

# 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 [Bernoat 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

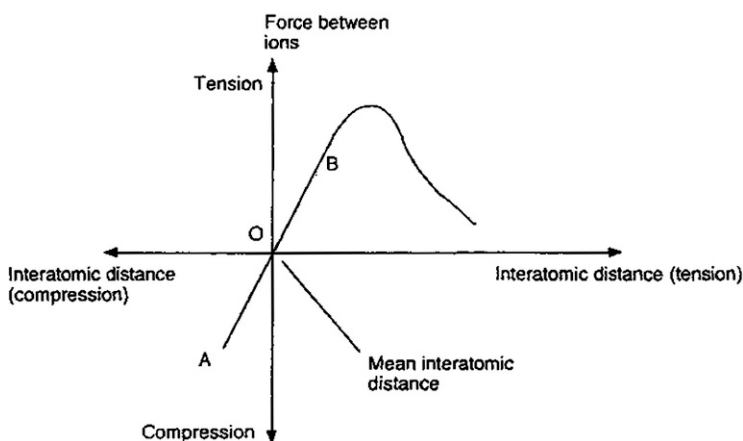
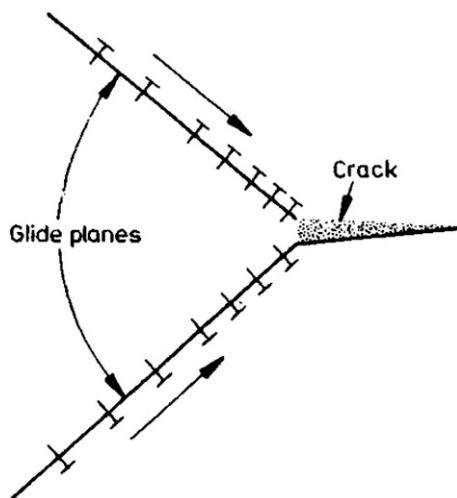


Fig. 2.1 Forces versus distance on an atomic scale [Rhodes 1998]

**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  $5\text{ Jm}^{-2}$ , for plastic solids it is  $10\text{ Jm}^{-2}$ , and for metals is approximately  $500\text{ Jm}^{-2}$ .

## 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  $\mu\text{m}$  particle to 1  $\mu\text{m}$  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  $\mu\text{m}$  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

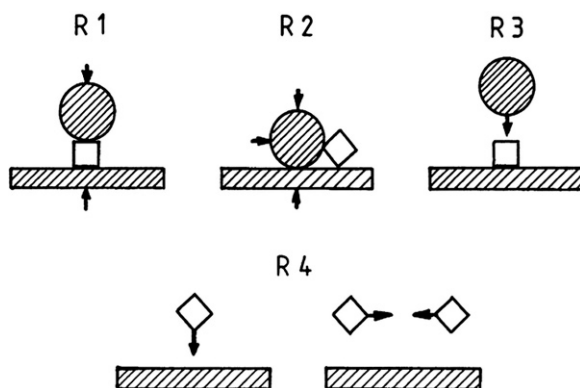
$N = 1.5$ ,  $C = C_B$  for Bond

## 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.



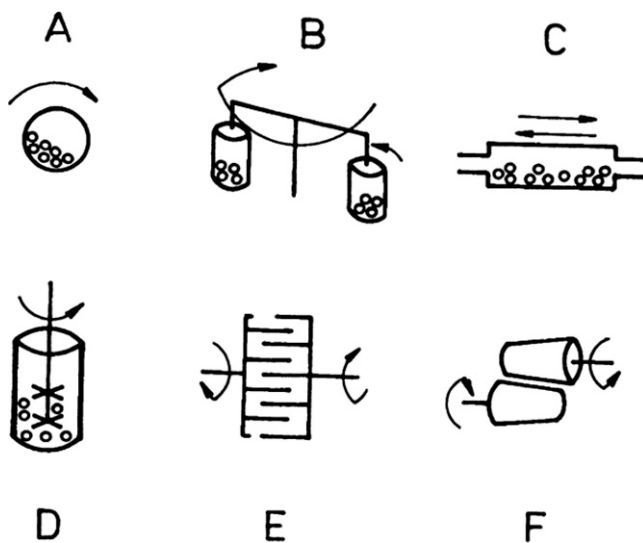
**Fig. 2.3** Main stress types in mills, R1 – compression, R2 – shear (attrition), R3 – impact (stroke), R4 – impact (collision), circle – mass of milling media, square – mass of material charge, rectangle – mass of mill wall [Heinicke 1984]

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  $25 \text{ rev s}^{-1}$ ) but low amplitudes (2–4 mm).

