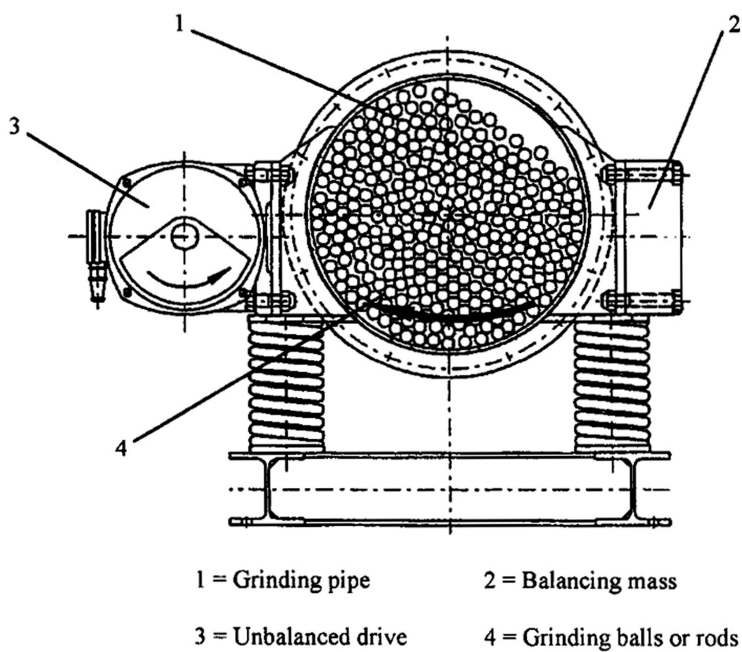


Fig. 2.7 Diagrammatic view of the eccentric vibration mill [Gock and Kurrer 1999]

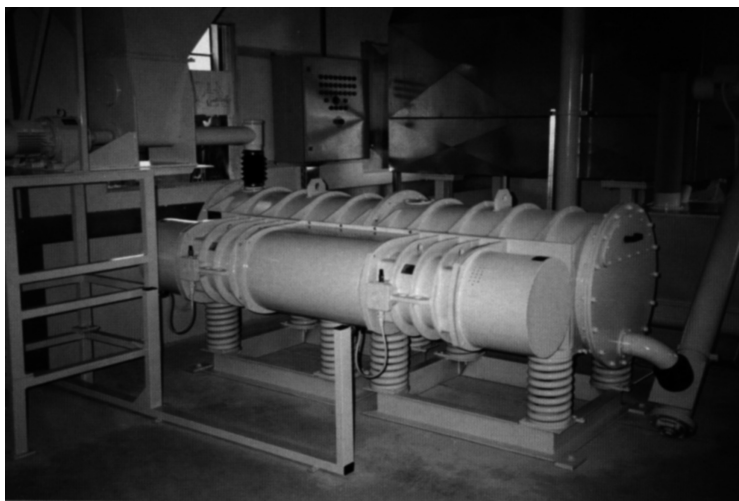


Fig. 2.8 Industrial eccentric vibration mill ESM 656 (Siebtechnik, Germany) [<http://www.siebtechnik.com>]

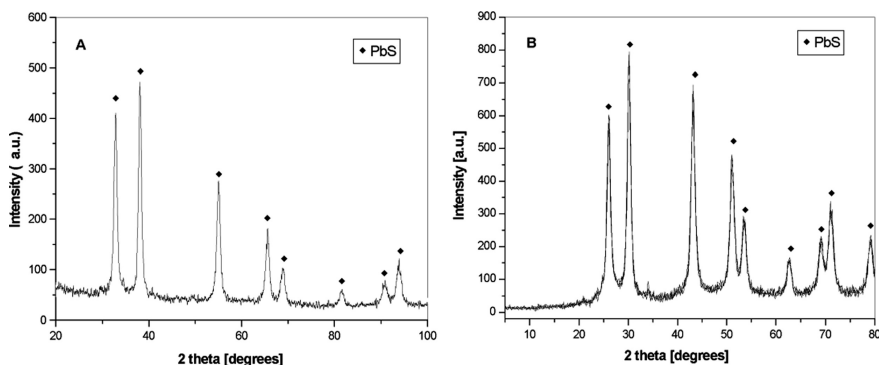


Fig. 2.9 XRD patterns of PbS nanoparticles mechanochemically synthesized in a laboratory (A) and in an industrial mill (B) [Baláž et al. 2004]

Recently, various mechanochemical synthesis of the new nanosized materials have been performed with this type of mill [Baláž et al. 2004, 2005; Godočková et al. 2006]. XRD patterns of synthesized PbS semiconductor particles are given in Fig. 2.9. The values of 18 nm and 13 nm were estimated for PbS nanocrystallites prepared in laboratory mill and industrial mill, respectively.

The grain size of the ball-milled solids are found to decrease with milling time down to a constant value. An advantage of the use of high-energy milling is the possibility to introduce large strains and produce nanocrystalline structures. The product of milling is powder, typically a few micrometers in diameter, with the internal nanocrystalline structure [Koch 1993].

2.4.2 Planetary Mills

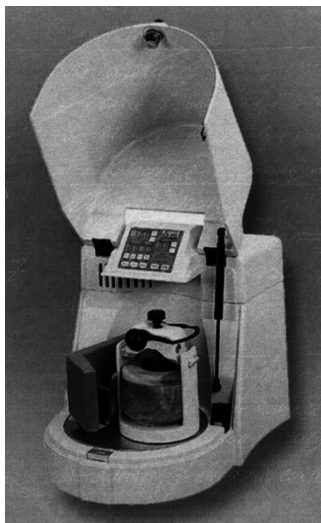
The planetary ball mill (Fig. 2.10) owes its name to the planet-like movement of its vial (s) (Fig. 2.4). Since the vials and the supporting disc rotate in opposite directions, the centrifugal forces alternatively act in like and opposite directions. This causes the milling balls to run down the inside wall of the vial – the friction effect, followed by the material being milled and milling balls lifting by of and travelling freely through the inner chamber of the vial and colliding against the opposite inside wall [Suryanarayana 2001].

Planetary mills exploit the principle of centrifugal acceleration instead of gravitational acceleration. The enhancement of the forces acting on the balls in relation to the conventional ball mill is achieved by the combined action of two centrifugal fields [Golosov 1971; Molčanov et al. 1988].

The charge inside vials performs two relative motions: a rotary motion around the mill axis and a planetary motion around the vial axis (Fig. 2.11).

The application of laboratory-scale planetary mills for mechanical activation has been studied intensively by Russian scientists [Golosov 1971; Molčanov et al. 1988;

Fig. 2.10 Laboratory planetary mill Pulverisette 6 (Fritsch, Germany) [<http://www.fritsch.com>]



Molčanov and Jusupov 1981; Avvakumov 1986]. Their general conclusion was that, by observing certain conditions, these mills produce high mechanical activation after a relatively short milling time. In principle, it is possible to obtain the gravitational accelerations in values 50–100 g. The energy density in these mills is 100–1000 higher than the energy density used earlier in conventional milling equipments [Fokina et al. 2004].

However, it was noted that manufacturing of high throughput rate encounters design difficulties. During the past decades the problem of continuous feeding of

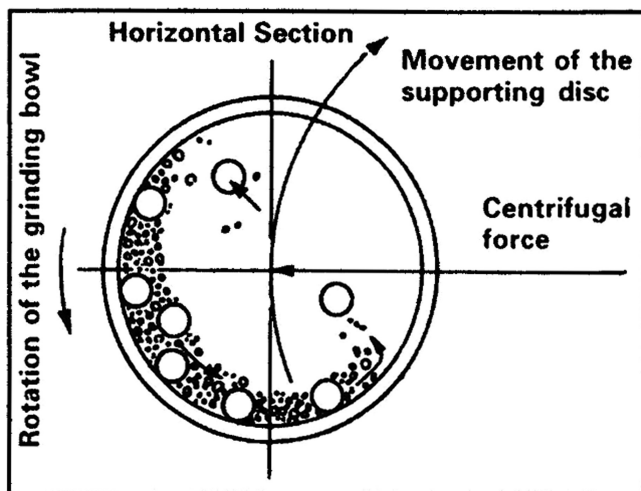


Fig. 2.11 Movements of working parts and balls in a planetary mill

a material into a planetary mill has been successfully solved and novel planetary mills of the industrial scale operating in a continuous mode are now manufactured [Kochnev 1992; Kochnev and Simakin 1994]. In this mode the initial material is continuously fed into the mill, with coarser powder returned for another cycle of milling and the final fine or nanoscale powder product continuously provided as a result of the milling process. The productivity per unit volume of the working chamber for these mills is significantly higher (at least ten times) than that of conventional ball mills. Industrial planetary mills of continuous action, characterized up to 20 g acceleration and by productivity up to 3–5 tons of powder (of minus 10 micrometers fraction) per hour, are now-commercially available [<http://www.ttd.spb.ru>].

