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# Mechanical activation of heterogeneous exothermic reactions in powder mixtures

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The review concerns the results of recent experimental, theoretical and applied studies on mechanical activation of reactive powder compositions and self-propagating high-temperature synthesis of materials using activated mixtures. We discuss the influence of activation regimes on the combustion temperature and velocity, self-ignition temperature, activation energy of the reaction, as well as the microstructure and atomic structure of the reactive compositions. Particular attention is paid to revealing structural transformations that lead to an increase in the reactivity of powder mixtures. Examples of practical application of the processes reviewed are presented.
The bibliography includes 229 references.

## Contents

1. Introduction 875
2. Influence of planetary ball milling on the reactivity of powder mixtures 877
3. Mathematical models and experimental observations of interaction between milling bodies and powders 883
4. Theoretical ideas about the causes of changes in reactivity: a comparison with experimental data 888
5. Role of structural transformations in the increase in reactivity 891
6. Application of mechanical activation to synthesis of materials 894
7. Conclusion 896

## 1. Introduction

Mechanical activation of powder compositions by treatment in planetary ball mills is an efficient method for the synthesis of inorganic compounds and materials. Indeed, there is considerable literature on the title topic and the number of original communications, analytical reviews [1–7] and monographs [8–12] concerned with research and development in this area continuously increases. Depending on the method used to carry out a chemical reaction, all studies in this field can be divided into two large classes.

The first class includes experiments where the chemical reaction between components of a powder mixture proceeds during the treatment in a planetary ball mill. This approach is termed mechanochemical synthesis,[2,8] mechanical alloying or mechanical doping since a mill is loaded with a mixture of starting powder reactants that are treated to give a product, that is, a chemical compound or an alloy. Vigorous exothermic reaction in the course of mechanochemical synthesis was for the first time reported for metal chalcogenide systems.[13]

The second class includes studies where mechanical treatment is arrested prior to the start of a chemical reaction. Usually, such a treatment has no effect on the chemical and phase compositions of powder mixtures, but the reactivity of the mixtures changes significantly. This approach is termed preliminary mechanical activation,[9,10] or arrested reactive milling.[14–16] Preliminarily mechanoactivated compositions can be used in various processes of the synthesis of materials and fabrication of items, in pyrotechnics, as additives to solid propellants and for other purposes,[16,17] but in all cases the chemical reaction follows the activation process and the activated composition is removed from the mill activator.

In spite of fundamental differences between the two approaches, they are practically implemented using the same activators under similar treatment conditions; therefore, it is impossible to separate studies on mechanochemical synthesis and preliminary mechanical activation. In this review we will consider both approaches. The emphasis is placed on the recent results concerning preliminary mechanical activation, since there are numerous issues to be solved in this area. In our opinion, most of them can be reduced to the following:

— what are the changes in mechanically treated solid reactants that influence the reactive properties of powder mixtures and the routes of heterogeneous reactions in them?

— what are the mechanisms of this influence?

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Urgent need to solve these issues was in a general way formulated by Academician V.V.Boldyrev in a review:[3] '... the information gathering step should be already replaced with the systematisation of the available information and construction of models for the mechanical activation and mechanochemical reactions. So far, this has been accomplished only in a few particular cases. The accumulation of experimental facts is still underway but it should not last forever'.

Mechanical activation is applicable to various chemical classes of compounds and uses various types of equipment. Being not intended to cover all aspects of mechanical activation in a single review, we restrict ourselves to consideration of treatment of exothermic powder mixtures of inorganic components in planetary and vibratory ball mills. An analysis of publications shows that at present high-energy ball milling in planetary ball mills is the main method of mechanical activation† for basic research and technology. Exothermic mixtures, *i.e.*, mixtures whose components can react with one another with release of a considerable amount of heat, attract the attention of researchers not only due to various practical applications of these systems. Mechanical treatment of such compositions allows one to obtain valuable information on high-temperature heterogeneous reactions involving solid particles and melts, on the influence of microstructure, grain boundaries, structural defects and other microscopic factors on the kinetics and mechanisms of these reactions. Recently, most research activity has focused on powder mixtures of elemental metals and nonmetals used in self-propagating high-temperature synthesis (SHS) technologies as well as on mixtures of metal oxides with aluminium or magnesium (thermite compositions). This review mainly concerns the SHS compositions. More comprehensive information on other systems can be obtained from original communications concerning metal–oxide thermite systems,[7,18–20] organic[21–23] and other systems.

We will discuss the most important results obtained in the last 10–15 years. Section 2 is devoted to critical analysis of experimental data on the combustion velocity and temperature and on the ignition temperature of reactive exothermic mixtures treated in planetary ball mills, aimed to determine the most reliable characteristics of the reactivity of the systems in question.

In Section 3 we will analyze the influence of mechanical factors on powder particles activated in planetary ball mills. Most mathematical models for mechanical activation are usually based on the assumption of intense plastic deformation of reactants under the action of impact load. Recent experimental data obtained using high-speed video recording inside the milling vials of planetary ball mills showed that impacts are not the main factor responsible for activation. A critical comparison of the mechanical mathematical models with experimental data allows one to quantify the impacts of grinding balls on the components of reactive mixtures. It is commonly accepted that impact load causes certain changes in the structure of chemical compounds and that these changes influence their reactivities. However, opinions are different as to the nature of the changes in question and on the mechanism of their action on reaction. We will consider such factors as a decrease in the activation energy of the reaction, grinding of reactants and an increase in the specific contact surface area, an increase in diffusion coefficients resulting from accumulation of structural defects, increasing role of grain boundary diffusion of reactants, seeding of product phases, *etc*.

Various hypotheses concerning an increase in the reactivity of mechanically activated powder mixtures are analyzed and compared in Section 4. Application of high-resolution transmission electron microscopy (HR TEM) in studies of activated compositions made it possible to detect nanosized precursors that are formed during mechanical activation and significantly influence the initiation of heterogeneous reactions in the powder mixtures. These new experimental data are presented in Section 5. Next, in Section 6, we will consider some examples of how mechanical activation is used in the synthesis of ceramic and intermetallic materials and in pyrotechnic compositions. In Conclusion, we briefly summarize the key trends of the development of the title field of research in the last decade and point to the issues to be solved in the nearest future.

Notations and abbreviations used in the review are as follows:

$\varepsilon$ — excess energy influencing the activation energy of reaction;

$\eta$ — dimensionless conversion;

$b$ — constant characterizing the properties of the material being ground;

$D_a$ — activation dose;

$E$ — activation energy of reaction;

$E_0$ — activation energy for the initial mixture before mechanical treatment;

$E_b$ — ball impact energy per hit (collision);

$E_t$ — total energy of milling that took the time $t$;

$F$ — friction force;

$f_b$ — frequency of impacts;

$F(\eta)$ — kinetic function;

$G_m$ — energy efficiency of mechanochemical reaction / mol MJ$^{-1}$;

$J$ — specific power density of activator;

$K$ — parameter of planetary ball mill;

$k$ — friction coefficient;

$k_0$ — pre-exponent;

$m_p$ — mass of powder being treated;

$n$ — order of chemical reaction;

$N$ — normal force pressing rubbing bodies to each other;

$n_b$ — number of balls in milling vial;

$q$ — heat release rate;

$Q$ — heat of reaction;

$r$ — radius of milling vial;

$R$ — universal gas constant;

$r_b$ — radius of grinding ball;

$R_d$ — radius of Sun Disk;

$S$ — specific contact surface area between reactants;

$S_0$ — maximum specific surface area of particles;

$T$ — temperature;

$t$ — activation time;

$T_{ad}$ — adiabatic temperature;

$T_c$ — combustion temperature;

$T_{ign}$ — self-ignition temperature;

$T_{max}$ — maximum temperature of products;

† In addition to 'mechanical activation', the term 'high-energy ball milling' is often used. Usually, the latter is indicative of the use of planetary rather than conventional ball mills.

$T_{ign}^{0}$ — self-ignition temperature of initial mixture (before activation);
$U$ — linear combustion velocity;
$V$ — friction velocity;
$W$ — angular velocity of Sun Disk;
$w$ — angular velocity of milling vial;
$x$ — fraction of activated particles in mixture;
DSC — differential scanning calorimetry;
MDS — molecular dynamics simulation;
SHS — self-propagating high-temperature synthesis;
SPS — spark plasma sintering.

## 2. Influence of planetary ball milling on the reactivity of powder mixtures

The main modes of self-sustained exothermic reactions in powder mixtures are the autowave and thermal explosion ones.[24] In the former case the reaction is initiated locally and spontaneously propagates from the heated region throughout the sample (powder mixture, compacted sample, *etc.*) in the form of a combustion wave. Usually, experimentalists measure the linear velocity of the combustion wave front ($U$) and the temperature of reaction products immediately behind the combustion wave front ($T_c$). These characteristics of an autowave process are termed the combustion velocity and combustion temperature, respectively.

In the thermal explosion mode, the entire reactive sample is heated homogeneously in order to minimize the nonuniformity of the temperature distribution inside the sample. Ideally, the temperature at any point of a reactive sample should be the same at any instant; therefore, a self-sustained reaction will be initiated at all points simultaneously (so-called volume self-ignition of the sample). This reaction mode corresponds to the thermal explosion model by N.N.Semenov[25,26] and is also called volume combustion. The key experimental parameter of this mode is the self-ignition temperature ($T_{ign}$); some authors also reported the maximum temperature of products after completion of the reaction ($T_{max}$). In the text below we will analyze the experimental dependences of these parameters on the mechanical activation condtions.