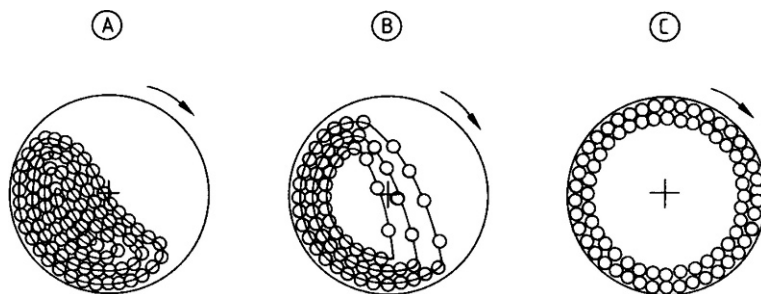


**Fig. 2.4** Types of mills for high-energy milling (the stress type is given in parenthesis): (A) ball mill (R1–R4), (B) planetary mill (R1–R4), (C) vibration mill (R1–R4), (D) attritor – stirring ball mill (R1–R4), (E) pin mill (R4), (F) rolling mill (R1–R2) [BOLDYREV 1986]

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

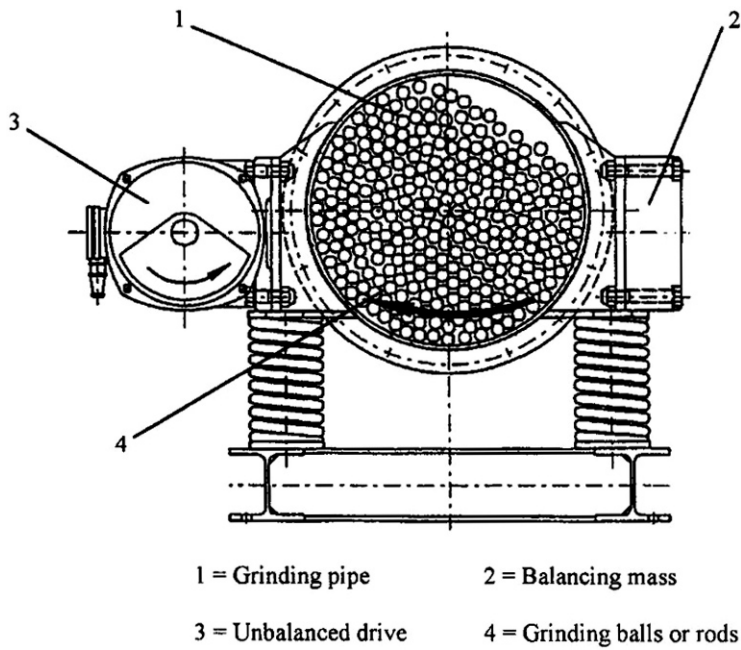
dimensions of the milling bodies should be adjusted to the strength and particle size of the feed [Rose and Sullivan 1961; Rose 1962]. In the opinion of Bernhardt and Heegn the amplitude of the vibration mill and the quantity of the feed is prime importance in mechanical and mechanochemical activation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

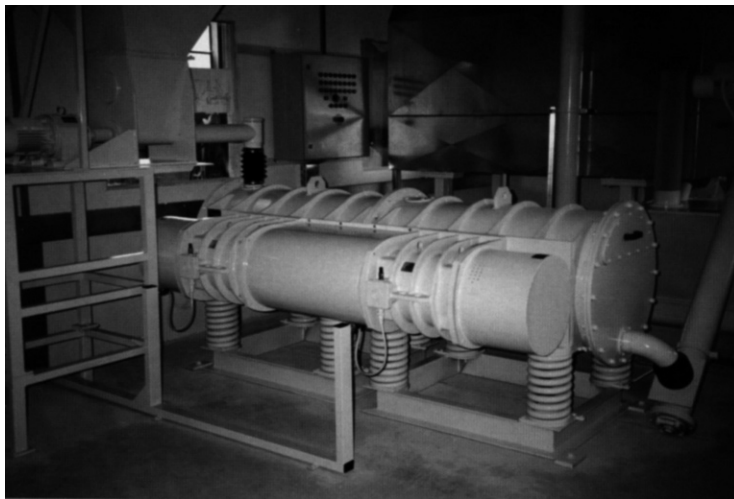
An important disadvantage of vibration mills is their low output. Because of the high-input of energy and the low throughput of material, the high temperatures are developing in the mill. The high temperature is caused by the fact that the mill is almost completely filled and by the complex trajectory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