2.4.3 Mixer Mills

Special mills have been developed in the USA under the trade name Spex mills (Fig. 2.12). The common variety of the mill has one vial containing the sample and milling balls, secured in the clump and swung energetically back and forth several thousand times a minute. The back- and- fourth shaking motion is combined with lateral movements of the end of the vial, so that the vial appears to be describing a figure eight or infinity sign as it moves. The vial is vibrated with an amplitude 50 mm and a frequency of 20 Hz. These mills can be considered as high-energy variety [Koch 1993].



Fig. 2.12 Laboratory mixer mill Spex 8000 (CertiPrep, USA) [<http://www.utk.edu>]

2.4.4 Attritors (*Stirred Ball Mills*)

The attritor was invented in 1922 by Szegvari in the USA for a quick dispersion of fine sulphur particles needed to complete the vulcanization of rubber. After patenting the principle of attritor in the fifties in the USA, in 1956 the license for their manufacturing was transferred to Germany. This type of mill originally used for applications in chemical and pharmaceutical industry was later applied for powder and extractive metallurgy. An attritor was the first high-energy mill used for preparation of materials by mechanical alloying [Benjamin 1970].

Attritors (attrition mills, stirred ball mills) consist of a cylindrical grinding chamber with a drive shaft having multiple impellers sticking out from the rotating shafts (Fig. 2.13). There is a wide variety of impeller types including flat discs, discs with various geometric openings, and concentric rings. This rotating shaft puts the fine media, particles and, possibly a liquid into a stirring motion. The impellers energize the balls charge, causing powder size reduction because of impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers [Baláz 2000]. Common media materials are glass, sand, alumina, zirconia, silicon carbide, steel, rubber, polyurethane and various plastics. Typical media sizes can range from 0.5 to 4 mm in diameter. The density of the media used is important because the media need to move through the mix of particles, media and fluids. Cover seals can be provided for processing under an atmosphere [Klimpel 1997].

Attritors use the comminution intensity between the contact surfaces of moving balls, similar to the operation of conventional ball mills, but without the disadvantages of the latter [Klimpel 1997; Püpke 1971; Netzsch 1974]. The most important

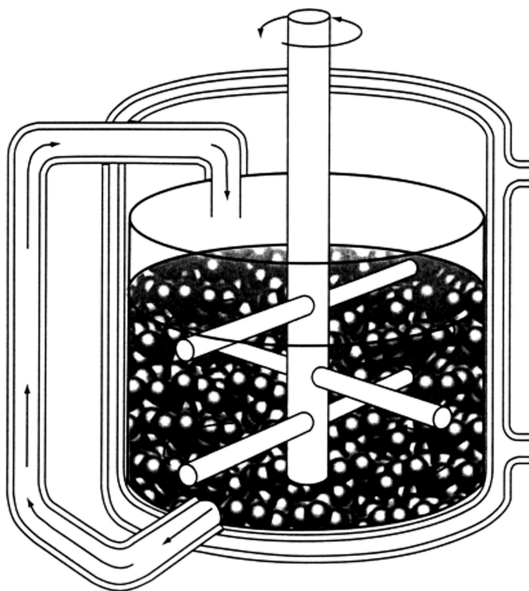
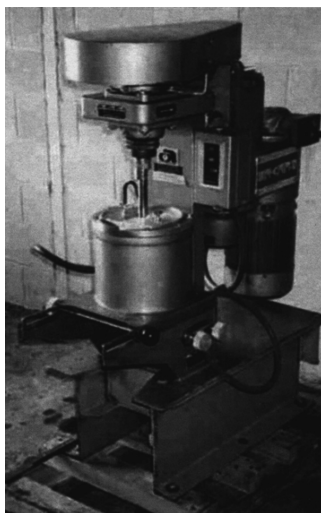


Fig. 2.13 Diagrammatic view of the attritor [Klimpel 1997]

Fig. 2.14 Laboratory attritor PC 2043 of batch mode of operation (Union Process, USA) [<http://www.unionprocess.com>]



concept in the attritor is that the power input is used directly to agitating media to achieve milling. It is not used for rotating or vibrating a heavy grinding chamber in addition to the media.

Attritors can be operated wet or dry, in batch, circulation a continuous mode. Batch attritors (Fig. 2.14) are used to process hard-to-mill materials, such as tungsten carbide, silicon carbide and various metals. The circulation attritor is a combination of an attritor and a holding tank.

The high circulation rate is achieved in this system. One advantage of the circulation is that large quantities of material can be handled. Continuous attritors are best suited for the continuous production of large quantities of material (Fig. 2.15).

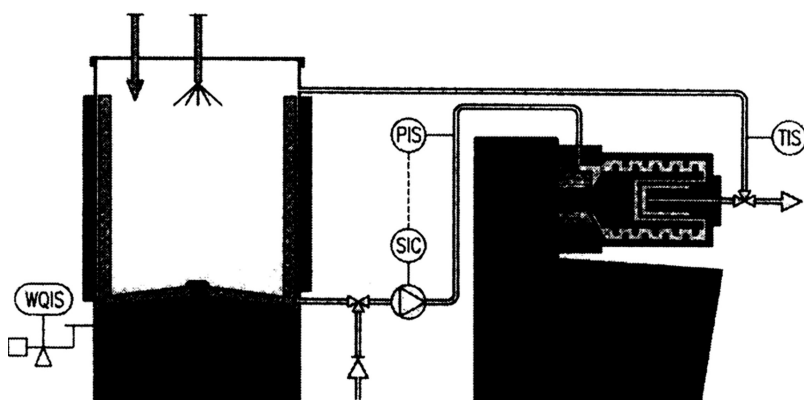


Fig. 2.15 Industrial attritor LMZ 25 of continuous mode of operation (Netzsch, Germany) [<http://www.netzsch.com>]

It was demonstrated that this type of mill may, in some instances, offer certain advantages in comparison to other mills, e.g. vibration mills [Heegn et al. 1974, 1980]. If strontium ferrate is activated in a vibration mill then extensive amorphisation takes place even after brief milling. This result was detrimental to the later use of this material because of deterioration of its magnetic properties. In contrast, when milling was carried out in an attritor, the specific surface increased monotonously while crystallinity was either preserved or it decreased much less than on milling in a vibration mill.

Balázš documented the differences in vibratory and attrition milling on changes of chalcopryrite milling (Fig. 2.16). From this Figure it is evident, that the products of milling in an attritor and vibration mill differ in specific structural disordering. According to the published data, these differences are due to the differences in milling environment and ball dimensions [Boldyrev 1983]. It is known that milling in aqueous environment and/or the use of small balls is more favourable for new surface formation whereas dry milling and/or the use of larger balls favour amorphization.

