

Mechanosynthesis of Nanophase Powders

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INTRODUCTION

Among the different processes able to produce nanocrystalline powders in bulk quantities, mechanosynthesis, i.e., the synthesis of nanograined powders by means of mechanical activation, is one of the most interesting from an industrial point of view. Mechanosynthesis of nanophase powders is one of the less sophisticated technologies—and, in such a sense, also the most inexpensive—to produce nanophase powders; in fact, it exploits devices and processes that have many aspects in common with mixing, fine grinding, and comminution of materials. However, it does have interest for applications, as, in principle, this is a very low cost process and its potential for industrial applications is very significant. This article describes the basis of the process, some possible applications and perspectives of mechanosynthesized nanophase powders, and some simple ideas that are able to depict part of the process, with a specific mind to the mechanosynthesis of nanocrystalline materials starting from elemental powder precursors. Mechanosynthesis belongs to the family of process technologies known as mechanical alloying, which are basically using the same or very similar apparatuses, i.e., milling or size reduction devices, which could be generally described as ball mills. A recent thorough analysis by Suranarayana^[1] of the processes related to mechanical alloying defines mechanosynthesis as a mechanochemical synthesis, attributing most of the research work in this field of mechanical alloying to Dodd and McCormick,^[2] Takacs,^[3] and Matteazzi et al;^[4] it is also necessary to quote the fundamental and pioneering work of Butyagin^[5] and Urakaev and Boldyrev^[6] and some important developments by Calka and Wexler.^[7] While, because of many different process parameters and conditions, a complete modeling of the mechanical alloying process and mechanosynthesis of nanophase materials would be an aim very difficult to reach, it is useful to identify the operating principle of the most common devices employed for the process, along with some kinematic aspects, some specific mechanical considerations, and thermodynamic and kinetic issues of the process as well. Finally, current production of mechanosynthesized powders and perspectives will be briefly discussed.

THE MECHANOSYNTHESIS PROCESS

The concept of the mechanosynthesis process is very simple: to seal in a vial some—usually powdered—materials along with grinding media, which are usually balls, and to reduce the size of the materials by mechanical action, providing at the same time an intimate mixing of the different materials introduced, so close that diffusion and chemical reactivity are greatly enhanced. For clarity, one could consider a mixture of elemental powders—for simplicity, we could limit to powders of element *A* and element *B*—introduced in a cylindrical container, the jar of a vibrating mill, with repeated and prolonged impacts imposed by mechanical energy imparted to grinding media (Fig. 1).

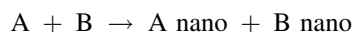
Depending on the nature of the reactants, different intermixing mechanisms are possible; generally speaking, the ductile phase tends to incorporate—if such a phase is present—a more brittle phase, with a tendency to form particles which are microscopically (to a scale of micrometers) folded.

With prolonged milling, the crystal size of both reactants decreases in an exponential way, following a decreasing trend with the processing time *t* of the type:^[8,9]

$$d = d_f + (d_i - d_f)e^{-c_1 t} \quad (1)$$

where *d* should be considered representative of the crystal size, being *d_i* the initial, *d_f* the steady-state crystal size, and *c₁* an empirical constant depending on the process parameter. Other possible trends of the crystal size evolution with milling time are discussed in the next paragraph, especially if exothermic effects of the reaction $A + B \rightarrow A_x B_y$ are to be taken into account.