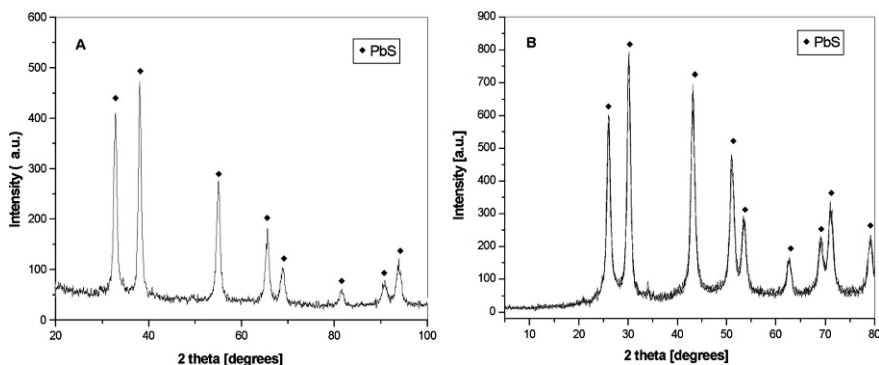


**Fig. 2.7** Diagrammatic view of the eccentric vibration mill [Gock and Kurrer 1999]



**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

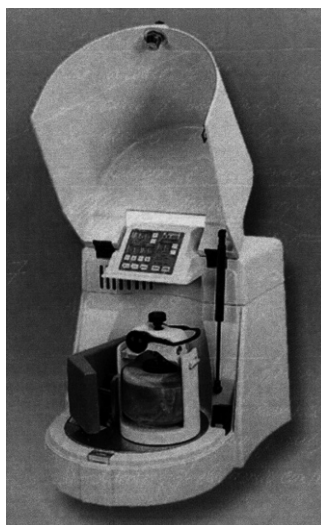
The planetary ball mill (Fig. 2.10) owes its name to the planet-like movement of its vial (s) (Fig. 2.4). Since the vials and the supporting disc rotate in opposite directions, the centrifugal forces alternatively act in like and opposite directions. This causes the milling balls to run down the inside 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).

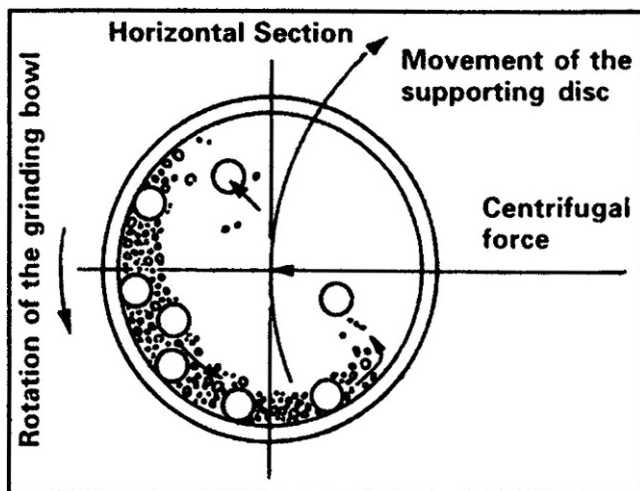
The application of laboratory-scale planetary mills for mechanical activation has been studied intensively by Russian scientists [Golosov 1971; Molčanov et al. 1988;