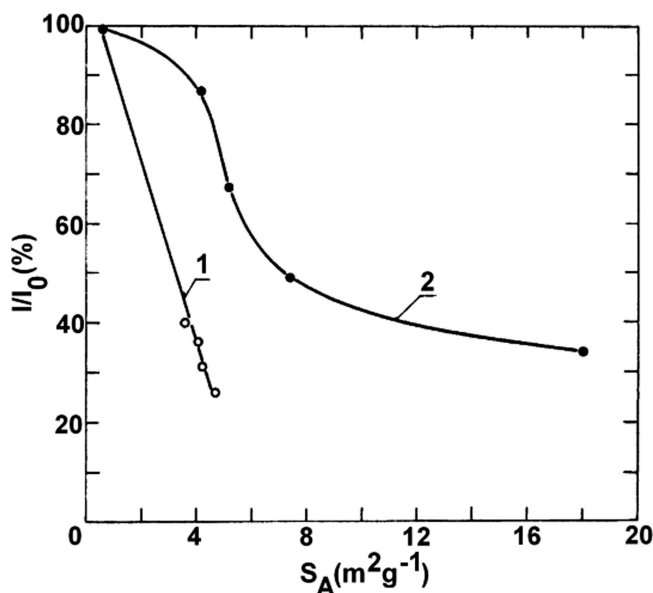


Fig. 2.16 The relative intensity of the selected diffraction line, I/I_0 vs. specific surface, S_A of chalcopryrite CuFeS_2 mechanically activated in a vibration mill (1) and in an attritor (2) [Balázš 2000]

2.4.5 New Mill Design

The brief review presented obviously could not cover all features of high-energy mills. Special new designs of mills have been developed in recent years for specialised purposes. The selected examples are given bellow and this list is, of course, not complete.

Nishin Giken (Tokyo, Japan) has developed the mill with the ability to control the temperature of milling from very low temperatures by spraying liquid nitrogen up to a high temperature of 300°C by electrical heating [http://www.nishineng.com]. In Australia concepts of magnetic mechanical milling and electric-discharge-assisted mechanical milling have been developed [Calka and Wexler 2002]. This concept of milling enhancement can result in both faster reactions and new synthesis and processing routes. In Italy a new high-energy mill for the synthesis of nanophase materials in large quantities has been designed and developed as described in [Miani and Maurigh 2004]. ZOZ company designed several new concepts of attrition mill scalable for production of nanosized materials [http://www.zoz.com].

2.4.6 Process Variables

There are several variables which influence the milling process (see e.g. Fig. 2.17).

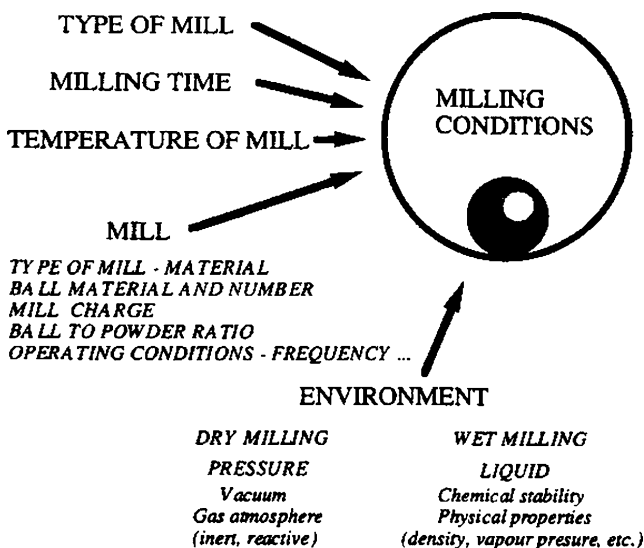


Fig. 2.17 An overview of the main factors to be considered in the milling process [Campbell and Kaczmarek 1996]

2.4.6.1 Type of the Mill

Usually specially designed mills are applied for special purposes. Sometimes the stress mechanism is decisive for particle size reduction in the mill, sometimes it is the size of the feed and the product size distribution which are most important [Rhodes 1998].

2.4.6.2 Material of Milling Media

The material used for the milling media (milling chamber, vial, balls) is important due to impact of the milling balls on the inner walls of the milling chamber. Some specific materials are used for specialized purposes [Suryanarayana 2001]. Commonly materials include various steels (stainless, tool, hardened chromium, tempered, bearing steel and tungsten carbide lined), tungsten carbide, zirconia, agate, alumina and silicon nitride. The specific gravity plays an important role. In general, high-density and larger balls give better results because of high impact forces on the powders. The balls should be more dense than the material to be milled.

Even though most of the investigators generally use only one size of the milling medium, there have been instances where different size balls have been used in the same investigation. It has been predicted that the highest collision energy can be obtained if balls with different diameters are used [Suryanarayana 2001].

Use of milling balls of the same size has been shown to produce tracks. Consequently, the balls roll along a well-defined trajectory instead of hitting the end surfaces randomly. Therefore, it is necessary to use several balls, generally a combination of smaller and larger balls to “randomize” the motion of the balls [Rhodes 1998; Suryanarayana 2001; Takacs and Pardavi-Horvath 1994].

The properties of materials used as milling media are given in Table 2.1.

Table 2.1 Milling media in high-energy milling [<http://www.fritsch.com>]

Material	Main composition	Density (g cm^{-3})	Abrasion resistance
Agate	SiO_2	2.65	Good
Corundum	Al_2O_3	> 3.8	Fairly good
Zirconium oxide	ZrO_2	5.7	Very good
Stainless steel	Fe, Cr, Ni	7.8	Fairly good
Tempered steel	Fe, Cr	7.9	Good
Tungsten carbide	WC, Co	14.7–14.9	Very good

2.4.6.3 Ball-to-Powder Ratio

The ball to powder ratio (BPR) or charge ratio is another milling parameter and represents the weight ratio of the milling balls to the powder charge. A wide range of BPR have been used in a variety of investigations from values as low 1:1 to as high 220:1 [Suryanarayana 2001].

2.4.6.4 Extent of Filling of the Milling Chamber

It is necessary that there is enough space for the balls and the powder particles to move around freely in the milling chamber. The filling depends on type of mill. Generally about 50% of the space is left empty [Suryanarayana 2001] but in attritors this value is 20–30%.

2.4.6.5 Milling Atmosphere

The milling atmosphere can contaminate the powder and as a results milling is frequently carried out in evacuated, argon, or helium charged milling chambers [Suryanarayana 2001]. Other atmospheres can be used if particular effects are desired. Nitrogen and ammonia have been used to produce nitrides and hydrogen atmospheres to produce hydrides [Calka 1991; Calka and Wexler 2002; Calka and Radlinski 1991; Ogino et al. 1993; Chen et al. 1990, 1995; Schulz et al. 1995; Murty and Ranganathan 1998]. The intention application of hydrogen in milling chamber was a real breakthrough in hydrogen storage technology for synthesis of nanocrystalline hydrides. The presence of air in the milling chamber can result in the formation of oxides, oxisulphates or sulphates [Baláž 2000]. Contamination can be avoided by milling the powders with a milling media made up of the same material as that of the powders being milled.

2.4.6.6 Milling Speed

The milling speed can have an important influence but this varies with the type of mill. Above a certain critical speed, the balls will be pinned to the walls of the milling chamber and not exert any impact force on the powder. Below this critical speed, however, the higher the milling speed, the higher the milling intensity will be. For the higher speeds the temperature of the milling chamber may reach a high value [Suryanarayana 2001].

2.4.6.7 Milling Time

According to many researchers the milling time is the most important milling parameter. However, the level of contamination will increase with milling time and some undesirable phases may form if a powder is milled too long. Substantial reduction in particle size usually occurs with milling time and typically takes the form of exponential decay.

2.5 Accompanying Phenomena

2.5.1 Temperature Effects

Since diffusion processes are involved in the formation of a nanostructure, it is expected that the temperature of milling will have a significant effect. Two kinds of temperature effects during milling are usually taken into account: local temperature pulses due to ball collisions and the overall temperature in a vial. During the milling

process part of the milled powder is attached to the vial walls and, other part is attached to the balls. The remaining part is in a free state moving in the volume of the milling chamber. All these parts have different temperatures [Suryanarayana 2001].

The temperature of the powder influences the diffusivity and defect concentration in the powder thus influencing the phase transformations induced by milling. The results of measurement and calculation of the milling temperatures show that there is only a moderate temperature rise during milling and that local melting can be ruled out [Murty and Ranganathan 1998]. Bi powder was milled and the temperature of milling was calculated. The value was below its melting point 271°C [Koch 1997].