The gradual transformation of the milled powders from a rather coarse to a nanocrystalline grain size could be simply depicted as a formal reaction:



Miani and Fecht^[10] have been considering mechanical milling—i.e., the reduction of metal powders of elements and intermetallic compounds to nanocrystalline powders by grinding—and they have proposed empirical estimates for the enthalpy stored. These estimates could be a base

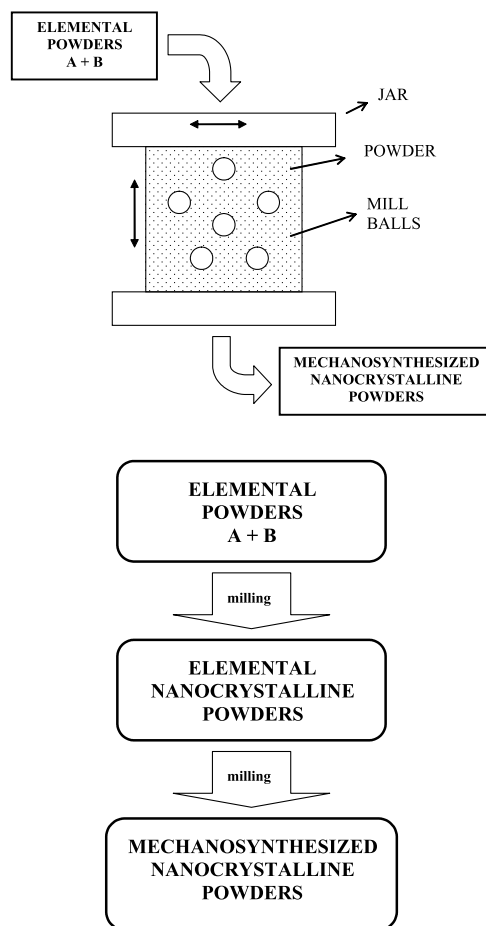


Fig. 1 Mechanochemical synthesis schematic process and steps.

for an evaluation of the mechanochemical energy transfer imparted to the powders. In mechanochemical processing, as time is increasing, along with the energy imparted to the materials, new phases/compounds tend to appear. It has been generally recognized, by different authors, that the generic reaction path linking the time evolution of the reactants with time is sigmoidal.^[8–10] We shall come back to this point dealing with the process kinetics. Here we could depict the second step of the reaction as:



This is an oversimplification, as the mechanochemical synthesis process occurs continuously. However, it may be useful to evaluate, for instance, energetic aspects.

KINEMATIC AND MECHANICAL ASPECTS

Milling devices are of different nature: vibrating mills, planetary mills, attritor mills, and tumbling mills—with

efficiencies in the process that are decreasing from vibrating to tumbling—have been employed successfully. The different devices employed for research purposes are described in Koch;^[11] there has been a tendency of different research groups^[5,12,13] to develop ad hoc mills for the synthesis by milling of nanophase materials. Fig. 2 describes a mill developed in the University of Udine, which has been scaled-up to be industrially employed.

The most important physical parameters involved are well described in a series of papers by Cocco and Delogu,^[8,9,14] in an attempt to propose a quantitative understanding of the mechanical alloying processes. These authors have underlined the importance of relating basic and phenomenological aspects, suggesting that the framework of solid-state chemistry and chemical kinetics should be the most fruitful to interpret results and develop new trends. For the sake of simplicity, considering a mill with just one ball, and adopting the terminology of Butyagin,^[5] one of the pioneers in the field of mechanochemistry, Table 1 was proposed. With such a situation, it



could be interesting to adopt the quantitative techniques used in engineering the deformation processes, as it has been proposed earlier by Courtney and Maurice.^[15] In any case, with the aid of simple kinetic trends, the milling time should be related to the energy dose, not only for device scale-up, but also for process control. This could help, for instance, in controlling exothermic mechanochemical reactions where combustion appears, imparting the completion of a mechanochemical synthesis of nanocrystalline materials.

A possible new design for a jar for laboratory milling is the one presented in Fig. 3, together with its constructional details. The purpose of the experimental jar is to use a diathermic oil to monitor heat release during processing. The jar has been produced with integral internal channels by means of selective laser sintering^[16] and it is available for experimentation on SPEX 8000 mills; typical dimensions of the main cylinder are 75 mm in height and 60 mm in outside diameter.