**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].



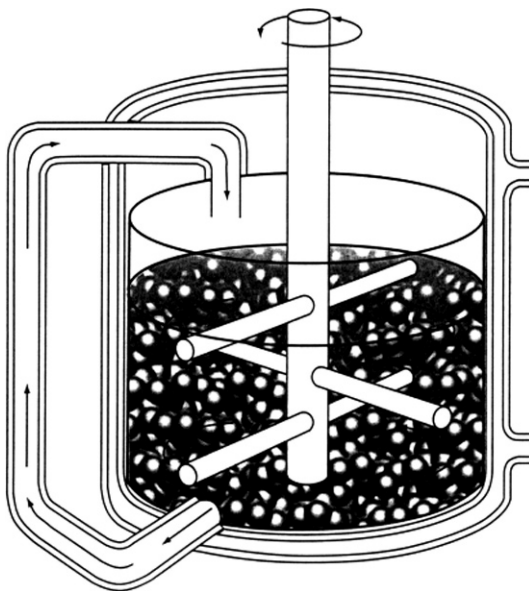
**Fig. 2.12** Laboratory mixer mill Spex 8000 (CertiPrep, USA) [<http://www.utk.edu>]

### 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].

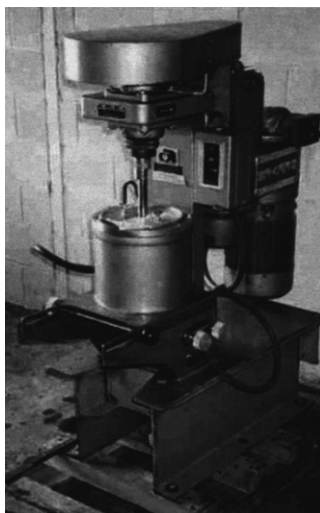
Attritors (attrition mills, stirred ball mills) consist of a cylindrical grinding chamber with a drive shaft having multiple impellers sticking out from the rotating shafts (Fig. 2.13). There is a wide variety of impeller types including flat discs, discs with various geometric openings, and concentric 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; Pöpke 1971; Netzsch 1974]. The most important



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

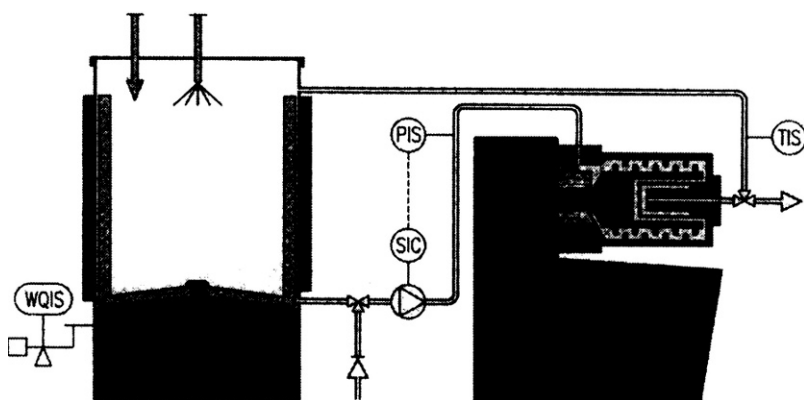
**Fig. 2.14** Laboratory attritor PC 2043 of batch mode of operation (Union Process, USA) [<http://www.unionprocess.com>]



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.

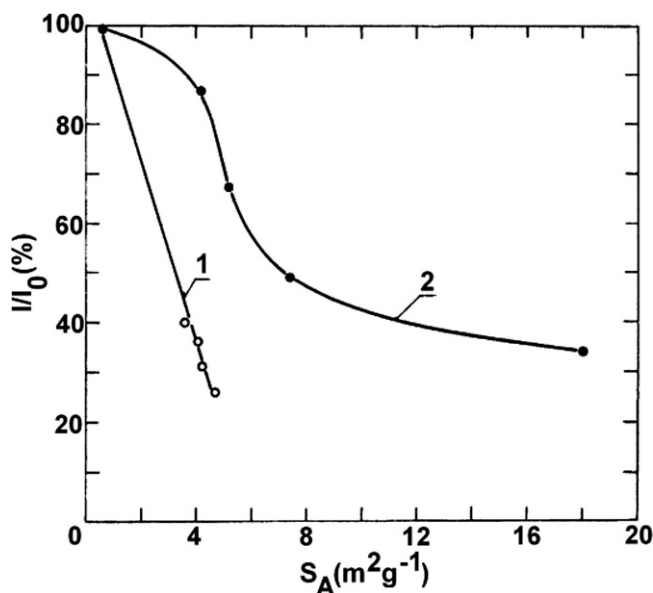


Fig. 2.16 The relative intensity of the selected diffraction line,  $I/I_0$  vs. specific surface,  $S_A$  of chalcopryrite  $\text{CuFeS}_2$  mechanically activated in a vibration mill (1) and in an attritor (2) [Balázš 2000]