The temperature increase of the milling balls in two laboratory mills was studied recently [Takacs and McHenry 2006]. The ball temperature remains below 100°C in a SPEX mixer mill and it is cooler when flat-ended rather than round-ended vial is used. Temperatures over 200°C are typical in a planetary mill operating at similar milling intensities. The results presented in Fig. 2.18 were obtained using a Fritsch P-5 mill with two vial sizes and rotational speeds. The final temperatures are indeed much higher than the temperatures obtained with the SPEX 800 mill. The temperature could be increased further via increasing the speed of the mill. In fact, the highest temperature obtained with the smaller bowl was 327°C at 318 rpm. A decrease of the temperature is expected at very high speeds, as the balls stay attached to the container wall for too long, reducing both heating and efficiency of milling [Abdellaoui and Gaffet 1996]. It is suggested that the higher ball temperatures result from more oblique collisions and friction, while the lower temperature but higher intensity of the mixer mill with flat-ended vial is due to the larger portion of frontal impacts.

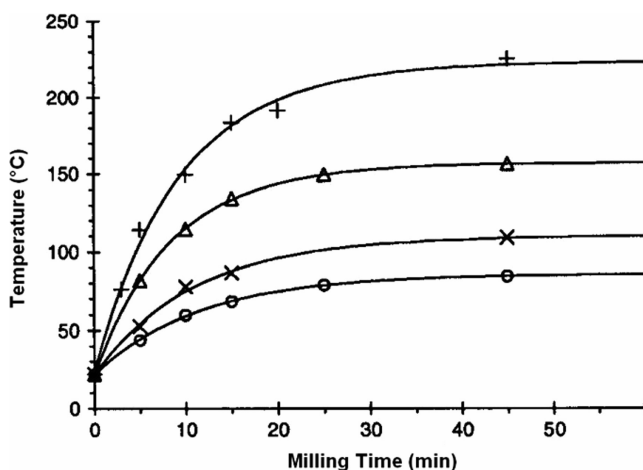


Fig. 2.18 Ball temperature-milling time curves obtained using a Fritsch P-5 planetary mill. The (+) and (x) symbols represent data with a 10-cm diameter milling bowl and 100 balls and 280 rpm (+) and 200 rpm (x) speeds and the (Δ) and (o) symbols correspond to a 7.5-cm bowl, 50 balls and 280 rpm (Δ) and 200 rpm (o) speeds [Takacs and McHenry 2006]

2.5.2 Contamination

The serious problem which is usually cited in mechanochemical research is contamination. The small size of milled particles, availability of large surface area, and formation of new surfaces during milling all contribute the contamination of the powder [Suryanarayana et al. 2001]. As mentioned above, the milling atmosphere can be one source. However, if steel balls and milling chambers are used iron contamination can contribute as a further factor. It is most serious for the high-energy mills. Low-energy mills result in much less, often negligible Fe contamination. Other milling media, such as tungsten carbide or ceramics, can be used but contamination from such media is also possible. Surfactants (process control agents) may also be used to minimize contamination. Using a “seasoned” milling chamber – i.e. media coated with the product powder – resulted in very low values for Fe contamination [Davis and Koch 1987; Koch 1997]. Application of shortest milling times and self-coating of the balls with milled material can be also helpful [Suryanarayana et al. 2001].

2.5.3 Amorphization

During high-energy milling, the size of crystals decreases to some critical values. Further energy supply to these crystals of limiting size causes further deformation of crystals, energy accumulation in the volume or at the surface of crystals, and subsequently amorphization [Boldyrev and Tkáčová 2001].

The occurrence of an amorphous phase is generally interfered by observing the presence of broad peaks in the X-ray diffraction patterns. It is not possible to distinguish among solids which are truly amorphous, extremely fine grained or a solid in which very small crystals are embedded in an amorphous matrix. Hence, it has been the practice to recognize such observations as “X-ray amorphous”, suggesting that the identification was done only by X-ray diffraction methods. It is desirable that the X-ray diffraction observations are confirmed by other techniques as well [Suryanarayana 2001].

2.5.4 Mechanochemical Equilibrium

The objective of high-energy milling is the preparation of a milled material having the finess suitable for further application. However, this particle size reduction is, in many cases, complicated by particle size enlargement where smaller particles are put together to form larger entities in which the original particles can still be identified. Experience shows that after achievement of a certain degree of dispersion further comminution is reduced, or there may even be an increase of particle size, due to the interaction of particles [Juhász and Opoczky 1990].

In a typical experiment, copper was milled in a mill loaded with steel balls for 110 hours followed by separation of milled material in a 60 μm sieve [Hüttig 1943]. Both the coarse and the fine fractions were milled for another 48 hours and a product of approximately the same sieve analysis was obtained because of the comminution of the coarse fraction and aggregation of the fines. Hüttig called the particle size distribution and he demonstrated the same phenomenon with other brittle materials. On the basis of these experiments Hüttig postulated the existence of an “equilibrium state of comminution”.

Tanaka suggested the following equation for characterizing the kinetics of milling

$$S_{\infty} = S_{\infty} \left(1 - e^{-kW_z} \right) \quad (2.5)$$

where W_z is the energy input, S_{∞} the specific surface at equilibrium and k a constant [Tanaka 1958].

Later the process of new surface area formation was described by equation

$$S = S_m \left(1 - e^{-k_2 t} \right) \quad (2.6)$$

where S is specific surface after time t and S_m is maximum specific surface [Chodakov 1972]. Constant k_2 implies the significance of rate constant of new surface formation. Equation (2.6) describes also processes in which the formation of new surface is limited by milling equilibrium after a certain time of milling.

Jimbo described the phenomenon characterized by the increase of the size, the decrease of the specific surface area and the specific total pore volume with the increase of milling time as “the negative grinding phenomenon” [Jimbo et al. 1990]. This phenomenon is in a very close relation to the aggregation and agglomeration effects discussed in the next paragraph.

2.5.5 Agglomeration and Aggregation

In the course of the milling process a gradual deterioration of effectivity is to be observed. The energy input proportional surface increase gets impossible to obtain. A first explanation in mechanochemistry was given in the year 1937: with decrease of particle size, the number of defect locations runs out hence the increase of milling resistance, at extreme dispersity is approached [Smekal 1936]. Equations (2.5) and (2.6) can be applied for the mathematical description of such process. As it is well known in mechanochemistry, attaining a certain value, the surface area begins to diminish. In Fig. 2.19 the characteristic plots are given for several sulphides after application of high-energy milling.

Thorough investigation of this process on several solids has shown [Opoczky 1977; Beke 1984; Juhász and Opoczky 1990] that three stages can be clearly distinguished:

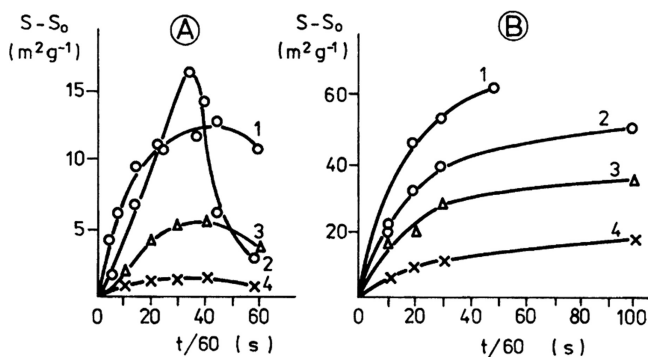


Fig. 2.19 Specific surface area, $S - S_0$ vs. time of mechanical activation, t: 1 – FeS_2 , 2 – ZnS , 3 – FeS , 4 – PbS , A – milling in air, B – milling in H_2O , S_0 – specific surface area of non-activated solid [Avvakumov 1986]

- the *Rittinger stage*, in which the interaction of particles can be neglected and the energy input is approximately proportional to the new surface area formation (Fig. 2.20a);
- the *aggregation stage* in which the new surface area produced is not proportional to the energy input because of particle interaction (aggregation). However, the degree of dispersion is still increasing significantly (Fig. 2.20b). The particles adhere on each other. This adherence takes place without structural changes in consequence of van der Waals forces of the magnitude $0.04\text{--}4 \text{ kJmol}^{-1}$. These aggregates can be dissolved by slight mechanical intervention;
- the *agglomeration stage* in which the increase in dispersion first drops to a negligible value then stops altogether; it may even give way to a decrease of surface area because of particle interaction (agglomeration). Here particles are grown

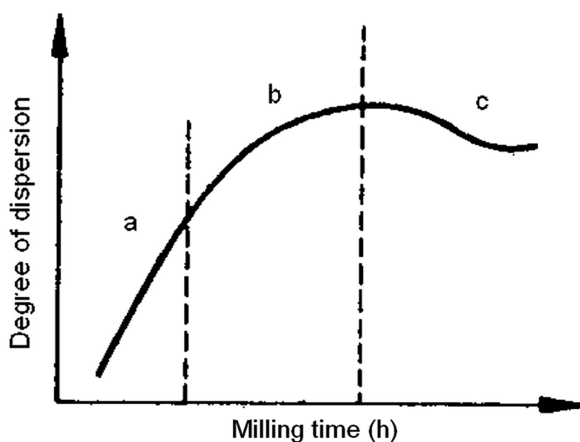


Fig. 2.20 Three stages during high-energy milling [Opoczky 1977]

together by chemical bonds of the magnitude $40\text{--}400\text{ kJmol}^{-1}$ and separation becomes impossible (Fig. 2.20c). Mechanochemical reactions and changes in the crystal structures mainly occur at this stage.