THERMODYNAMICS

Mechanosynthesis is a technique involving far from equilibrium processing; so, in principle, thermodynamics

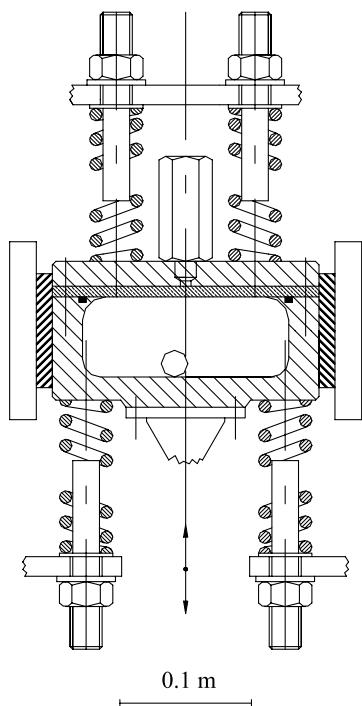


Fig. 2 Experimental vibrating mill for the synthesis of nanophase materials in significant quantities. (From Ref. [12].)

Table 1 Butyagin terminology for an elementary mechanochemical process: ball milling with one ball

Physical quantity	Expression	Units
Impact energy	$E = 1/2m_b v_{imp}^2$	J
Impact frequency	N	hits/sec
Milling intensity	$I = NE = 1/2Nm_b v_{imp}^2$	W
Energy dose	$D = It = NEt = 1/2Nm_b v_{imp}^2 t$	J
Specific dose	$D_m = NEt/m_p$	J/kg

m_b and m_p are the mass of the ball and of the powder, respectively.
Source: Ref. [14].

arguments should not be of help. However, it is possible to conceive the most simple reaction in the mechanochemical synthesis of nanocrystalline materials—the one involving elemental powders A and B—as a two-step process: the first could be thought of as a reduction of the crystal domains and the second as the formation of a nanophase compound or alloy. Miani and Fecht's^[10] extrapolation may be employed for the first step, and Miedema model for the second step, assuming that the enthalpy of alloy formation is the same also in the nanocrystalline status (Table 2). This approach is able to give order-of-magnitude correct results, as could be checked comparing these semiempirical calculations^[10] to the actual heat release.^[17]

Fecht proposed an empirical regression with an analysis by means of differential scanning calorimetry (DSC) data on nanocrystalline metals and intermetallic compounds obtained by 24-hr ball milling by SPEX milling. Scanning up to 870 K with 20 K/min, he obtained the results listed in Table 3.

These data allow to estimate the excess enthalpy stored ΔH :

$$\Delta H / \Delta H_f = 8.5 \times 10^{-5} T_m \quad (2)$$

where ΔH_f is the enthalpy of melting and T_m is the melting temperature.

KINETICS

For what concerns kinetic evolution, the situation is very complex. We have different and contrasting phenomena. Dealing with the mechanochemical synthesis of nanophase materials, we are interested to obtain a crystal size of the order of tens of nanometers, which is usually considered an effective value for applications. The crystal size evolution with time could be depicted with Eq. 1 reported above. If thermal effects are present, i.e., if the enthalpy of re-