### 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).

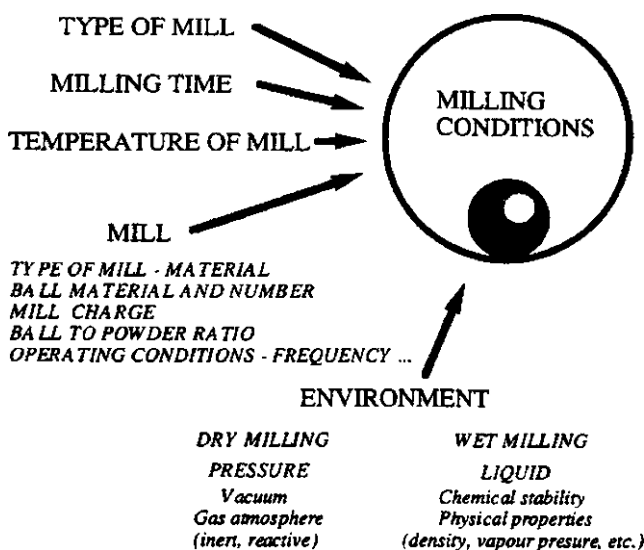


Fig. 2.17 An overview of the main factors to be considered in the milling process [Campbell and Kaczmarek 1996]

#### 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 ( $\text{g cm}^{-3}$ )	Abrasion resistance
Agate	$\text{SiO}_2$	2.65	Good
Corundum	$\text{Al}_2\text{O}_3$	> 3.8	Fairly good
Zirconium oxide	$\text{ZrO}_2$	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 [Baláz 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**

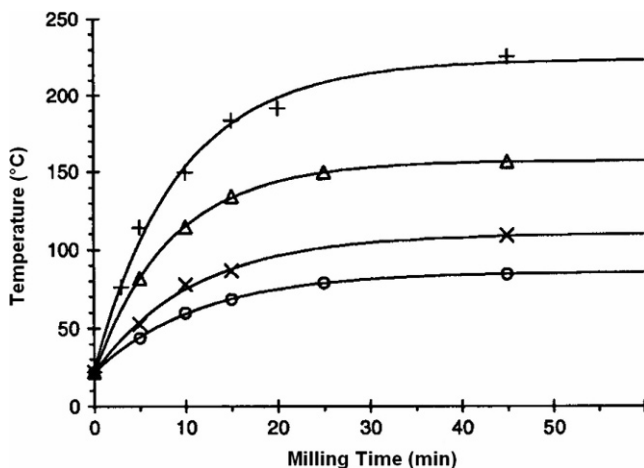
### ***2.5.1 Temperature Effects***

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  $271^{\circ}\text{C}$  [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  $100^{\circ}\text{C}$  in a SPEX mixer mill and it is cooler when flat-ended rather than round-ended vial is used. Temperatures over  $200^{\circ}\text{C}$  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  $327^{\circ}\text{C}$  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 (○) symbols correspond to a 7.5-cm bowl, 50 balls and 280 rpm (Δ) and 200 rpm (○) 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 interferred 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  $\mu\text{m}$  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,  $S_{\infty}$  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:

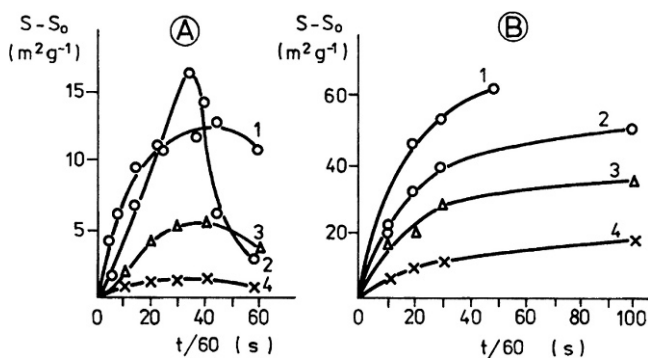


Fig. 2.19 Specific surface area,  $S - S_0$  vs. time of mechanical activation, t: 1 – FeS<sub>2</sub>, 2 – ZnS, 3 – FeS, 4 – PbS, A – milling in air, B – milling in H<sub>2</sub>O,  $S_0$  – specific surface area of non-activated solid [Avvakumov 1986]