To obtain agglomerates, binding forces must act between the particles. The possible mechanism can be divided into the following major groups: solid bridges (1), interfacial forces and capillary pressure at freely movable liquid surfaces (2), adhesion and cohesion forces at not freely movable binder bridges (3), attraction forces between solid particles (4) and form-closed bonds (5) [Rumpf 1962]. Another classification into only two groups distinguishes between the presence of material bridges between the primary particles in the agglomerate and attraction forces [Pietsch 1972, 1984].

The most important characteristic of all forms of agglomerates is their strength. Rumpf defined the tensile strength as the tensile force at failure divided by the cross section of the agglomerate. Because with high probability failure occurs as the result of the highest tensile strength in all stressing situations, this proposal is justified.

Figure 2.21 illustrates the relative magnitude of the different bonds discussed above as a function of particle size. We see that van der Waals forces become important only for particles below $1\text{ }\mu\text{m}$ in size, adsorbed vapour forces are relevant below $80\text{ }\mu\text{m}$ and liquid bridge forces are active below about $500\text{ }\mu\text{m}$ [Rhodes 1998].

Van der Waals forces act between atoms and molecules without the transfer of electrons from one partner to the other. Adhesion forces between solid particles can be classified as long-distance forces (Coulombian-electrostatic and van der Waals forces) or a short-distance attractive forces (chemical and intermediate bonds, e.g. hydrogen bonds). Experiments and calculations support the view that the major role in adhesion of solids is played by attractive electrostatic and van der Waals forces [Juhász and Opoczky 1990].

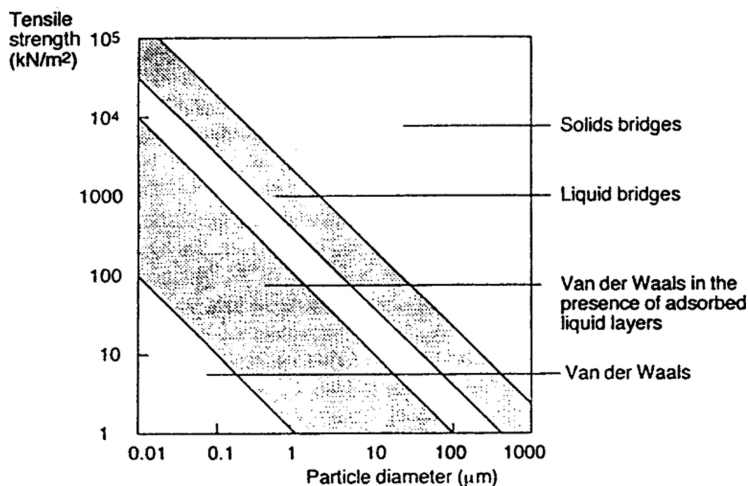


Fig. 2.21 Theoretical tensile strength of agglomerates with different bonding mechanism [Rumpf 1962]

According to many authors, the formation, rupture and severance of surface bonds that are characteristic for particle interactions in high-energy milling can be summarized as follows. After a relatively short period of milling and at relatively low fineness the adherence of particles sets in as a consequence of van der Waals adhesion forces. The distance between particles and the number of contacts plays an important role in the appearance of adhesion. In real polydisperse systems the presence of very fine particles along with relative coarse particles will greatly promote the formation of aggregates, and this accounts for the marked tendency for aggregation in milled products that have a broad range of particle sizes. Plastic deformation at contact points greatly increases both the area of the adhesion forces and, thereby increases the strength, compactness, and resistance to mechanical effects of particle agglomerates [Rumpf 1962, 1966, 1972–1974; Rumpf and Herrmann 1970; Krupp 1967; Juhász and Opoczky 1990].

In the course of adhesion of particles in mechanochemically activated systems the chemical interactions may also proceed at the contacting surfaces. These interactions result in a very compact, irreversible adhesion of the particles and forming of agglomerates. Agglomerates can be formed by various processes, e.g. by welding, coalescence of crystals, by direct initiation at the contacting surfaces, or by means of “melt-bridges” [Juhász and Opoczky 1990]. A typical agglomerate formed by mechanical activation is given in Fig. 2.22.

In nanoparticles, van der Waals forces are extremely important. Particles in the nanometer size range have a strong tendency to agglomerate owing to their relatively large specific surface area and other properties, which in turn accentuates their van der Waals interactions. Nanoclusters are only kinetically stable. They must be stabilized against aggregation into larger particles. This is frequently performed by adding further substances into the system (see next paragraph).

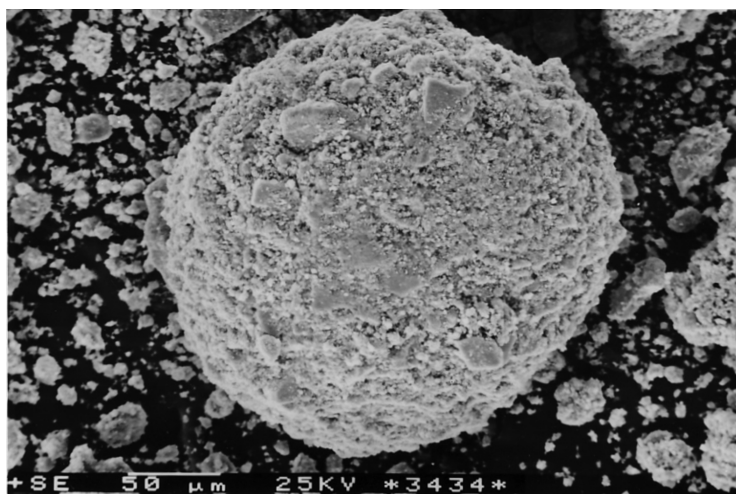


Fig. 2.22 A typical agglomerate of chalcopyrite CuFeS_2 particles formed by mechanical activation

2.6 Surfactants

There are several expressions used in literature for substances which preferentially adsorb onto the interfaces, prevent aggregation and stabilize the separated nanoparticles. The terms such as *surfactants*, *surface active agents*, *process control agents* and *lubricants* are most frequently applied.

In principle, stabilization can be accomplished by *electrostatic* (charge, or “inorganic”) stabilization or *steric* (“organic”) *stabilization* [Overbeeck 1981].

Steric stabilization is achieved by surrounding particles with a layer of substances which are sterically bulky such as polymers. These large adsorbates provide a steric barrier that prevents close contact of the fine particles (Fig. 2.23). The coil dimensions of surfactants are usually larger than the range over which the attraction forces between nanoparticles are active [Dutta and Hofmann 2004].

The water molecule plays here a special role. If a surfactant is added to water, its hydrocarbon chain tend to self-associate to minimize contact with water molecules. If the water is able to solubilize the polar head and the alkyl chains equally, no aggregates are formed.

The shape of the surfactant (Fig. 2.24) plays an important role in forming the assembly [Pileni 2003]. If the surfactant molecules have a very large polar head and a small chain forming a cone shape (Fig. 2.24a), the chains tend to self-associate to form a spherical aggregate called a normal micelle (Fig. 2.24b). If the surfactant has a shape of a champagne cork (Fig. 2.24c) spherical reverse micelles are formed (Fig. 2.24d). This is termed a water-in-oil droplet. In surfactant systems containing large amounts of both oil and water, the shape and dimension of the aggregates changes (Fig. 2.24e). Adding more water induces a new phase transition, with the surfactant molecules reorganizing as a planar or lamellar film (Fig. 2.24f). The other types of surfactant shapes are also possible as an onion shape on Fig. 2.24g.