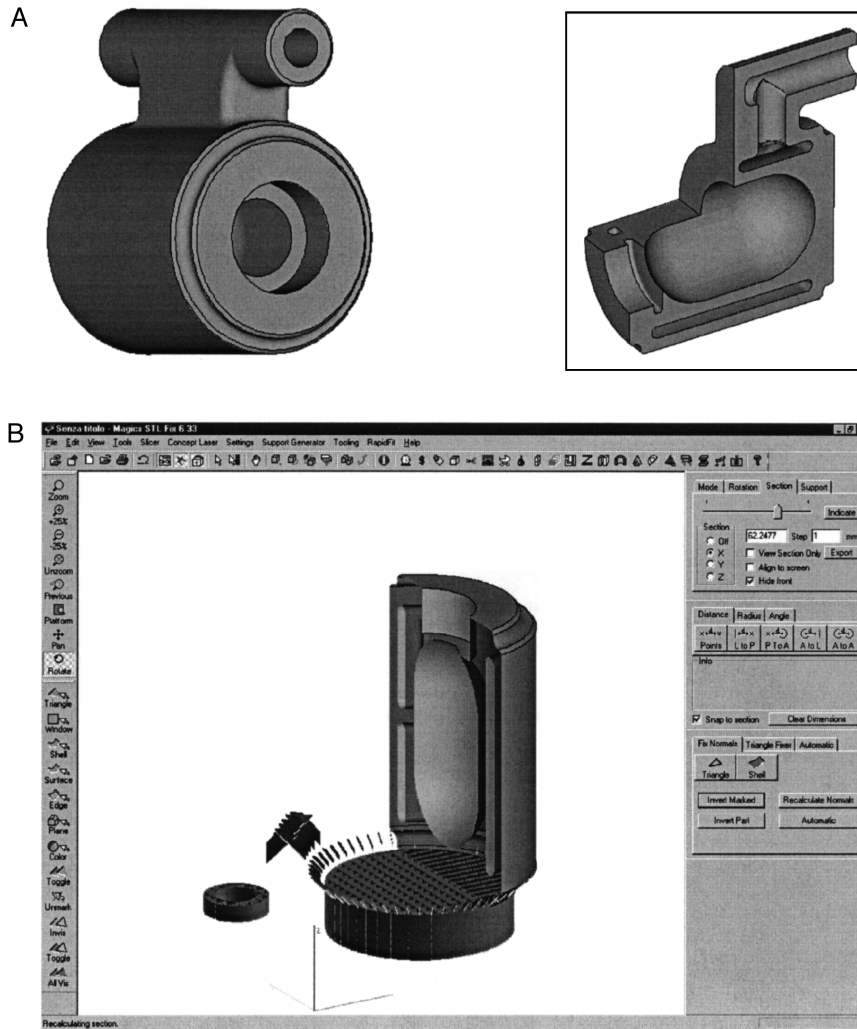


Fig. 3 (A) Prototype vial for the SPEX 8000 Mill, along with a section view of internal channels. (B) Prototype vial for the SPEX 8000 Mill: constructional details for the direct metal-selective laser sintering processing.

action $A + B$ is high enough to increase temperature, we should introduce a term:

$$\frac{\partial}{\partial t} d(t, T) = f(t) + g(t) e^{\left(-\frac{E}{RT}\right)} \quad (3)$$

where E is an activation energy, R is the gas constant, and T is the absolute temperature. This leads to an integrated form of the type:

$$d(t) = \int_0^t f(u) + g(u) e^{\left(-\frac{E}{RT}\right)} du + d_0 \quad (4)$$

where d_0 is the initial grain size. Although this is a hypothesis which neglects chemistry and assumes the existence of just one chemical species or compound, still, this equation is too general to be exploited on a practical

Table 2 Miani and Fecht's^[10] data for the empirical extrapolation of the excess enthalpy stored in mechanically milled nanocrystalline powders

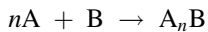
Material	Structure	T_m (K)	d (nm)	ΔH (kJ/mol)
Fe	bcc	1809	8	2.1
Cr	bcc	2148	9	4.2
Nb	bcc	2741	9	2.1
W	bcc	3683	9	4.6
Co	hcp	1768	14	1.0
Zr	hcp	2125	13	3.4
Hf	hcp	2495	13	2.2
Ru	hcp	2773	13	7.2
NiTi	CsCl	1583	5	5
CuEr	CsCl	1753	12	6.8
SiRu	CsCl	2073	7	10.1
AlRu	CsCl	2300	8	5.2



Table 3 Iron conversion ratio α in the mechanosynthesis of nanophase iron carbides using a SPEX 8000 mill