### 2.1. Influence of activation on the combustion velocity and temperature

The influence of activation on the combustion velocity of SHS compositions was for the first time observed in the experiments on mechanical treatment of titanium powder and its mixtures with carbon black in conventional (non-planetary) ball mills.[27] A two- or threefold increase in the combustion velocity and a considerable decrease in the self-ignition temperature of the hybrid system Ti–$N_2$ (solid–gas) and the gasless system Ti–C was found. Interestingly, the combustion velocity of the Ti + C composition increased equally both for an individually treated Ti powder that was manually mixed with carbon black and for a treated mixture of titanium and carbon black. However, mixing titanium and soot in the same milling vial without grinding balls had no effect on the combustion velocity. A noticeable increase in the combustion velocity required prolonged (up to 120 h) treatment in ball mills.

Experiments using planetary ball mills allow the treatment time to shorten by a factor of 1 000 and more. This is an interesting feature of high-energy mechanical activation since, in spite of higher power density of planetary ball mills, the ball impact energies in them are comparable with the impact energies in conventional mills that are usually equipped with heavier balls (see below). More information on the influence of low-energy treatment on the combustion parameters can be found in a review;[28] here we restrict ourselves to activation in planetary ball mills.

The dependences of combustion velocity on the treatment duration (Fig. 1) were measured for various powder compositions. The most complete data obtained for the Ni–Al systems (see Fig. 1 *a*) do not allow one to reveal a trend that could be treated as common to all systems studied. Most often, curves passing through a maximum are observed, that is, the combustion velocity initially increases and then gradually decreases (see curves *1–3*, *8–10*, *12*, *14*, *15* in Fig. 1).

Activation, *i.e.*, an increase in combustion velocity, depends on various factors and can be achieved in different manner (see below). Deactivation (decrease in combustion velocity after mechanical treatment) is most often explained by the formation of some amount of products in the reactive mixture during mechanical treatment; this leads to reduction of the specific heat release of the activated mixture and to blockage of the contact surface of the reactants.[10] Although such an explanation is obvious, it seems to be unsatisfactory. The experimentally observed considerable decrease in combustion velocity requires that the fraction of such products be rather high (tens of per cent), but this contradicts the results of chemical analysis or X-ray powder diffraction studies of activated mixtures. For instance, activation of the 5 Ti + 3 Si mixture is accompanied by the appearance of trace amounts of the product $Ti_5Si_3$ (diffraction peaks of negligible intensity against the background) in the activated mixture after vacuum annealing; clearly this cannot be responsible for the fourfold decrease in the combustion velocity (see curve *16* in Fig. 1 *b*).[38] Contrary to this, a study of 3 Ti + $B_4C$ mixture revealed a noticeable amount of product (TiC) after 5 min of treatment, but the combustion velocity increased twofold rather than decreased as the treatment duration increased from 3 to 9 min (untreated mixture does not burn, see curve *11* in Fig. 1 *b*).[34]

An interesting feature was observed in a study of the 3 Ti + 2 BN composition (see curve *12* in Fig. 1 *b*).[35] Namely, the combustion velocity of the mixture activated from 0 to 1 min initially increases and then decreases; the composition activated from 1 to 4 min does not burn at all (this corresponds to the dashed line). Eventually, activation over four minutes and more causes the composition to combust, but the combustion velocity decreases considerably. Noteworthy, the X-ray diffraction patterns of the samples activated for 1 and 10 min exhibit no traces of crystalline intermediates or final reaction products.

It should be noted that the authors of many studies on correlations between the combustion velocity and activation time do not report the dependences of the composition of the mixture on the treatment duration. Moreover, even for the same mixture Ni + Al and similar mechanical activation modes, different dependences of the combustion velocity on the treatment duration were obtained (see Fig. 1 *a*). In addition, the combustion velocity of activated Ni + Al compositions depends on the external pressure of inert gas (Ar), and the dependences obey different patterns for different mechanical treatment modes.[40] Activation of a Ni + Al

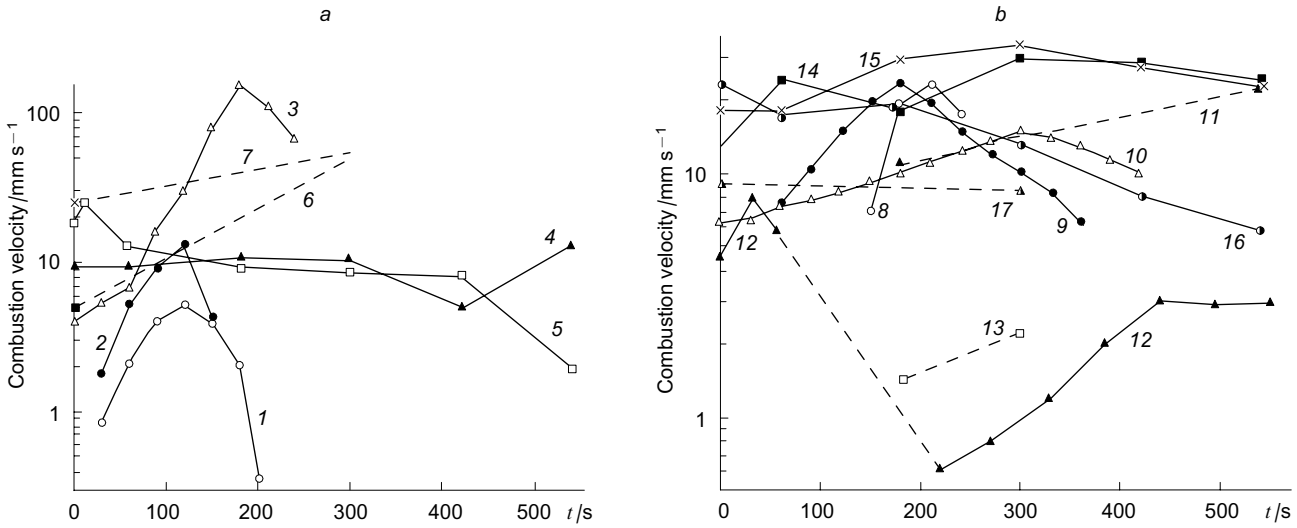



**Figure 1.** Combustion velocity plotted *vs.* duration ($t$) of mechanical activation in planetary ball mills for Ni + Al mixtures (*a*) and other compositions (*b*):
3 Ni + Al (*1*);[29] 3 Ni + Al (*2*);[30] Ni + Al (*3*);[30] Ni + Al, mechanical activation in air (*4*);[31] Ni + Al, mechanical activation in argon (*5*);[31] Ni + Al, loose powder (*6*);[32] Ni + Al, pressed sample (*7*);[32] Ti + Ni (*8*);[30] 40 mass % (Ti + 2.1 B) + 60 mass % Cu, ball acceleration of 60 g (*9*);[33] 40 mass % (Ti + 2.1 B) + 60 mass % Cu, ball acceleration of 40 g (*10*);[33] 3 Ti + $B_4C$ (*11*);[34] 3 Ti + 2 BN (*12*);[35] Ta – Zr – C (*13*);[36] 5 Ti + 3 Si, fine titanium (*14*);[37] 5 Ti + 3 Si, ultrafine titanium (*15*);[38] 5 Ti + 3 Si, fine titanium, vacuum annealing (*16*);[38] and 80 mass % (Ti + C) + 20 mass % Ni (*17*).[39]

mixture along with some amount of hexane in a planetary ball mill for 10 and 40 min led to an increase in the combustion velocity from 12.7 to 22.5 cm s$^{-1}$, respectively.[41]

Without claiming a final explanation of the experimental data presented above, one can assume the following. In the classical theory of combustion the combustion front propagation velocity is unambiguously determined by the heat release rate.[42] Theoretical[43,44] and experimental[45,46] studies of gasless combustion of powder mixtures showed that the reaction wave propagation velocity can depend on the time of heat transfer between particles in the mixture. Thus, there are two stages of the process and each of them can be the limiting stage for the combustion front propagation. This creates prerequisites for realization of complex-shape nonmonotonic dependences of combustion velocity on mechanical activation parameters. The rate of a chemical reaction should increase in mechanically activated mixtures owing to milling of reactants, an increase in the contact surface area between particles of the mixture, cleaning of the contact surface from contaminants and oxide films, as well as intensification of bulk and grain boundary diffusion. However, mechanical activation can lead to either increase or decrease in the efficiency of heat exchange between particles, which depends on the particle shape and size, on the particle size distribution, the interparticle contact surface area and the thermal resistance of interparticle contacts. For instance, a feature of mechanically activated mixtures Ni + Al, Fe + Al and Ti + Al consists in the formation of layered composite particles with submicrometre-thick internal layers of metallic reactants, the composite particle size being as large as hundreds of micrometres.[31,47–51]

Composite particles were also detected in Ta + C (Refs 52 and 53) or TiN + B (Ref. 52) mixtures containing no highly ductile components, *e.g.*, aluminium. As a consequence, the reaction involving a single particle is very fast, while heating and ignition of a neighbouring particle requires much longer time; this was shown using high-speed micro video recording.[35,41] Macroscopic combustion velocity is limited by heat exchange between the composite particles rather than the chemical reaction rate. Therefore, in this case the experimentally observed linear combustion velocity cannot characterize the reactivity of the powder composition. This conclusion also seems to be applicable to other compositions for which data on the morphology of activated particles are unavailable or fragmentary. Thus, mechanical activation influences the linear velocity of the combustion wave of SHS compositions through the shape and size of the composite particles, which determine interparticle heat exchange.