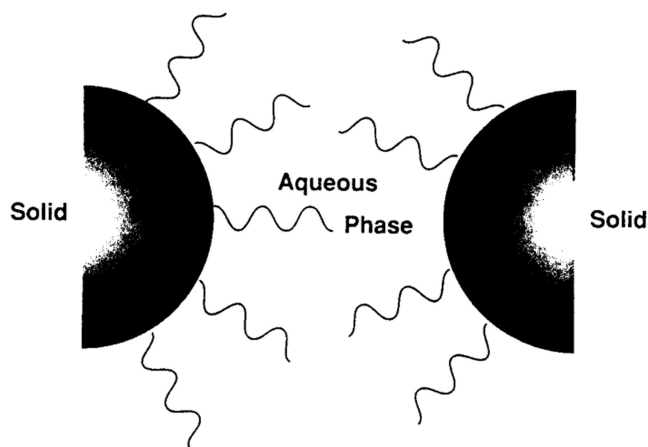


Fig. 2.23 Steric stabilization of nanoparticles by polymeric surfactants [Klimpel 1997]

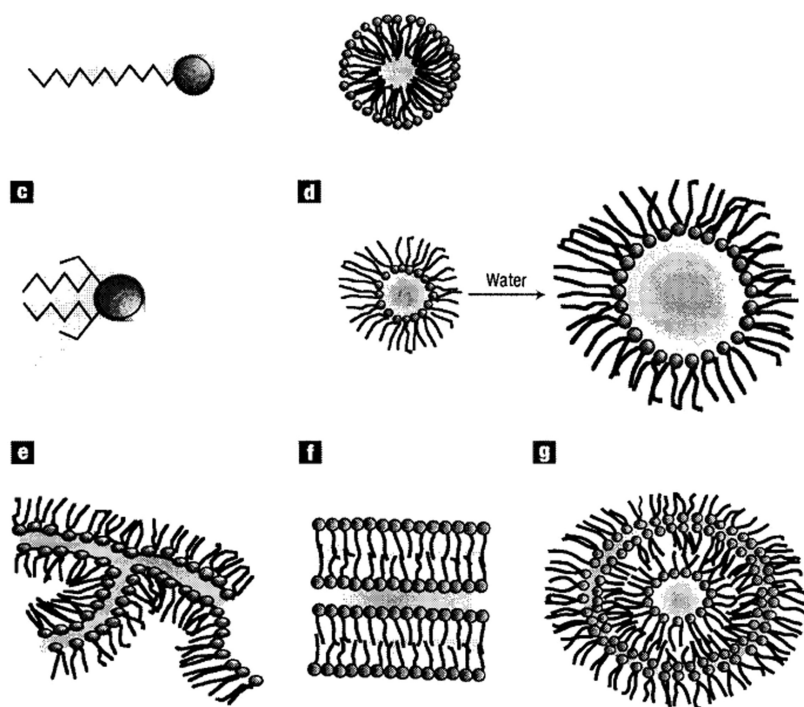


Fig. 2.24 Surfactant shapes and various self-assemblies in colloidal solution [Pileni 2003]

Electrostatic stabilization (Fig. 2.25) occurs by the adsorption of ions to the electrophilic surface [Hunter 1987]. Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counterions which surrounds the particle [Dutta and Hofmann 2004].

Surfactant chemicals as a group have some unusual chemical and physical properties. In addition to the tendency for their adsorption at phase interfaces, they

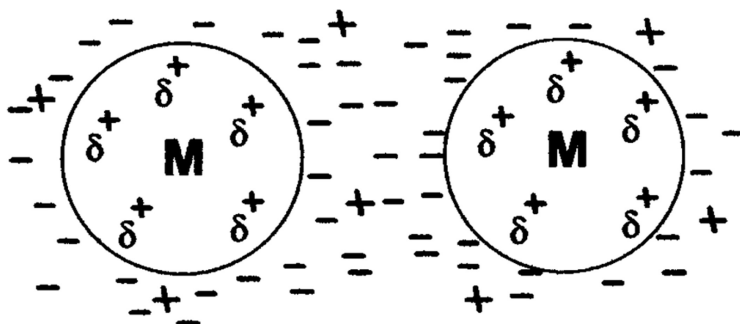


Fig. 2.25 Electrostatic stabilization of nanoparticles by polymers [Aiken III et al. 1996]

also demonstrate several other important properties. One of these properties is self-association between surfactant molecules of exactly the same structure leading to the formation of micelles [Klimpel 1997].

In high-energy milling, surfactants have been used at a level of about 1–5 wt.% of the total powder charge into the mill [Suryanarayana 2001]. The nature and quantity of surfactants used and the type of powder milled would determine the final size, shape, and purity of the powder particles. Use of a larger quantity of surfactants normally reduces the particle size by 2–3 orders by magnitude. For example, it was reported that milling aluminium for 5 hours produced a particle size of about 500 μm when 1% stearic acid was used as a surfactant. However, when 3% of stearic acid was used, the particle size was only 10 μm [Lai and Lu 1998]. Several surfactants are given in Table 2.2.

The choice of polymer surfactants varies from case to case. They must be mobile enough to provide access for the addition of monomer units, while stable enough to prevent the aggregation of nanocrystals [Mana et al. 2002]. By using surfactants (or mixtures of surfactants) that bind differently to the different crystallographic faces, we can control the shape of the nanocrystals [Puntes et al. 2001]. However, it should be realized that there is no universal surfactant.

There have been several reports in literature that milling can be influenced by the addition of surfactants into the mill [El Shall and Somasundaram 1984]. The most of the results have been interpreted in terms of two major mechanisms.

The first mechanism is called *Rebinder effect*. According to this concept, the adsorption of surfactants results in a decrease of the surface energy of solids where by their strength and resistance to mechanical effects decrease [Rebinder and Kalinovskaja 1932]. The classical explanation of the chemomechanical effect is based on the Griffith's theory of fracture of solids weakened by a priori cracks. Molecules and ions of the surfactant intrude into the microcracks. The concept of Rebinder effect comprises the whole complex of phenomena promoting deformation and fracture. The essential feature is that, because of the reversible interaction of the solid with the surfactant, less work is required for the generation of new surface. After Juhász and Opoczky, Rebinder concept about the reduction of surface energy and the consequent decrease of fracture energy is untenable, since it is known that fracture energy is primarily determined by plastic deformation at the crack front and that stresses arising on fracture surfaces can only marginally, if at all, influence the propagation of cracks [Juhász and Opoczky 1990].

Table 2.2 Surfactants and the quantity used (adapted after Suryanarayana 2001)

Benzene	–	Octane	1%
Ethanol	4%	Polyethyleneglycol	–
Methanol	–	Sodium chloride	2%
Graphite	0.5%	Stearic acid	1%
Heptane	0.5%	Toluene	5 ml

The second mechanism states that adsorption of surfactants influences the properties of fragments created by milling. This mechanism is based on the empirical observation that surfactants alter the conditions of energy and mass transport by high-energy milling.