- *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

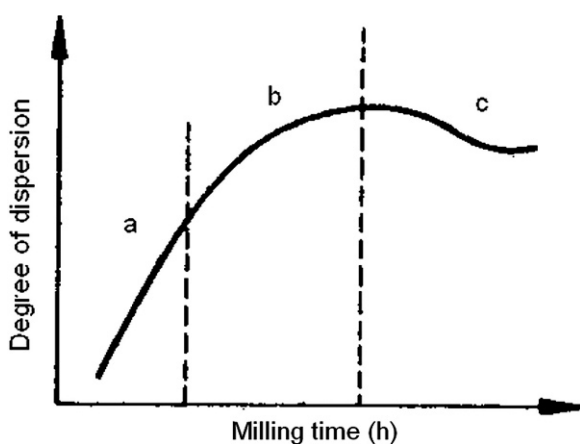


Fig. 2.20 Three stages during high-energy milling [Opoczky 1977]

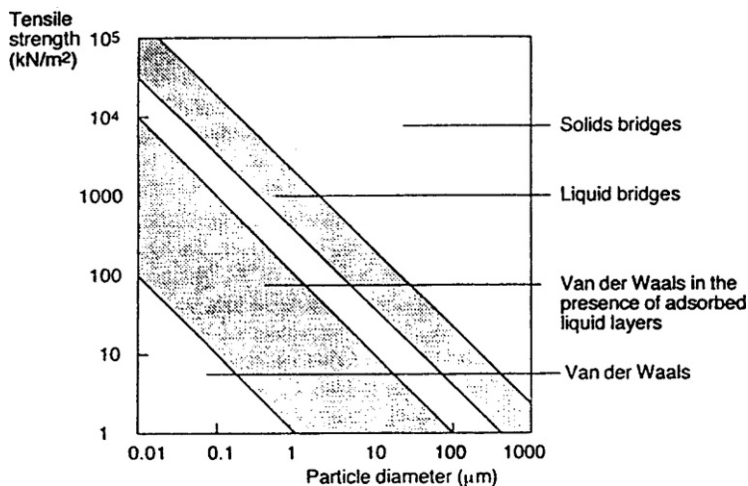
together by chemical bonds of the magnitude  $40\text{--}400\text{ kJmol}^{-1}$  and separation becomes impossible (Fig. 2.20c). Mechanochemical reactions and changes in the crystal structures mainly occur at this stage.

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].

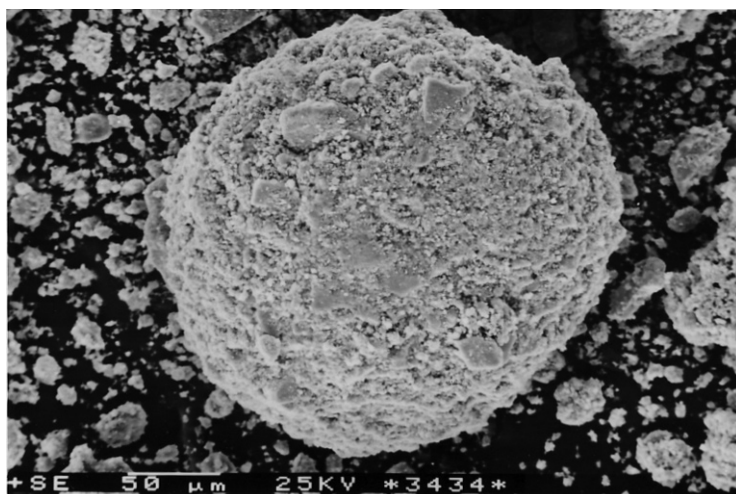


**Fig. 2.21** Theoretical tensile strength of agglomerates with different bonding mechanism [Rumpf 1962]

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  $\text{CuFeS}_2$  particles formed by mechanical activation