The apparent combustion velocity can also be influenced by the elongation of the samples, which is often observed in SHS processes. Gases that were initially present in pores of the sample or formed as a result of desorption and evaporation of impurities create an internal pressure that can expand the plastic zone of the combustion wave, which was formed as a result of partial melting of components, and thus lead to elongation of cylindrical samples immediately during combustion.[40,54] Mechanical activation causes the intensity of gas production and the extent of elongation of the samples to increase. Owing to elongation the medium becomes more porous, the conditions deteriorate for heat transfer from combustion products to the initial mixture, and the distance for the combustion wave to travel also increases. Taken altogether, these factors can lead to a decrease in the apparent combustion front propagation velocity. An analysis of experimental data on the combustion velocity of mechanically activated compositions showed that this parameter cannot be used as a reliable characteristic of the reactivity of compositions.

**Table 1**. Changes in maximum combustion temperature after mechanical activation.

| Reaction mixture | Character of changes in combustion temperature with increasing duration of mechanical activation | $T_{ad}$ /K (see [a]) | $T_c$ /K | Combustion temperature of activated composition /K | Ref. |
|---|---|---|---|---|---|
| 3 Ni + Al | Maximum at $t$ = 60 s | 1586 | 990 | 1040 | 29 |
| 3 Ni + Al | Maximum at $t$ = 120 s | 1586 | 900 | 975 | 30 |
| Ti + Ni | Maximum at $t$ = 180 s | 1418 | 690 | 910 | 30 |
| Ti + 2.1 B + 1.66 Cu | Monotonically decreases | 2239 | 1800 | 1500 ($t$ = 360 s) | 33 |
| $x$ Ti + $B_4C$ ($x$ = 3–5) | Monotonically decreases as $t$ increases from 3 to 10 min | 3193–3169 | – | From 2370 ($t$ = 3 min) to 1970 ($t$ = 10 min) | 34 |
| 3 Ti + 2 BN | Maximum at $t$ = 30 s | 2624 | 2300 | 2350 | 35 |
| Ta + Zr + 2 C | Increases as $t$ increases from 3 to 5 min | 3206 | – | 2133 ($t$ = 180 s), 2284 ($t$ = 300 s) | 36 |
| Cr + 2 B | – | 1942 | – | 1570 | 55 |
| Ti + 0.46 Cr + 0.72 B | – | 2064 | – | 1770 | 55 |
| Ti + 0.71 Cr + 0.72 B | – | 1928 | – | 1645 | 55 |
| **W + C** | **Monotonically decreases as $t$ increases from 4 to 15 min** | **1340 (at $T_{ign}$ = 1223 K), 943 (at $T_{ign}$ = 298 K)** | **7** | **1350 ($T_{ign}$ = 1223 K)** | **56** |
| Ti + C | Increases as $t$ increases from 2 to 11 h (see [b]) | 3290 | – | 3088 | 57 |
| **Ti + 0.43 C** | **Increases as $t$ increases from 1 h to 6 h 30 min (see [b])** | **1995** | – | **2415** | **57** |
| Nb + 2 Si | Increases as $t$ increases to 9 h (see [b]) | 1870 | 1636 | 1881 | 58 |
| Nb + 0.6 Si | Increases as $t$ increases to 4 h (see [b]) | 2290 | – | 2185 | 58 |
| **Ta + 2 Si** | **Increases as $t$ increases from 2 to 8 h (see [b])** | **1794** | – | **1770 (2 h), 2030 (8 h)** | **59** |
| **Ta + 0.6 Si** | **Increases as $t$ increases from 2 to 8 h (see [b])** | **1823** | **After 2 h activation $T_c$ = 1992 K** | **2238** | **59** |
| Ti + 2 Si | Increases as $t$ increases to 216 min, then decreases and again increases (see [b]) | 1690 | 1612 | 1673 | 60 |
| Ti + 0.6 Si | Weak maximum at $t$ = 4 h (see [b]) | 2400 | 2133 | 2185 | 60 |
| $SiO_2$ + 1.4 Al | Decreases as $t$ increases from 5 to 15 min | 1464 | – | 1330 (5 min), 1260 (15 min) | 61 |
| 3 Ti + 3(1 – $x$) Si + 3$x$ Al | Decreases as $t$ increases from 3 to 6 h and $x$ increases | From 2550 ($x$ = 0) to 1900 ($x$ = 0.6) | – | From 2150 ($x$ = 0, $t$ = 3 h) to 1450 ($x$ = 0.6, $t$ = 6 h) | 62 |
| Ta + C | Remains below the adiabatic value after 4 min of activation; mixtures activated for more than 6 min do not ignite | 2743 | – | 2487 | 53 |

[a] The adiabatic combustion temperature ($T_{ad}$) was calculated using the Thermo program.
[b] Treatment in conventional (not planetary ball) mill.

Published data on the combustion temperature of various compositions (Table 1) are also contradictory since either an increase or a decrease in the combustion temperature are observed after activation. It should be noted that the $T_c$ value determined from the maximum on the temperature profile of the combustion wave can differ from the so-called leading temperature that, theoretically, should influence the combustion wave propagation velocity.[63] At present, we have no experimental data on the fine structure of the temperature profiles of combustion waves in mechanically activated SHS compositions measured using microthermocouples. Studies of powder mixtures carried out in the 1980s involved no mechanical activation. It would be interesting to perform a similar research into mechanically activated compositions; however, this has not been done so far since this experimental method is rather complicated and requires thermocouples less than 10 μm in diameter that can operate under the combustion wave conditions. Optical methods based on high-speed video recording[24,40,45] or infrared thermal imaging[41] revealed significant thermal micro-heterogeneities in the structure of the combustion wave, which also complicate the determination of the 'leading temperature'. Thus, the values listed in Table 1 characterize the temperature of the final reaction product, *i.e.*, the total heat of exothermic reaction minus the heat loss (if exists); here, listed are the data for compositions activated in conventional ball mills but the results of experiments with additional chemical, electrical or thermal activation are not included.

Often, an increase in $T_c$ is explained by accumulation of additional energy in the material during the activation process,[55,56] while a decrease in $T_c$ is thought to be a consequence of partial product formation. Clearly, only the fact that the combustion temperature of an activated

mixture is higher than the adiabatic combustion temperature of this mixture provided a 100% transformation (combustion) of reactants in the absence of heat sink to the environment can be considered as a direct proof of accumulation of additional energy in the reactive mixture. If the combustion temperature remains lower than the adiabatic value, its increase as a result of mechanical activation is most likely indicative of higher degree of combustion due to the milling of reactants and to an increase in the specific contact surface area. As far as we know there are only three publications [56, 57, 59] whose authors detected superadiabatic combustion temperatures of activated compositions (these data are given in bold in Table 1).

The results of a study [56] on high-energy activation of the W + C reactive mixture in planetary ball mills allowed the authors to conclude that $T_c$ is 'almost twice higher' (!) than the adiabatic temperature. We believe this is an incorrect conclusion. The case in point is that the $T_{ad}$ value was calculated assuming that the initial temperature of the mixture equals room temperature; this led to $T_{ad}$ = 963 K.[56] However, the reaction proceeded in the thermal explosion mode, *i.e.*, the entire sample was heated to the self-ignition temperature (1223 K) at which thermal explosion occurred. If this value is taken as the initial temperature of the sample, the calculated adiabatic combustion temperature appears to be nearly equal to the experimentally measured one (see Table 1). It was also reported [56] that heating to temperatures above 973 K causes the formation of $W_2C$ as intermediate product while heating above 1000 K leads to the appearance of trace amounts of WC. However, even if the initial temperature of the reaction is set to 973 K, the adiabatic combustion temperature will still be almost equal to the experimentally measured value. Therefore, at present there are no studies of compositions activated in planetary ball mills reporting the combustion temperatures exceeding the corresponding adiabatic values.

Consider compositions that were exposed to long-term mechanical treatment in conventional ball mills.[57–60] Information on 'super-adiabatic' temperatures determined after treatment of Ta + Si mixtures in conventional ball mills over long periods of time [59] was discussed earlier in a review [28] and a monograph.[24] We pointed out that the initial temperature of the samples was not specified (ignition was achieved after prolonged heating of samples, so their temperature could increase), the pyrometric technique used includes errors due to uncertainties in the emissivity of samples during the combustion process [59] and that the thermodynamic functions of tantalum silicides at high temperatures are not known with certainty. These arguments are also applicable to the Ti + 0.43 C composition.[57] In addition, mention may be made that the Thermo software does not allow one to calculate nonstoichiometic compounds and solid solutions, which can introduce additional errors into calculations of adiabatic combustion temperatures. Indeed, the calculated $T_{ad}$ value of stoichiometric composition Ti + C is higher than the measured combustion temperature of the activated stoichiometric composition.

The combustion temperatures of activated mixtures reported in all other studies known to date do not exceed and are often much lower than the adiabatic combustion temperatures at 100% conversion of reactants (probably, due to heat loss or incomplete combustion). Summing up, accumulation of rather high additional energy in mechanically activated reactive mixtures leading to an increase in the combustion temperature seems to be improbable.