References

- Abdellaoui, M. and Gaffet, E. (1996) The physics of mechanical alloying in a modified horizontal rod mill: mathematical treatment. *Acta Materialia* 44, 725–734.
- Aiken III, J.D., Lin, Y. and Finke, R.G. (1996) A perspective on nanocluster catalysis: polyoxoanion and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ stabilized $\text{Ir(0)} \sim 300$ SD nanocluster soluble heterogeneous catalysts. *Journal of Molecular Catalysis A: Chemical* 114, 29–51.
- Avvakumov, E.G. (1986) *Mechanical Methods of Chemical Processes Activation*. Nauka, Novosibirsk (in Russian).
- Bachmann, D. (1940) Über den Einfluss des Mahlvorganges auf die Eigenschaften von Hochpolymeren Zellulose und Polystyrol. *Verfahrenstechnik Zeitschrift, VDI-Beiheft* 2, 43–55.
- Baláz, P. (1981) *Intensification of Chalcopyrite Oxidative Leaching*. PhD. Thesis, Mining Institute of Slovak Academy of Sciences, Košice.
- Baláz, P. (2000) *Extractive Metallurgy of Activated Minerals*. Elsevier, Amsterdam.
- Baláz, P., Godočiková, E., Kril'ová, L., Lobotka, P. and Gock, E. (2004) Preparation of nanocrystalline materials by high-energy milling. *Materials Science Engineering A* 386, 442–446.
- Baláz, P., Godočiková, E., Takacs, L. and Gock, E. (2005) Mechanochemical preparation of metal/sulphide nanocomposite particles. *International Journal of Materials Products Technology* 23, 26–41.
- Beenken, W., Gock, E. and Kurrer, K.E. (1996) The outer mechanics of the eccentric vibration mill. *International Journal of Minerals Processing* 44–45, 437–446.
- Beke, B. (1984) Considerations about the energetic effectivity of fine grinding. In: K. Inoya, J.K. Beddow and G. Gimbo (Eds.) *Proc. Int. Symp. on Powder Technology*. Kyoto, 1981, Hemisphere Publishing Corporation, Washington, pp. 373–379.
- Benjamin, J.S. (1970) Dispersion strengthened superalloys by mechanical alloying. *Metallurgical Transactions* 1, 2943–2951.
- Bernhardt, C. and Heegn, H.P. (1976a) Contribution to the investigation of the mechanical activation in fine grinding mills. In: H. Rumpf and K. Schönert (Eds.) *Proc. IVth European Symp. on Comminution*. Nürnberg 1975, Dechema Monographien, Bd. 79, Verlag Chemie, Frankfurt am Main, pp. 213–225 (in German).
- Bernhardt, C. and Heegn, H.P. (1976b) Zur mechanischen Aktivierung von Ton. *Folia Montana*, extraordinary number 296–307.
- Bernotat, S. and Schönert, K. (1998) Size reduction. In: *Ullmann's Encyclopedia of Industrial Chemistry*. VCH Verlagsgesellschaft, Weinheim, Vol. B2, pp. 5.1–5.39.
- Boldyrev, V.V. (1983) *Experimental Methods in Mechanochemistry of Solid Inorganic Materials*. Nauka, Novosibirsk (in Russian).
- Boldyrev, V.V. (1986) Mechanochemistry of inorganic solids. *Proceedings of Indian National Science Academy* 52, 400–417.
- Boldyrev, V.V. and Tkáčová, K. (2001) Mechanochemistry of solids: past, present and prospects. *Journal of Materials Synthesis* 8, 121–132.
- Bond, F.C. (1952) The third theory of comminution. *Transactions of AIME, Minerals Engineering* 193, 484–494.
- Calka, A. (1991) Formation of titanium and zirconium nitrides by mechanical alloying. *Applied Physics Letters* 59, 1568–1569.

- Calka, A. and Radlinski, A.P. (1991) Universal high performance ball milling device and its application for mechanical alloying. *Materials Science and Engineering A*, 134, 1350–1353.
- Calka, A. and Wexler, D. (2002) Mechanical milling assisted by electrical discharge. *Nature* 419, 147–151.
- Campbell, S.J. and Kaczmarek, W.A. (1996) Mössbauer effect studies of materials prepared by mechanochemical methods. In: G.J. Long and F. Grandjean (Eds.) *Mössbauer Spectroscopy Applied to Materials and Magnetism*. Plenum Press, New York Vol. 2, pp. 273–330.
- Charles, R.J. (1957) Energy-size reduction relationships in comminution. *Transactions of AIME* 208, 80–88.
- Chen, Y., Fitzgerald, J., Williams, J.S. and Willis, P. (1990) Mechanochemical synthesis of boron nitride nanotubes. *Journal of Metastable and Nanocrystalline Materials* 2, 375–380.
- Chen, Y., Li, Z.L. and Williams, J.S. (1995) The evolution of hydriding and nitriding reactions during ball milling of titanium in ammonia. *Journal of Materials Science Letters* 14, 542–544.
- Chodakov, G.S. (1972) *Physics of Milling*. Nauka, Moscow (in Russian).
- Cottrell, A.M. (1958) Intercrystalline creep fracture. *Transactions of AIME* 212, 192–203.
- Davis, R.M. and Koch, C.C. (1987) Mechanical alloying of brittle components: silicon and germanium. *Scripta Metallurgica* 21, 305–310.
- Dutta, J. and Hofmann, H. (2004) Self organization of colloidal nanoparticles. In: H.S. Salva (Ed.) *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publishers, California, Vol. 9, pp. 617–640.
- El-Shall, H. and Somasundaran, P. (1984) Physico-chemical aspects of grinding: a review of use of additives. *Powder Technology* 38, 275–293.
- Fokina, E.L., Budim, N.I., Kochnev, V.G. and Chernik, G.G. (2004) Planetary ball mills of periodic and continuous action. *Journal of Materials Science* 39, 5217–5222.
- Gock, E. and Kurrer, K.E. (1996) Eccentric vibratory mill—a new energy-efficient way for pulverisation. *Erzmetall* 49, 434–442.
- Gock, E. and Kurrer, K.E. (1998) Increased efficiency of the vibratory milling process with the eccentric vibratory mill. *Aufbereitung-Technik* 39, 103–111.
- Gock, E. and Kurrer, K.E. (1999) Eccentric vibratory mills—theory and practice. *Powder Technology* 105, 302–310.
- Godóčiková, E., Baláz, P., Criado, J.M., Real, C. and Gock, E. (2006) Thermal behaviour of mechanochemically synthesized nanocrystalline CuS. *Thermochimica Acta* 440, 19–22.
- Golosov, S.J. (1971) *Introduction to Ultrafine Milling in Planetary Mills*. Nauka, Novosibirsk (in Russian).
- Griffith, A.A. (1920) The phenomena of rupture and flow in solids. *Philosophical Transactions of the Royal Society (London) A* 221, 163–198.
- Heegn, H.P., Bernhardt, C., Gottschalk, J. and Hussemann, K. (1974) Activation effects on the comminution of quartz and calcite in various laboratory mills. *Chemische Technik (Leipzig)* 26, 696–701.
- Heegn, H.P., Bernhardt, C. and Ludwig, G. (1980) Zur Feinstmahlung von Strontiumferrit. *Folia Montana, extraordinary number*, 195–200.
- Heegn, H.P. (1989) On the connection between ultrafine grinding and mechanical activation of minerals. *Chemie Ingenieur Technik* 62, 458–464.
- Heinicke, G. (1984) *Tribochemistry*. Akademie-Verlag, Berlin.
- Holmes, J.A. (1957) A contribution to the study of comminution: a modified form of Kick's law. *Transactions of Institute Chemical Engineers (London)* 35, 125–138.
- <http://www.fritsch.com>
- <http://www.netzsch.com>
- <http://www.nishineng.com>
- <http://www.siebtechnik.com>
- <http://www.ttd.spb.ru>
- <http://www.unionprocess.com>
- <http://www.utk.edu>
- <http://www.zoz.com>