Milling time (hr)	Fe conversion ratio α
0.25	12.2
0.5	12.7
0.75	14.8
1	13.6
1.25	14.1
1.5	13.2
1.75	13.9
2	16.6
2.5	26.2
3	26.9
3.5	32.4
5	51.8
7.5	68.4
10	82.1
15	91.0

ground; however, it does take into account the mechanism of grain reduction as a result of milling action in the term $f(t)$ and the grain growth in the second term. If the reaction $A+B$ is exothermic enough, adiabatic temperature T , for the sake of simplicity, may be evaluated considering a simple first-principle calculation. In the case the temperature is low enough, the integral equation will coincide with Eq. 1. Avvakumov^[18] has proposed a kinetic equation for mechanochemical synthesis; Cocco et al.^[8,9,14] have validated it in some applications of mechanical alloying. One should consider the elements A and B that react to form the compound A_nB at the initial ratio of A on B reactant in the reaction:



By considering α as the degree of reaction atoms reacted on the initial atoms, n as the stoichiometric number, m as the initial atomic ratio of A atoms on B atoms, and ε as n/m ratio, a generalized Avvakumov equation is proposed here:

$$\frac{\partial}{\partial t} \alpha(t) = (1 - \alpha(t))(1 - \varepsilon\alpha(t)) f(t) \quad (5)$$

With the initial condition $\alpha(t=0)=0$, it is possible to integrate then the equation to:

$$\alpha(t) = \frac{e\left(-\int_0^t f(u)du + \int_0^t f(u)du\varepsilon\right) - 1}{-1 + \varepsilon e\left(-\int_0^t f(u)du + \int_0^t f(u)du\varepsilon\right)} \quad (6)$$

which is still a complicated expression. More insight could be given if the elemental powders are introduced in the vial with an initial ratio m of A on B species equal to the stoichiometric ratio of the formed compound A_nB , n . In such a case, $\varepsilon = n/m = 1$, and the equation simplifies to:

$$\frac{\partial}{\partial t} \alpha(t) = (1 - \alpha(t))^2 f(t) \quad (7)$$

which may be integrated as:

$$\alpha(t) = \frac{\int_0^t f(u)du}{\int_0^t f(u)du + 1} \quad (8)$$

Now it is possible to make the position

$$F = \int_0^t f(u)du \quad (9)$$

and formally calculate α as a function of F .

$$\alpha = \frac{F}{F + 1} \quad (10A)$$

It is possible to invert such a relationship to estimate the unknown function $f(t)$ on the basis of experimental evolution.

$$F = \frac{\alpha}{1 - \alpha} \quad (10B)$$

Coming back to the general solution, one could consider Eq. 6 as a function of F as:

$$\alpha_\varepsilon = \frac{e^{(F(\varepsilon - 1))} - 1}{\varepsilon e^{(F(\varepsilon - 1))} - 1} \quad (11)$$

In general, the two F functions will be different; however, it is likely that the $f(t)$ function does not depend strongly on composition, as it physically takes into account the mechanical response at a microstructural level of the mixture to the repeated impacts of the balls. This is equivalent to assuming that the crystal size evolution does not change too much with slight variations of composition. It is then possible, by algebraic substitution, to link the more simple kinetics, described by Eq. 8 at initial stoichiometric ratio, to the general described by Eq. 6 in such a way as:

$$\alpha_\varepsilon = \frac{e\left(\frac{\alpha(\varepsilon - 1)}{1 - \alpha}\right) - 1}{\varepsilon e\left(\frac{\alpha(\varepsilon - 1)}{1 - \alpha}\right) - 1} \quad (12)$$

where α may be computed using the values of the mixture at initial stoichiometric composition.