### 2.2. Influence of activation on the ignition temperature

Unlike contradictory data on the influence of mechanical activation on the combustion velocity and temperature, the decrease in the self-ignition temperature of activated mixtures was reported in almost all publications. According to theory of combustion,[25, 26, 42] the self-ignition temperature is a kinetic parameter rather than a constant of a chemical compound or a mixture of individual compounds. As a consequence, it depends on the heating rate and heat exchange with the environment, as well as on the reaction kinetics and other external and internal factors. The decrease in $T_{ign}$ was observed under different heat exchange conditions [fast heating in thermal explosion experiments, slow heating in differential scanning calorimetry (DSC) studies, *etc.*] and at different modes of preliminary mechanical activation. The effect can be more or little pronounced depending on the chemical composition and external conditions.

A very strong effect was reported for Ti + C mixtures activated in a ball mill for 10 h,[57] *viz.*, $T_{ign}$ decreased from 1600 (for the non-activated mixture) to 770 K. The self-ignition temperature of Ti + Si mixture decreased by 900° from 1670 to 870 K after a few hours of milling.[64] The self-ignition temperature of Ti + Si + C mixture was 1190 K before activation and decreased to 430 K after 90 min of milling. The further milling led to self-ignition of the mixture in the 106th minute inside the milling vial.[65]

When using high-energy planetary ball mills, it takes a much shorter time, from tens of seconds to a few minutes, to achieve a similar effect. An analysis of the plots of $T_{ign}$ *vs.* activation time (Fig. 2) reveals two trends. One of them, *viz.*, a monotonic decrease in the self-ignition temperature of preactivated compositions to a critical value with increasing activation time, is characteristic of highly exothermic

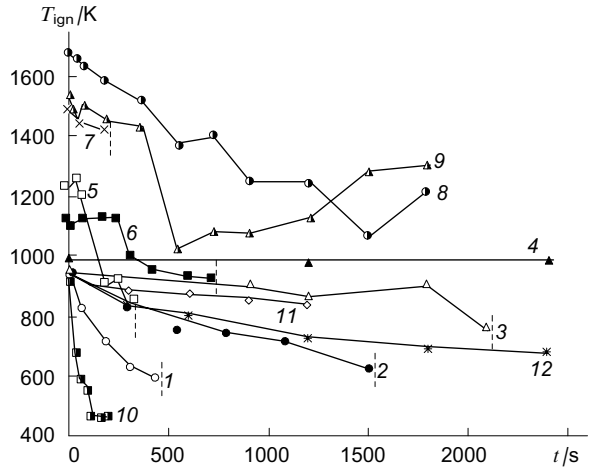



**Figure 2.** Self-ignition temperature plotted *vs.* duration of activation in planetary ball mills:
Ni + Al, ball acceleration of 90 g (*1*);[66] Ni + Al, 60 g (*2*);[66] Ni + Al, 30 g (*3*);[66] Ni + Al, 8 g (*4*);[66] Ti + Ni (*5*);[67] Ti + Al (*6*);[67] Ti + 0.6 Si (*7*);[67] 2 Ti + 3 BN (*8*);[67] 3 Ti + SiC + C (*9*);[67] 3 Ni + Al (*10*);[68] $SiO_2$ + 1.4 Al (*11*);[68] and Ni + Al, activation in the presence of hexane (*12*).[40]

compositions (curves *1–3*, *5–7*). As the critical value is reached, a self-sustained reaction occurs in the milling vial and the entire mixture of reactants is transformed into a product. The limiting values of activation times are denoted by vertical dashed lines in Fig. 2. A similar dependence is also observed for the Ni + Al mixture activated along with hexane (see curve *12*), although no self-sustained reaction is initiated in this case.[41] Shortening of the ignition delay time of activated mixtures was observed in addition to the decrease in $T_{ign}$.

The other trend (see curves *8* and *9*) is characteristic of low-exothermic mixtures. In this case, $T_{ign}$ also initially decreases, but a self-sustained reaction is not initiated and therefore the self-ignition temperature reaches a certain minimum value and then slowly increases but remains lower than the ignition temperature of the non-activated composition. Probably, the increase in $T_{ign}$ can be explained by local formation of reaction products, as is confirmed by X-ray powder diffraction data, but the amount of heat liberated is insufficient to initiate the reaction in the entire mixture.

The efficiency of the influence of mechanical treatment in planetary ball mills on the initiation temperature of a reaction depends on both the composition of the mixture and the treatment conditions. For instance, a significant decrease in $T_{ign}$ from a few hundreds to a thousand of degrees was reported for the Ti + C (Ref. 69) and 70 mass % (Ti + C) + 30 mass % Ni (Ref. 70) compositions. Using high-energy planetary ball mills, this effect is achieved much faster than using slowly rotating conventional ball mills.[63] However, $T_{ign}$ of $SiO_2$ + 1.4 Al composition decreases by less than 100° under high-energy treatment conditions[60] (see curve *11* in Fig. 2). Taking the Ni + Al composition as an example, it was shown that the efficiency of mechanical treatment rapidly increases with increasing mill rotation rate and acceleration of grinding balls (see curves *1–4*).[66] Indeed, the ignition temperature remains unchanged even after 1h of activation at an acceleration of 8 g but decreases by 300–350° within 5–7 min as the acceleration increases.[66] Noteworthy, it is the velocity and acceleration rather than the mass of balls that do influence, that is, the use of heavier balls does not compensate the slow rotation of the milling vial.

The key parameter characterizing the operating mode of a planetary ball mill is the ratio

$$K = \frac{w}{W} \quad (1)$$

where $w$ is the angular velocity of the milling vial rotating about its axis in the laboratory coordinate system and $W$ is the angular velocity of rotation of the vials about the common axis of the mill. For instance, the case $K = 2$ means that the milling vial makes two revolutions about its own axis during one revolution about the axis of the mill; at $K = 0$, the milling vial moves about the axis of the mill with retention of its own spatial orientation relative to the environment. The kinematics of motion will be discussed in more detail in the text below; here we will consider only how the parameter $K$ influences the self-ignition temperature.

The influence of the parameter $K$ on the efficiency of activation, in particular, on the self-ignition temperature was studied (Fig. 3).[71] Experiments were carried out at variable angular velocity $w$ and constant angular velocity

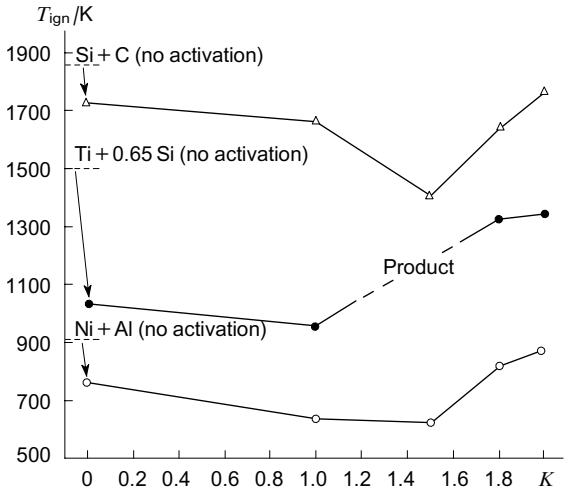



**Figure 3.** Self-ignition temperature plotted *vs.* dimensionless parameter $K$ that characterizes the operating mode of the planetary ball mill.
Treatment duration is 5 min. The plot is constructed using the data taken from Ref. 71.

$W$ and activation time. Horizontal dashed lines near the vertical axis denote the $T_{ign}$ values of corresponding non-activated mixtures. As can be seen, activation causes a considerable decrease in $T_{ign}$ (shown by arrows) at any $K$ values, but the efficiency of mechanical treatment is different depending on $K$. The most efficient mode is characterized by $K = 1.5$ and combustion of the Ti + 0.65 Si mixture with the formation of a reaction product inside the milling vial. Probably, nonlinear character of the dependences shown in Fig. 3 can be explained by specific features of the interaction between the reactive mixtures and the grinding balls (see below).

A rather complex pattern of the influence of mechanical activation on the initiation temperature was revealed by DSC for the $ZrO_2 + H_3BO_3$ + Al thermite mixture treated in a planetary ball mill for 15 h.[72] At a milling speed of 350 rpm, the ignition temperature was lower than at 200 and 450 rpm. The shift of the temperature peak in the DSC traces was up to 40°. Unfortunately, the $K$ value was not specified[72] and therefore it is unknown what is the milling speed, $W$ or $w$. A similar effect was reported for the $TiO_2 + H_3BO_3$ + Al mixture and it was concluded that the activation time has a stronger impact that the milling speed.[73]

A simultaneous decrease in the ignition and combustion temperatures as a result of mechanical activation was found for the thermite composition $MoO_3$ + 3 Zn (combustion experiments using DSC).[74] It was reported that the ignition temperature of the Mo + 2.2 Si composition equal to 931 K is independent of the activation time.[75] However, the authors[75] presented only the data for the activation times from 240 to 319 min and no comparison was made with the behavior of the non-activated composition. Therefore, the influence of activation on this mixture can be considered as quite probably relying on the comparison with the other two mixtures, Ti + Si (Refs 67 and 71) and Nb + Si.[76] The ignition temperature of the Nb + 2 Si composition equal to 750 K after 2 min of activation in a planetary ball mill decreased by ~100° upon activation over a period of 4 min

and then gradually increased up to 1140 K after further activation for 28 min.[76]

A recently proposed ball milling at cryogenic temperatures, which allows one to carry out high-energy ball milling in chambers cooled with liquid nitrogen, was used to study the reactivity of Ni + Al composites.[77] It was found that ball milling at room temperature for 90 min caused $T_{ign}$ to decrease to 675 K, while cryogenic milling led to a decrease in $T_{ign}$ to 600 K after 3 h of activation. A comparison of these data with the available results for nickel–aluminium mixtures treated in the highest-energy mills[66, 68] showed that $T_{ign}$ = 600 K and lower can also be achieved without cryogenic milling and in a shorter time. Nevertheless, cryogenic activation seems to be a rather promising technique since it allows one to process mixtures of ductile metals by reducing their sticking to walls of the milling vial and to the surface of grinding balls.