## 2.6 Surfactants

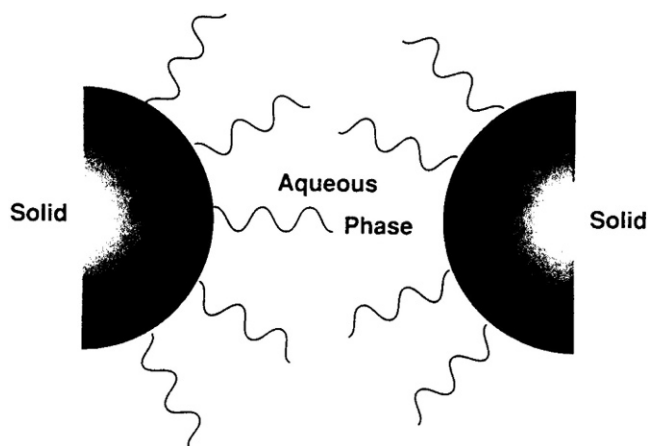
There are several expressions used in literature for substances which preferentially adsorb onto the interfaces, prevent aggregation and stabilize the separated nanoparticles. The terms such as *surfactants*, *surface active agents*, *process control agents* and *lubricants* are most frequently applied.

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].

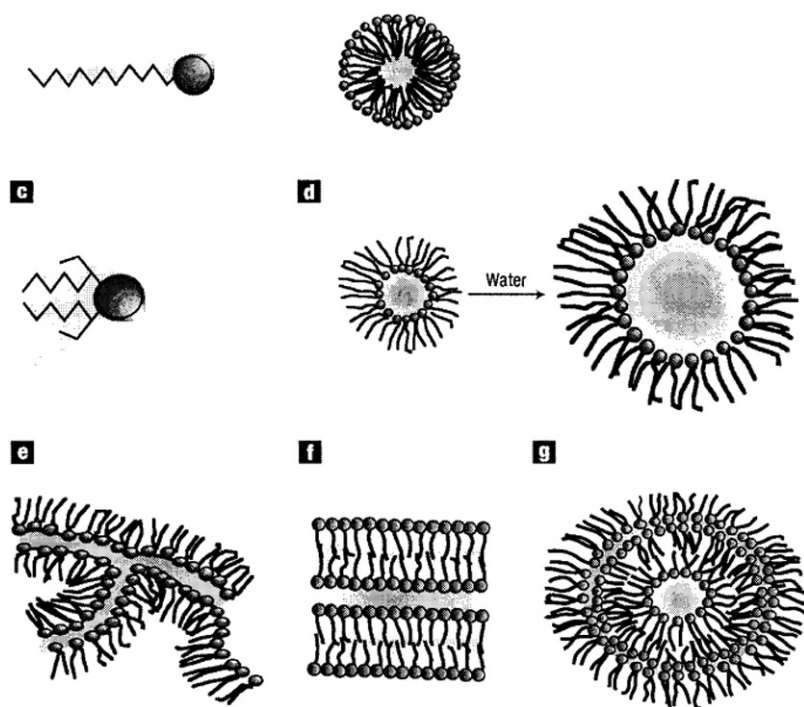
The water molecule plays here a special role. If a surfactant is added to water, its hydrocarbon chain tend to self-associate to minimize contact with water molecules. If the water is able to solubilize the polar head and the alkyl chains equally, no aggregates are formed.

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]

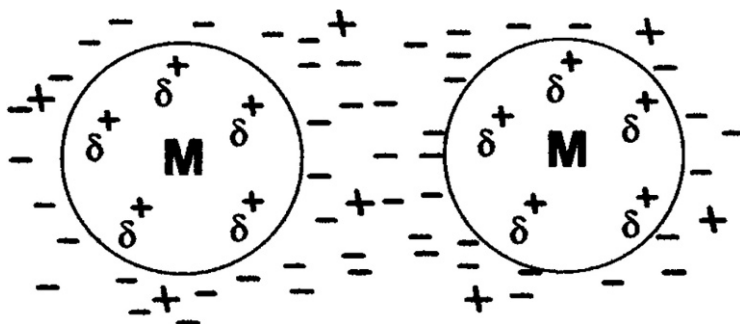




**Fig. 2.24** Surfactant shapes and various self-assemblies in colloidal solution [Pileni 2003]

*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  $\mu\text{m}$  when 1% stearic acid was used as a surfactant. However, when 3% of stearic acid was used, the particle size was only 10  $\mu\text{m}$  [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.

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