AN EXAMPLE IN THE MECHANOSYNTHESIS OF Fe₃C

Kinetic quantitative studies are not very common in mechanosynthesis of nanophase materials. A set of experiments was performed several years ago, and results were published in Ref. [19]. In such a system,^[20,21] experimental results suggest that fracturing of graphite crystal progresses by steps: fracturing along the hexagonal plane and subsequent fracturing of the hexagonal networks. Most of the experiments were performed at a fixed initial stoichiometric composition, 3 Fe 1 C; this composition corresponds to that of cementite Fe₃C. In such conditions, in the modified Avvakumov Eq. 5 reported above, $\varepsilon = 1$ holds, and it is possible to consider the simpler Eq. 7 and its solution Eq. 8. Using a SPEX 8000 vibrating laboratory mill, with 6 g of powder charge and a ball-to-powder weight ratio 10:1, it was possible to identify by appropriate microstructural analysis—Mössbauer spectroscopy and X-ray diffraction—several phases, Fe, C, a low carbon martensite-like alloy, and three main types of carbides. If we simplify the kinetic trend considering Fe₃C, cementite, as the unique carbide present, and we neglect the martensite-like alloy, we have to take into account just three chemical species: Fe, C, and Fe₃C. In such a way, the real kinetic evolution is simplified; experimental results are reported for iron in Table 3.

The $F(t)$ function presented above is shown as in Fig. 4.

The R^2 value for a quadratic fit is high indeed and a good correlation is found linking $[\alpha/(1-\alpha)]$ to $F(t)$. The almost parabolic trend of $F(t)$ means that the derivative of the $F(t)$ function, $f(t)$, could be linear. It is possible that an approach decoupling the two main contributions

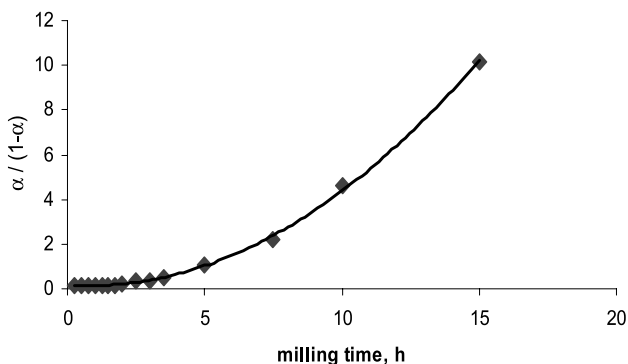


Fig. 4 Mechanosynthesis of nanocrystalline iron carbides: plot of Eq. 10B suggests a possible parabolic trend of $F(t)$ function; squares are experimental data. (View this art in color at www.dekker.com.)

Table 4 Iron and carbon crystal size evolution in the mechanosynthesis of nanophase iron carbides with a laboratory SPEX 8000 mill

Milling time (hr)	Fe crystal size (nm)	C crystal size (nm)
0.25	38	24.6
0.5	32.5	20.4
0.75	34.2	15.7
1	31.3	10.8
1.25	27.9	
1.5	23.6	
1.75	18.1	
2.5	11.6	
3	13.4	
3.5	8.8	
5	9.3	

to reaction rates in mechanosynthesis would be found in the future, linking $f(t)$ to the crystal size evolution. Considering such a hypothesis, Eq. 7 could become:

$$\frac{\partial}{\partial t} \alpha(t) = \frac{c(1 - \alpha(t))^2}{d} \quad (13)$$

which one may solve as:

$$\alpha(t) = \frac{\int_0^t \frac{1}{d(u)} du}{\int_0^t \frac{1}{d(u)} du + \frac{1}{c}} \quad (14)$$

The crystal size evolution $d(t)$ may be evaluated by means of X-ray diffraction line broadening; experimental results for these specific systems are presented in Table 4.

One might check that the crystal size evolution could be assumed as a simple reciprocal function of time. In this case, $1/d_{\text{Fe}} = 0.0259t + 0.0111$ and $1/d_{\text{C}} = 0.0682t + 0.0189$, where d_{Fe} and d_{C} are the iron and carbon crystal size, respectively. The reciprocal of the grain size d could be assumed as^[10] $1/d = 1/d_{\text{Fe}} + 1/d_{\text{C}}$ and, in this case, by summing $1/d_{\text{Fe}}$ and $1/d_{\text{C}}$ contribution, as $1/d = 0.0941t + 0.03$. Substituting this expression in Eq. 13 and integrating as in Eq. 14, one could obtain:

$$\alpha(t) = \frac{ct(941t + 600)}{941ct^2 + 600ct + 20\,000} \quad (15)$$

where c should be evaluated by data fitting. With the choice $c = 0.81$, the data fitting is excellent, apart the first three or four points of the kinetics; this could be a result of an erroneous attribution of the hyperfine field distribution in the Mössbauer spectra at early milling times.