Thus, mechanical treatment has a strong and proven activating effect on such an important kinetic parameter of reactive mixtures as the self-ignition temperature.

### 2.3. Slow reaction and self-ignition during activation

As mentioned above, activation can be accompanied by either an instantaneous self-propagating reaction resulting in transformation of the entire mixture into the product or a slow reaction characterized by gradual accumulation of a product (this is the classical regime of mechanochemical reactions). At present, there is no answer to the question which of the pathways will be followed by a particular mechanochemical reaction. Often, reactive mixtures demonstrate an unpredictable behaviour. Atzmon[78] treated a Ni + Al mixture in a shaker ball mill and observed the following unusual phenomenon. If treatment was carried out continuously over a period of a few hours, a noticeable amount of product (NiAl phase) was observed only after 180 min of activation and then gradually increased as ball milling continued. However, if the process was stopped after 100–120 min, the milling vial was cooled within 30 min or more under a fan, and then the ball mill was switched on again, the restart was followed in 30–60 s (!) by an instantaneous reaction that converted the entire mixture into NiAl within less than a second. Atzmon[78] assumed that arresting the ball milling process and cooling the powder (with possible oxidation) leads to a decrease in ductility and to concentration of energy in a smaller volume upon the impact of a grinding ball and, consequently, to a higher local temperature upon impact. However, this assumption was not confirmed experimentally.

A study of Mo + Si mixture showed that instantaneous reaction with transformation of the entire mixture into $MoSi_2$ occurred abruptly after two or three hours of continuous milling and that no chemical transformations of the system under study were observed during the milling time.[79] Unlike the situation with Ni + Al mixture, arresting the process was not required. It was assumed that prolonged milling is needed to reduce the reactant particle size to a certain critical value at which ignition becomes possible; accumulation of a considerable excess enthalpy in the activated particles was rejected as highly unlikely event. A mechanical alloying study of a Cu + Al mixture using a shaker ball mill demonstrated that only a slow reaction occurred during treatment of the mixture for 8 h.[80] As the duration of mechanical activation increased, the content of solid solution and intermetallic phases in the mixture gradually increased while the reaction heat release of the treated compositions gradually decreased by one of two orders of magnitude according to DSC measurements. This is indicative of almost complete transformation in the slow reaction regime within 8 h. The existence of both regimes, slow reaction and instantaneous transformation, was established for the Ti + $x$C compositions depending on the reactant ratio.[81, 82] A fast self-sustained reaction was observed only at $0.39 \leqslant x \leqslant 1.22$, whereas a slow reaction proceeded at $0.25 \leqslant x \leqslant 0.39$ and $1.22 \leqslant x \leqslant 4$.[82]

Emphasize that studies[78–82] were carried out using a 'Spex 8000' shaker mill with a small number of relatively heavy grinding balls (at most 11 and even only one[81, 82]) for activation and that the milling vial executed a reciprocating motion. Probably, this provides an explanation for the difference of the results obtained in Refs 78–82 from the data obtained using planetary ball mills for activation. In the planetary ball mills the slow reaction mode is realized only for weakly exothermic and difficult-to-initiate mixtures, such as Ti + BN, Nb + Si or Ti + SiC + C,[67, 76, 83] whereas an explosive reaction of highly exothermic compositions Ti + C, Ti + Si, Ni + Al, *etc.* occurs a few minutes after the activation began (see Fig. 2). No coexistence of both modes in a single system, as well as the 'Atzmon effect' in the activation in planetary ball mills has been reported so far.

A common fact independent of the activation mode is as follows. Activated mixtures are characterized by enhancement of a certain (activating) factor that reduces the threshold self-ignition temperature of the mixture and can lead to self-ignition during the milling process. This cannot be mechanical heating through impacts and friction of grinding bodies because, first, cooled mixtures retain high reactivity and, second, measurements of the milling vial temperature in the vibrating mill showed that it remains low (at most 50–60 °C) even after many hours of milling, up to the ignition of the mixture.[78, 81] It is logical to assume, like in the early studies on mechanochemistry,[84–87] that it is structural transformations of the powder particles that play the role of the activating factor.

From this point of view, studies of mixtures composed of activated and non-activated powders of the same chemical composition are of interest. What happens if an initial mixture of reactants is mixed with mechanically activated mixture of the same chemical composition having a much lower self-ignition temperature? Clearly, two scenarios are possible. According to one of them, the properties of the mixtures will be 'averaged' and the combined composition will be more reactive than the initial mixture but less reactive than pure activated mixture. According to the second scenario, particles of the activated mixture will ignite at low temperature and thus ignite the surrounding non-activated mixture, so the self-ignition temperature of the combined mixture will approach $T_{ign}$ of the activated mixture. At present, few relevant experimental data are available and all of them support the first scenario.

A Ti + 0.43 C composition was activated[81] almost until ignition (~15 h), but the process was arrested prior to self-ignition. The activated composition was mixed, in different ratios, with the initial untreated mixture of the same chemical composition and the combined composition was again mechanically activated until self-ignition. The time necessary for additional activation of the combined composition until self-ignition (Fig. 4 *a*) was measured. Note that

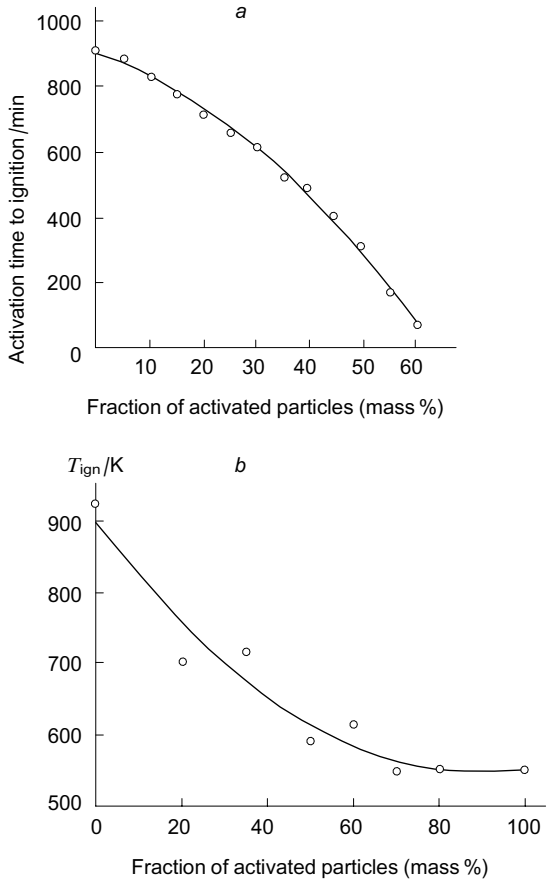



**Figure 4.** Time necessary for additional activation of the composition Ti + 0.43 C until self-ignition [81] (*a*) and self-ignition temperature of Ni + Al mixture [83] (*b*) plotted *vs.* mass ratio of activated and untreated particles in the mixture.

in the original study [81] the duration of the process was measured as the number of collisions between the steel ball and the wall. For convenience, in Fig. 4 *a* it was converted to minutes based on the fact that the collision frequency in those experiments was 29.2 Hz. As can be seen, the time of additional activation gradually decreases with increasing fraction of activated particles; as this fraction becomes as high as 61%, a fast self-sustained reaction occurs.

A somewhat different experimental design was used for the combined composition Ni + Al.[83] The mixture was activated in a planetary ball mill for 5 min (self-ignition occurred in the sixth minute). The activated and untreated compositions were mixed in a porcelain mortar and then the self-ignition temperature of the combined compositions was measured at different fractions of activated particles (see Fig. 4 *b*). It was found that $T_{ign}$ gradually decreases with increasing this fraction and becomes equal to the self-ignition temperature of activated composition as the fraction of activated particles reaches a value of 70% and more. It should also be noted that the measurements of the self-ignition temperatures of certain fractions of activated powder Ni + Al gave equal $T_{ign}$ values for large and small particles.[88] Thus, by mixing compositions of different reactivity one can gradually vary the self-ignition temperature, the additional activation time to ignition and other properties of reactive mixtures.

## 3. Mathematical models and experimental observations of interaction between milling bodies and powders

### 3.1. Theoretical models for motion

The operating principle and design of various planetary ball mills have been described in detail in monographs (see, *e.g.*, Refs 9, 10, 89, 90). A typical illustration of milling media motion in a planetary ball mill is shown in Fig. 5. The milling vials of radius $r$ are mounted on a common disk of radius $R_d$ called the Sun Disk.‡ Often, there are two (in some cases, four) vials. They are arranged symmetrically with respect to the axis of the Sun Disk and have equal masses to avoid strong vibrations.