- Hukki, R.T. (1961) Proposal for a Solomonic settlement between the theories of von Rittinger, Kick and Bond. Transactions of AIME 220, 403–408.
- Hunter, R.J. (1987) *Foundations of Colloid Science*, Vol. 1. Oxford University Press, New York.
- Husemann, K., Wolf, R., Hermann, R. and Hoffmann, B. (1976) Erhöhung der Effektivität trockener Feinstmahlprozesse durch grenzflächenaktive Zusätze. *Aufbereitungstechnik* 35, 393–403.
- Hüttig, G. (1943) Intermediate steps at solid-state reactions and their significance in catalysis. In: G.M. Schwab (Ed.) *Handbook of Catalysis*. Springer Verlag, Wien, Vol. 4, pp. 318–577 (in German).
- Jimbo, G., Zhao, Q.Q., Yokoyana, T. and Taniyana, Y. (1990) The grinding limit and the negative grinding phenomenon. In: *Proc. IInd World Congress Particle Technology, Society of Powder Technology*, Kyoto, Part II, pp. 305–312.
- Juhász, A.Z. and Opoczky, L. (1990) *Mechanical Activation of Minerals by Grinding: Pulverizing and Morphology of Particles*. Ellis Horwood, Chichester.
- Kick, F. (1883) A critique of industrial methods of measurement of strength. *Dinglers Polytechnik Journal* 247, 1–15.
- Kirpičev, V.L. (1874) Similarity in elastic phenomena. *Žurnal Russkogo Fiziko-chimičeskogo Obščestva, časť fizičeskaja IX*, 152–158 (in Russian).
- Klimpel, R.R. (1997) *Introduction to the Principles of Size Reduction of Particles by Mechanical Means*. Engineering Research Center at the University of Florida, Gainesville, pp. 1–41.
- Koch, C.C. (1993) The synthesis and structure of nanocrystalline materials produced by mechanical attrition: a review. *Nanostructured Materials* 2, 109–129.
- Koch, C.C. (1997) Synthesis of nanostructured materials by mechanical milling: problems and opportunities. *Nanostructured Materials* 9, 13–22.
- Kochnev, V.G. (1992) Planetary mill. Russian Patent 1358990.
- Kochnev, V.G. and Simakin, S.A. (1994) Planetary mill feeder. Russian Patent 2094120.
- Krupp, H. (1967) Particle adhesion theory and experiment. *Journal of Colloid Interface Science* 1, 111–239.
- Kurrer, K.E. and Gock, E. (1997) Eccentric vibratory mills for ultrafine comminution. *Zement-Kalk-Gips International* 50, 362–373.
- Lai, M.O. and Lu, L. (1998) *Mechanical Alloying*. Boston, Kluwer Academic Publishers.
- Mana, L., Scher, E.C. and Alivisatos, A.P. (2002) Shape control of colloidal semiconductor nanocrystals. *Journal of Cluster Science* 13, 521–532.
- Miani, F. and Maurigh, F. (2004) Mechanochemical synthesis of nanophase powders. In: J.A. Schwarz, C.J. Contescu and K. Putyera (Eds.) *Dekker Encyclopedia of Nanoscience and Nanotechnology*. Marcel Dekker, New York, pp. 1787–1795.
- Molčanov, V.I. and Jusupov, T.S. (1981) *Physical and Chemical Properties of Fine Milled Minerals*. Nedra, Moscow (in Russian).
- Molčanov, V.I., Selezneva, O.G. and Žirnov, E.N. (1988) *Activation of Minerals by Milling*. Nedra, Moscow (in Russian).
- Murty, B.S. and Ranganathan, S. (1998) Novel materials synthesis by mechanical alloying/mixing. *International Materials Review* 43, 101–143.
- Netzsch Feinmahltechnik GmbH-Technical Information FT 002, 1974. Zirkulationsmühle System ZETA.
- Ogino, Y., Yamasaki, T., Atzumi, N. and Yoshioka, K. (1993) Nitriding of transition metal powders by ball milling in nitrogen gas. *Materials Transactions JIM* 34, 1212–1216.
- Opoczky, L. (1977) Fine grinding and agglomeration of silicates. *Powder Technology* 17, 1–7.
- Overbeek, J.T.G. (1981) *Colloidal Dispersions*. Royal Society of Chemistry, London.
- Pietsch, W.B. (1972) Über Grenzflächenvorgänge in der Agglomerationstechnik. *CZ Chemie-Technik* 1, 116–119.
- Pietsch, W.B. (1984) Agglomerate bonding and strength. In: N.E. Fayed and L. Otten (Eds.) *Handbook of Powder Science and Technology*. Van Nostrand, New York, pp. 231–251.
- Pileni, M.P. (2003) The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals. *Nature Materials* 2, 145–150.

- Puntes, F., Krishnan, K.M. and Alivisatos, A.P. (2001) Colloidal nanocrystal shape and size control: the case of cobalt. *Science* 291, 2115–2117.
- Püpke, I. (1971) Construction and operating method of an attrition mill in powder metallurgy. *Powder Metallurgy International* 3, 94–96.
- Rebinder, P.A. and Kalinovskaja, N.A. (1932) Lowering of strength of solid surface layers at surfactants adsorption. *Žurnal tehničeskoj fiziki* 2, 286–302.
- Rhodes, M. (1998) *Introduction to Particle Technology*. John Wiley and Sons, Chichester.
- Rittinger, P.R. (1867) *Lehrbuch der Aufbereitungskunde*. Ernst und Korn, Berlin.
- Rose, H.E. and Sullivan, R.M. (1961) *Vibration Mills and Vibration Milling*. Constable and Company Ltd., London.
- Rose, H.E. (1962) Hochleistungsschwingmühlen. *Chemie Ingenieur Technik* 34, 414–417.
- Rumpf, H. (1961) Problemstellungen und neuere Ergebnisse der Bruchtheorie. *Materialprüfung* 3, 253–265.
- Rumpf, H. (1962) The Strength of granules and agglomerates. In: W.A. Knepper (Ed.) *Agglomeration*. John Wiley, New York, pp. 379–418.
- Rumpf, H. (1966) Struktur der Zerkleinerungswissenschaft. *Aufbereitungstechnik* 7, 421–435.
- Rumpf, H. and Herrmann, H. (1970) Eigenschaften Bindungsmechanismen und Festigkeit von Agglomeraten. *Aufbereitungstechnik* 11, 117–127.
- Rumpf, H. (1972) Haftung und Festigkeit von Agglomeraten Vergleich zwischen Modellrechnung und Experiment. *Die Pharmaceutische Industrie* 34, 270–281.
- Rumpf, H. (1973) Physical aspects of comminution-a new formulation of a law of comminution. *Powder Technology* 7, 148–159.
- Rumpf, H. (1974) Die Wissenschaft des Agglomerierens. *Chemie Ingenieur Technik* 46, 1–11.
- Smekal, A. (1922) Technische Festigkeit und molekuläre Festigkeit. *Naturwissenschaften* 10, 799–804.
- Smekal, A. (1936) Bruchtheorie spröder Körper. *Zeitschrift für Physik* 103, 495–525.
- Schönert, K. and Weichert, A. (1969) Die Wärmetönung des Bruches in Eisen und ihre Abhängigkeit von der Ausbreitungsgeschwindigkeit. *Chemie Ingenieur Technik* 41, 295–300.
- Schönert, K. and Steier, K. (1971) Die Grenze der Zerkleinerung bei kleinen Korngrößen. *Chemie Ingenieur Technik* 43, 773–777.
- Schönert, K. (1974) Über die Eigenschaften von Bruchflächen. *Chemie Ingenieur Technik* 46, 711–715.
- Schubert, H. (1989) *Aufbereitung fester mineralischer Rohstoffe*. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, Band I.
- Schulz, R., Boily, S., Zaluski, L., Zaluska, A. and Ström-Olsen, J.O. (1995) Nanocrystalline Mg-based hydrides: hydrogen storage for the zero-emission vehicle. *Innovations in Metallic Materials*, 529–535.
- Suryanarayana, C. (2001) Mechanical alloying and milling. *Progress in Materials Science* 46, 1–184.
- Suryanarayana, C., Ivanov, E. and Boldyrev, V.V. (2001) The science and technology of mechanical alloying. *Materials Science and Engineering A*, 304–306, 151–158.
- Takacs, L. and Pardavi-Horvath, M. (1994) Magnetic properties of nanocomposites prepared by mechanical milling. In: R.D. Shull and J.M. Sanchez (Eds.) *Nanophases and Nanocrystalline Structures*. Warrendale, Pa, pp. 135–144.
- Takacs, L. and McHenry, J.S. (2006). Temperature of the milling balls in shaker and planetary mills. *Journal of Materials Science* 41, 5246–5249.
- Tanaka, T. (1958) *Staub* 18, 157–168.
- Tkáčová, K. (1989) *Mechanical Activation of Minerals*. Elsevier, Amsterdam.
- Tkáčová, K., Heegn, H.P. and Številová, N. (1993) Energy transfer and conversion during comminution and mechanical activation. *International Journal of Mineral Processing* 40, 17–31.
- Welch, A.J.E. (1953) The reaction of crystal lattice discontinuities to mineral dressing. In: *Developments in Mineral Dressing*. The Institution of Mining and Metallurgy, London, pp. 387–392.



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