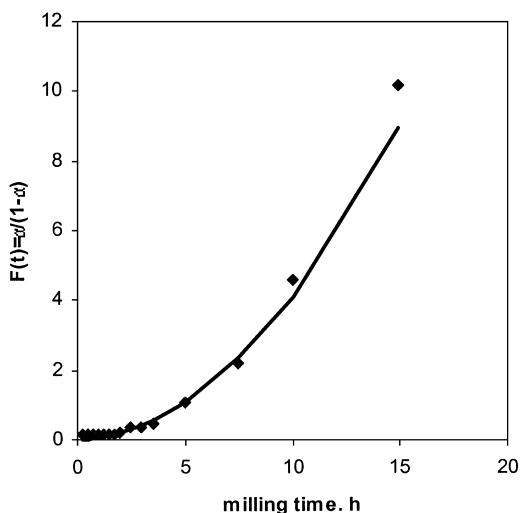


Fig. 5 Experimental results (in squares) in mechanosynthesis of iron carbide compared with values calculated according to real crystal size evolution (Eq. 15).

The agreement with the $F(t)$ function is also excellent, as reported in Fig. 5.

INDUSTRIAL TRENDS AND RESULTS

At the moment of writing this entry, there are two companies that are exploiting successfully the mechanochemical synthesis of nanocrystalline powders: Advanced Powder Technology Pty Ltd.^[22] of Perth, Western Australia, and M.B.N., Italy.^[23] Both companies have strong connections with the university field and could be considered as spin-offs of the research group of Matteazzi et al.^[4] and Dodd and McCormick.^[2] Matteazzi has pioneered the works in the mechanochemical synthesis of nanophase powders, and, along with Le Caer, he was the first to employ the terminology “mechanosynthesis” in obtaining nanocrystalline carbides and silicides^[24] and aluminides.^[25] These compounds, and especially carbides, have remarkable industrial applications in the field of cutting tool materials. Matteazzi chose the Fe–C system as a model for the mechanosynthesis of nanocrystalline carbides for the availability of a powerful tool in microstructural analysis, Mössbauer spectroscopy,^[26] which is applicable to Fe-containing systems. Subsequently, he studied alumina-based nanocomposites^[27] and the solid-state reduction of oxides such as the transformation of hematite to nanocrystalline wustite.^[28] Further work includes the first reported applications of mechanosynthesized materials to catalysis^[29,30] and the

development of a vibrating mill^[12,13] scaling up the possibilities of mechanosynthesizing of the SPEX 8000 mill. Latest developments include the study of grain growth and of consolidation by means of cold isostatic pressing (CIP) and hot isostatic pressing (HIP).^[31] The Italian company M.B.N.^[23] has now developed and scaled-up, with an industrial production capacity of 200 t/years of materials, several of the earlier works by Matteazzi. The company is now focusing on the Mechanomade[®], which is basically a mechanosynthesis technique, and on consolidation technologies such as forging and extrusion with the processes of Mechanoforge[®] and Mechano XT[®]. These techniques have led, for instance, to the production of an Al₂O₃ doped copper alloy (99% Cu, 1% Al₂O₃), which has outstanding mechanical properties (yield strength of 800 MPa, ultimate tensile strength of 900 MPa).