The vials execute a circular motion with the Sun Disk about the common axis of the mill with angular velocity $W$. In addition, each vial rotates about its own axis with angular velocity $w$. The angular velocity ratio [see expression (1)] is the key parameter determining the operating mode of the mill. At small $K$ values, a ball inside a milling vial, rolls along the inner wall of the vial, always remaining at the maximum possible distance from the axis of the Sun Disk. These balls will be called 'stagnant' since they retain their positions in the coordinate system of the Sun Disk. The angular velocity of rotation (rolling) of a stagnant ball is given by

$$\omega \approx \frac{WR_d}{r_b} \qquad (2)$$

where $r_b$ is the radius of the ball. If the parameter $K$ increases, the friction force on the wall of the milling vial causes the ball to leave its equilibrium position, to get carried 'up' the wall, and then to separate from the wall at a certain point and to go to free fall (if the milling vial contains more than one ball, rolling over other grinding balls can occur). Eventually, at even larger $K$ values, the ball is pressed against the vial wall by centrifugal force and executes a circular motion with the wall. This is a centrifugating ball. What is the motion that has activating effect on

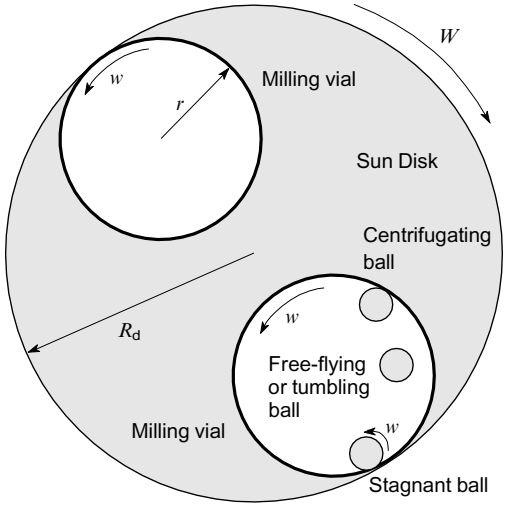



**Figure 5.** Operating principle of a planetary ball mill activator.

‡ The shape of the Sun Disk can be different in some cases.

the powder mixture of reactants placed in a milling vial along with grinding balls?

Most mathematical (mechanical) models for combustion treat collisions of grinding balls with one another and with the milling vial wall as the main activating factor, while friction of grinding balls is considered as additional activating factor. Diagrams of various grinding ball motion modes developed for conventional ball mills where an increase in $K$ is followed by transition from tumbling motion of balls to free fall and then to centrifugal (supercritical) motion (Fig. 6) are almost commonly accepted. In spite of certain differences in details of the motion modes and terminology, this scheme is reproduced in many monographs and reviews devoted to treatment of powders in planetary ball mills.[10,91,92] This approach is often used as a basis for comparison of the efficiencies of different activators.[8,93] The models for planetary ball mills differ from those developed for conventional ball mills in that the former take into account the centrifugal force that is created by the motion of the Sun Disk, plays the role of artificial gravity force and is many times higher than conventional gravitation.

A modern trend in theoretical modelling is to perform a more detailed analysis of the collision event and energy dissipation. Often, models are based on the Hertz problem of direct central collisions of balls and on the Kelvin–Voigt viscoelastic model (spring–damper), while the finite element method (FEM) is used as research tool.[94] Based on the results of kinematic modelling of a planetary ball mill, it was concluded that the activation efficiency is directly related to the impact (shock) power[95,96] that was defined as the product of the impact (collision) frequency and the kinetic energy of balls flying after a hit. Depending on the impact angle, the kinetic energy was divided into the impact energy (direct impact) and the friction energy (oblique impact, rotating balls).

A similar approach was used for comparative analysis of the kinematics of tumbler and planetary ball mills.[97] According to calculations, the shock power should pass through a maximum with increasing parameter $K$ and this maximum can be observed at $1.7 < K < 3.2$ depending on the ratio of the radii $r$ and $R_d$ (see Fig. 5). Based on detailed mathematical treatment of all components of the velocity and forces acting at the instant of impact, it was concluded that the impact efficiency is determined by the tangential component of the impact force, which monotonically decreases as $K$ decreases.[98] An FEM analysis of the effect of the velocity and direction of rotation of the milling vial on the specific impact energy of balls in a planetary ball mill showed[99] that this energy is much higher if the Sun Disk and the milling vial rotate in opposite directions. The dependences on $K$ pass through a maximum at $K = 2.4$, but the maximum specific impact energy for rotation in opposite directions is as high as 15.5 kJ $s^{-1}$ $kg^{-1}$ *vs.* only 3 kJ $s^{-1}$ $kg^{-1}$ for unidirectional rotation of the disk and milling vial. The FEM approach was improved to simulate the motion of grinding balls and forces acting at the instant of impact taking account of their real mass, density, elastic modulus and other properties.[100] Numerical simulation showed that normal impacts dominate at short times of milling (to 0.3 s) while the sliding motion of the balls along the vial wall becomes the main type of motion at longer times.

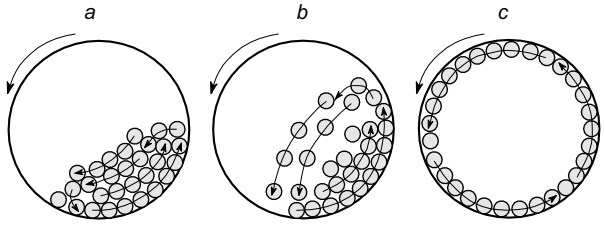



**Figure 6.** Different motion modes of grinding balls in a ball mill according to kinematic models.
Friction mode (*a*), tumbling mode (*b*) and centrifugal, or supercritical, mode (*c*).

The model with allowance for heating of grinding balls and powder mixtures was constructed under the following assumptions:[101]

— the maximum possible increase in temperature occurs if 100% of the kinetic energy of the motion of ball is converted to heat; and

— self-ignition of mixtures occurs if the heat release rate initiated locally (at the impact points) is higher than the rate of heat dissipation into massive parts of the mill.

Calculations using this model showed that the mechanical activation time necessary for self-ignition of a mixture is shortened as the rotation velocity of the milling vials, the ball size, density and mass, as well as the enthalpy of formation of reaction product increases. The results obtained were in good agreement with experimental data on activation of Ti + C mixtures with different intensity. Conversion of kinetic energy of grinding balls to internal energy of powder mixtures upon collisions is the key point of a number of recent models.[102,103] In particular, it was concluded[102] that the maximum impact energy and activation efficiency are achieved at $K = 1.15$ and $W = 800$ rpm. Attempts were also reported to take account of liquid media[104] and abrasive wear[105] on mechanical activation.

### 3.2. Experimental observations

The authors of experimental studies on validation of activation models use three different approaches. One of them involves establishment of dependences of the phase composition, structure and properties of activated mixtures on the operating modes of ball mills[81,82,101,102,106] under the *a priori* assumption of dominant role of impacts which serves a basis for most theoretical models of activation. For instance, the composition of products of mechanochemical synthesis was plotted *vs.* impact energy and collision frequency for the Ni + Zr mixture,[106] but no direct data on the collision frequency and impact energy were obtained since all data were plotted *vs.* the parameters $w$, $W$ and $K$. The dependences of the properties of mixtures on the number of collisions are available;[81,82] however, the collision frequency was assumed to be equal to the doubled oscillation frequency of the shaker mill-mixer and no direct observation of the motion of grinding balls was done.

An experimental study of the effect of collisions using a free falling ball[107] provides an example of the second approach. A steel grinding ball was released from a specified height to impact upon a thin layer of steel powder particles located in a recess of a steel plate. This method has clearly seen advantages, *viz.*, the possibility of direct measurement of the velocity and the kinetic energy of the ball, the impact force, the rebound height, as well to study the

effect of the impact of prescribed specific impact energy on the powder particles. Based on the results of these measurements, it was concluded that the impact force, *i.e.*, the force with which the ball presses on the steel plate, is a relevant parameter for assessing the efficiency of collisions during the activation process. The porous powder layer dampers impacts, thus reducing the impact force and increasing the time of contact between colliding bodies. Therefore, the simple Hertz model of colliding balls was thought to be inapplicable in this case and a modified Kelvin–Voigt viscoelastic model was proposed instead.[107]

It should be noted that a similar but improved model approach was tested in a study of mechanochemical synthesis in organic system glycine–oxalic adid dihydrate.[108] In this case, a solid body inside a solenoid was lifted under the action of magnetic field when the solenoid was switched on and fell freely onto the sample placed at the anvil when the solenoid was switched off. Numerous repetition of the cycle made it possible to study the dynamics of the mechanochemical reaction. Probably, the model experimental procedures are most appropriate to study the activation modes in vibratory (shaking) mills where a relatively small number of massive grinding balls fall from one end of the milling vial to the other end and back, thus following the reciprocating motion of the mill. The results obtained can also be used to analyze processes occurring in planetary ball mills, but one should know parameters of collisions that occur under planetary motion of the milling vials.

The third approach, which is based on direct observations of the behaviour of grinding balls during the activation process, seems to be the most promising. Indeed, even the pioneering study [109] on direct observation of processes occurring in a planetary ball mill gave unexpected results. The motion of grinding balls was monitored through transparent lids of milling vials and photographs were taken (exposure duration 1 ms) and high-speed video recording (exposure duration of 0.25 and 0.5 ms) was used. It was found that actual ball trajectories do not agree with the theoretical models based on the kinematic schemes. Free fall and ball–ball collisions were not observed for all operating modes of the planetary ball mill, friction or rolling of the balls being predominant. As a result, a conclusion was drawn for the first time that mechanical activation processes should be analyzed in terms of attrition and wear in accordance with the results of *in situ* observations [109] rather than collisions (as in most theoretical models).

A complex planetary motion makes a detailed quantitative analysis of trajectories and velocity vectors for each ball difficult; therefore, the first experimental data were obtained for a ball mill.[110] A mill with an internal diameter of 0.8 m and transparent lid was alternately illuminated using blue and red flashes and photographs were taken at each flash. Pairs of successively taken colour photographs were processed using a computer and a velocity field at the instance of flash was constructed for each of a total of 190 grinding balls 30 mm in diameter. It was found that the rolling mode dominates at all values of rotation speed. The fraction of free falling balls that do not contact other bodies was at most 5% even at maximum rotation speed and their distance from the main group of low mobile balls was merely 2–3 cm and their velocity was about 1 m $s^{-1}$, which corresponds to free fall from a height of nearly 5 cm. Thus, the motion of a small fraction of 'active' balls can be characterized as low jumps when rolling down the layer of low mobile balls rather than free fall.

In the subsequent experiments aimed to determine actual trajectories of grinding balls a video camera mounted immediately on the milling vial of a planetary ball mill made a circular motion about the common axis of the mill with the milling vial.[111] Like earlier, the results of a study of changes in the parameter $K$ at different number of balls and different types of powders in the milling vial led to the conclusion that the observed picture of the motion of grinding balls is fundamentally different from the trajectories calculated using kinematic models. It is believed that the discrepancies are due to neglect of friction and sliding in the early kinematic models. Therefore, a model taking account of differences between the sliding friction and rolling friction coefficients was proposed. Corresponding FEM calculations showed good agreement between this model and experimental observations. Both the experiment and numerical simulation revealed no free-falling balls; the grinding balls were always grouped and the average relative rolling collision velocity was ~0.1 m $s^{-1}$.

Recently,[71] it was shown that a technically complicated procedure for mounting a video camera inside a planetary ball mill can be replaced by computerized image processing. A high-speed video camera is mounted stationary along the axis of the Sun Disk and the motion of the Sun Disk with two milling vials (Fig. 7) is recorded. In each video frame, two square windows were selected, each window centred at the axis of the milling vial. The window was referenced to the coordinate system of the Sun Disk and rotated about the axis of the Sun Disk. Thus, the milling vial is always at the centre of the window, as if the video camera was mounted above the vial. The results of observations of the ball trajectories were compared with the data on the activation efficiency that was evaluated from the self-ignition temperatures and structural transformations of the mixtures. The most intense activation occurred at $K = 1.5$; as $K$ further increased, the activation efficiency decreased (see Fig. 3).

Examples of the ball arrangement patterns, ball motion trajectories and velocity fields are shown in Fig. 8. As can be seen, the most intense activation

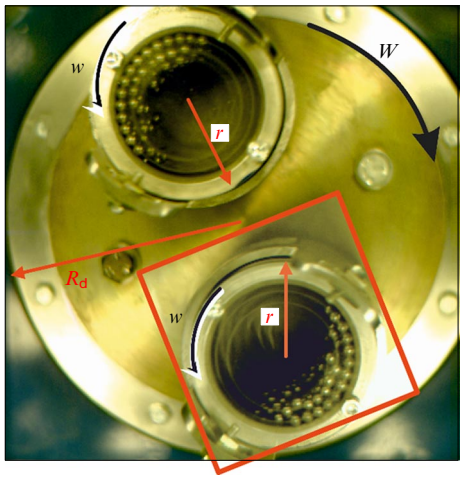



**Figure 7.** Analysis of digital images obtained by high-speed video recording: a schematic.[71]

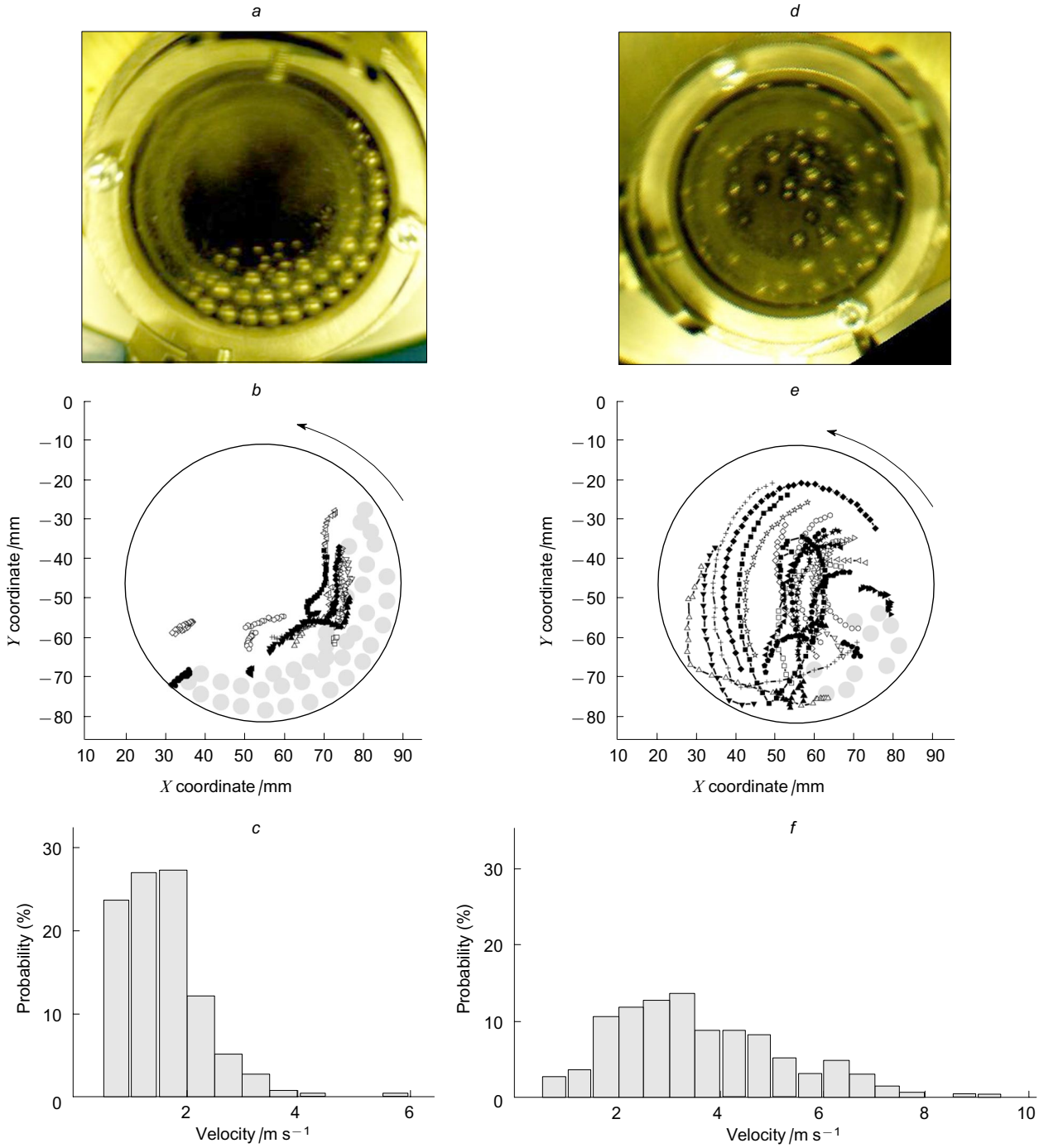



**Figure 8.** High-speed video recording of the motion of grinding balls at $K = 1.5$ (*a*–*c*) and 1.9 (*d*–*f*).[71] Digital images (*a*, *d*); trajectories of the moving balls ('stagnant' balls are shown as grey circles) (*b*, *e*); and statistical distributions of ball velocities in the coordinate system of the Sun Disk (*c*, *f*).

($K = 1.5$) occurs when most balls are 'stagnant', *i.e.*, almost do not change their positions, the motion trajectories of other balls correspond to the rolling mode and the ball motion velocity is at most 4 m s$^{-1}$ (Fig. 8 *a*–*c*). The fraction of free falling balls increases at $K = 1.9$, and their velocity increases up to 8 m s$^{-1}$ (see Fig. 8 *d*–*f*), but the activation becomes less pronounced (see Fig. 3). It follows that ball friction against one another and against the vial wall is a stronger activating factor compared to impacts of free falling balls.

### 3.3. Conditions in the vicinity of ball – reactant contact region

Irrespective of the type of mechanical activation (impact or friction), it is microscopic reactant particles localized in the gap between the colliding or rubbing balls (or between the ball and the vial wall) that are activated. Therefore, one has to consider conditions in this gap.