McCormick has obtained the most interesting results in the field of mechanochemical synthesis of nanocrystalline materials. With different coauthors and collaborators, along the years, he has started studying the mechanical alloying process, considering further some constructional detail of vibrating mills. He has recently exploited some results in the field of displacement mechanochemical reactions, which are interesting for the industrial field to patent a specific process—now property of an industrial spin-off of the University of Western Australia, Advanced Powder Technology Pty Ltd.^[23]—that has been called mechanochemical processing MCP[®]. Mechanochemical processing consists in solid-state displacement mechanochemical reactions caused by collisions between particles and balls inside mills. At the end of the reactions, nanocrystalline powders (grain size ~10 nm) within a soluble salt matrix are obtained. Thermal treatments, at low or intermediate temperatures, are typically performed depending on the specific nanocrystalline powders to be obtained. The final step is washing the salt matrix with appropriate solvents, allowing to obtain separated nanoparticles.

The use of a diluent phase may be necessary to:

1. Avoid combustion reactions during milling.
2. Reduce the volume fraction of nanoparticles (in this way, it is possible to avoid nanoparticles being agglomerated).
3. Control the particle size distribution.

Comparing it to the more simple mechanochemical reaction which has been presented in previous paragraphs, it is harder to model the physicochemical process. McCormick has obtained main results by using single ($A + BC \rightarrow AB + C$) or double ($AB + CD \rightarrow AD + BC$) displacement reactions.



For instance, in the production of ultrafine Co and Ni particles^[32] with a narrow particle size distribution of 10–20 nm, the reactions:

Reaction	ΔH (kJ/mol)
$\text{CoCl}_2 + 2\text{Na} \rightarrow \text{Co} + 2\text{NaCl}$	–495
$\text{NiCl}_2 + 2\text{Na} \rightarrow \text{Ni} + 2\text{NaCl}$	–507

were obtained by SPEX 8000 processing with a ball-to-powder ratio 3:1 and with typical processing times of the order of 24 hr. Here and in other previous works, a remarkable effect of the diluent phase NaCl was observed on the influence of the mean particle size, being of the order of nanometers in case 25–50 wt.% diluent and increasing it to the micron range when not present.

Further examples include the synthesis of metal sulfide nanoparticle^[33] reaction of the type $\text{ZnCl}_2 + \text{CaS} \rightarrow \text{ZnS} + \text{CaCl}_2$, with a mean particle size, observed by TEM, of 12 nm.

The synthesis of metal-oxide nanoparticles was described in Ref. [34]. A representative reaction is:

Reaction	ΔH (kJ/mol)
$\text{CeCl}_3 + 3\text{NaOH} \rightarrow \text{Ce(OH)}_3 + 3\text{NaCl}$	–345

Finally, one should also consider the activities of the Institute of Solid State Chemistry and Mechanochemistry of Novosibirsk, Russia,^[35] which has a research experience in field of mechanochemistry dating back to 1970s. Several applications, which span from the metal industry to the field of medical and cosmetic, are now directed to the mechanochemical synthesis of ceramic powders such as, for instance, nanocrystalline Al_2O_3 .^[36]

CONCLUSION

This article has presented some aspects of mechanochemical synthesis of nanophase powders, with an elementary modeling of the process^[37] and a general description of the results in the field. Mechanochemical synthesis is one of the most appealing technologies for the synthesis of nanophase materials, and, at an industrial and commercial level, it is already exploited for sintered products,^[23] abrasive processing,^[22] catalysis,^[22,23] medical,^[23] cosmetic,^[23,35] and even cleaning applications. Among different mechanochemical processes, MCP[®] process—which combines mechanochemical synthesis with appropriate thermal posttreatments—appears the most interesting for its capability to obtain nanocrystalline

powders of the order of 10–20 nm of many different materials. Possible research activities, related to applications in the field, would likely include the study of the influence of diluents in mechanochemical reactions and techniques for engineering, controlling, and sizing particles which have dimensions 2 orders of magnitude less than the finest powders used in metal powder technologies.

More details of the technologies of nanostructured material synthesis by mechanical attrition, in which mechanochemical synthesis should be inserted, are described in the entry by Koch^[38] in this encyclopedia; the reader is referred there not only for a more thorough description of these technologies, but also to appreciate shortcomings of this methodology, mainly represented by powder contamination during milling, which have not been discussed here.

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