At present, no procedures for measuring instantaneous local temperatures at the ball–ball contact points are available; therefore, indirect methods are used. For instance, the temperature of cooling water was measured [112]

at the inlet and outlet of a planetary ball mill (mechanical power dissipated into heat was calculated from the temperature difference); the temperature of the outer surface of the milling vial was also measured. Within 30 s after stopping the mill the milling vials were transferred into a calorimeter where the total heat content of the vials along with the grinding balls and powder was determined.[112] Those data were used to calculate the temperature of the grinding balls assuming that they accumulate 80% of the total heat during the milling process. It was found that the temperature of the grinding balls can be as high as 885 K in the absence of powder; however, this value decreased to 470 K taking into account the presence of alumina powder. The temperature of grinding balls calculated using this approach increased as the ball diameter increased from 3 to 9 mm at a constant total mass of balls in the milling vial. Direct ball temperature measurements were carried out with a thermocouple that was inserted into the vial immediately after stopping the mill (time necessary to stop and open the mill was 50 s).[67] The average ball temperature after 6 min of activation of Ni + Al mixture in argon atmosphere was as high as 570 K. Interestingly, heating in argon atmosphere occurred faster than in air, *viz*., the ball temperature after milling the same mixture in air was only 320 K.

Continuous measurements of the temperature and pressure during the milling of Ti + C mixture were carried out using a special wireless temperature and pressure monitoring system located inside the milling vial of a planetary ball mill.[101] In the course of milling the vial temperature increased by only 10–12° (from 300 to 312 K) A temperature peak at 325 K (self-ignition point) was accompanied by a gas pressure peak of nearly 400 kPa. However, calculations of heating of a porous powder medium in the gap between colliding balls showed that the local temperature at the point of collision can reach a value of 870 K. This corresponds to an increase in the average temperature of the milling vial to 350 K under assumption that the heat released at the points of collision is uniformly distributed in the bulk of the vial. Similar results were obtained for a vibratory mill using a temperature sensor mounted on the outer surface of a milling vial executing a reciprocating motion.[81] The temperature of the outer wall of the vial was at most 320 K after a few hours of treatment of a Ti + C powder mixture; self-ignition of the mixture was accompanied by the detection of a temperature peak at ~380 K.

Thus, it was experimentally shown (although based on the results of indirect measurements and calculations) that the local temperature at ball–reactant contact points can exceed the self-ignition temperature of the mixture. What is the driving force of such a heating, impacts or friction? Common sense tells that dry friction leads to more intense heating of the contact points than impacts. For instance, one can make fire by friction of two dry pieces of wood, but it is hardly possible to light these pieces by hitting them against each other. However, we will not rely on intuition and consider this question more strictly, based on the rather scarce data available in the literature.

The maximum ball motion velocity observed in the experiments with planetary ball mills[71,110,111] is in the range of 1 to 5 m $s^{-1}$, which corresponds to free fall of ball from a height of ~0.05–1.25 m. In the model experiments with free-falling balls[82] the balls were released from a height of 0.006 m to 0.25 m to acquire the velocity equal to that of ball motion in a vibratory mill. At a ball weight of 5 N (steel ball 3 cm in diameter) and a ball velocity of 1 m $s^{-1}$, an impact force of about 1000 N was measured. As the thickness of the powder layer onto which the ball fell increased from 0 to 2.7 mm, the impact force decreased nearly tenfold. The impact duration was in the range of 0.5–2.5 ms and increased as the thickness of the powder layer increased. The restitution coefficient, that is, the fraction of kinetic energy retained by the ball upon rebound from the steel plate covered with the powder layer decreased from 0.8 (clean steel plate) to 0.2 (powder layer 1.85 mm thick). Taking into account this fact, let us assume that 80% of the kinetic energy of the ball dissipated into heat upon the impact. For the ball in question (mass 0.5 kg, velocity 1 m $s^{-1}$), one gets an energy of 0.2 J. Even considering a highly activated mixture, *e.g.*, Ti + C, its initiation requires heating by at least 500–600° above room temperature.[57] It is easy to calculate that a heat of 0.2 J is high enough to heat a ~0.75-mg titanium particle 0.6 mm in diameter by 500 degrees provided that no heat loss occurs.

Thus, using extreme and non-obvious assumptions, *viz*., (i) 100% of heat is accumulated in a microscopic spatial domain, (ii) a ball mass of 500 g, (iii) 80% of kinetic energy dissipates into heat, and (iv) balls remain cold, we found conditions for impact initiation of the reaction. However, considering actual operating modes of planetary ball mills, the following should be taken into account. The mass of a conventional grinding ball is only 3 to 5 g, the fraction of balls involved in direct impacts is low, and activated powder particles are not always available in the gap between the colliding balls since a ball–ball collision takes about ~1 ms. Therefore, initiation of a reaction through ball–ball collisions seems to be unlikely. This is also confirmed by the results of experiments on shock initiation of reactions in powder metallic mixtures.[113–116] Indeed, it was found that even in the case of preliminarily mechano-activated mixtures (*e.g.*, Ni + Al) with low self-ignition temperatures the collision velocity necessary for ignition should be of the order of hundreds metres per second.

Compared to the influence of impact loads, the effect of friction on local heating of activated powders has been much less studied. Up to 90% of friction power defined as

$$P = kNV \tag{3}$$

where $k$ is the friction coefficient; $N$ is the normal force pressing rubbing bodies to each other; and $V$ is the relative velocity of the motion of rubbing surfaces, can dissipate into heat.

When analyzing collisions, one can restrict himself to the action of a single ball. Considering friction, the whole totality of grinding balls should be taken into account. Indeed, if grinding balls are grouped inside the milling vial as shown in Figs 6 and 8, the normal force $N$ depends on the total weight of all balls rather than that of a single ball, namely, upper balls press on the lower layer of balls, those transmit pressure to the underlying balls, *etc*. At a total mass of all balls of 0.2 kg and a normal acceleration of up to 100 g, the effective weight of all balls can be as high as 200 N, which is comparable with the impact force, but the impact force acts within a few milliseconds, while the grinding balls press against one another continuously as the ball mill is in operation.

The effect of the ratio of the total mass of grinding balls to the mass of activated powder has been well studied; this

ratio is one of the key parameters characterizing the activation mode. For instance, experiments showed that the extent of activation of Ni + Al mixture increases as the total mass of balls increases provided a constant mass of a single ball.[117] Ball grouping is also of crucial importance for the friction velocity. A single ball can roll on the inner surface of the milling vial and experience a rolling friction that is much lower than sliding friction. But two contacting balls cannot roll on the vial surface without sliding friction since the ball surfaces at the point of contact move in opposite directions.

The velocities of mutual friction of the surfaces of a large number of balls have almost not been studied as yet and no experimental data on the angular velocities of ball rotation about their centres are available (theoretical models also usually ignore rotation of balls and often treat balls as mass points). One can assume that the friction velocity is of the same order of magnitude as the linear velocity of the motion of the inner surface of the milling vial. For the most efficient operating mode of the Activator-2S planetary ball mill (see above) this velocity is 4.36 m $s^{-1}$ ($W$ = 694 rpm, $K$ = 1.5, $r$ = 4 cm), being higher than the average velocity of colliding balls. Assuming a friction coefficient of 0.15 (dry friction of steel on steel) and a normal force of 100 N (rough estimate since no better data are available), one gets a power friction of ~65 W. Since the milling vial makes a revolution every 0.058 s, a work of 3.7 J per rubbing ball is done and transformed into heat, which is tenfold higher than the energy dissipating into heat through collisions of a massive ball with the steel wall.

Understanding the approximate character of the estimates made, we nevertheless come to the conclusion that friction has a stronger effect on energy dissipation than impacts of free-falling balls in the case of mechanical activation in planetary ball mills. Drawing more accurate conclusions requires additional experimental and theoretical data on the actual motion modes of grinding ball and powder mixtures.

## 4. Theoretical ideas about the causes of changes in reactivity: a comparison with experimental data

The extent of activation of an exothermic reactive mixture can be characterized as the chemical heat release rate in a given mixture at a specified temperature

$$q = QSF(\eta)k_0 e^{(-E/RT)} \quad (4)$$

where $q$ is the specific chemical heat release rate, J $kg^{-1}$ $s^{-1}$; $Q = -\Delta H$ is the heat of reaction, J $kg^{-1}$; $S$ is the specific contact surface area between reactants, $m^2$ $kg^{-1}$; $F(\eta) = (1-\eta)^n$ is the kinetic function; $\eta$ is the dimensionless conversion; $n$ is the order of the reaction; $k_0$ is the pre-exponent, kg $m^{-2}$ $s^{-1}$; $E$ is the activation energy; $R$ is the universal gas constant; and $T$ is the absolute temperature.

In accordance with the theory of combustion and thermal explosion,[25,26,42] the higher the heat release rate $q$ the lower the self-ignition temperature. This is a measure of the extent of activation of a given reactive mixture. Consider the influence of mechanical activation on the parameters and functions appearing in Eqn (4).

The idea that mechanical energy can be converted into chemical energy $Q$ dates back to studies by Matthew Carey Lea (1823–1897), who is considered to be the founder of mechanochemistry.[118,119] In his works Lea, on the one hand, stated the fact that almost nothing was known about the interrelation between the two forms of energy (mechanical and chemical).[120] On the other hand, he considered experimentally proven the possibility of conversion of mechanical energy into chemical energy.[121] This approach was developed in studies of Butyagin and Pavlichev,[84–87] who introduced the notion of the energy yield of mechanochemical reaction ($G_m$), which was defined as the ratio of the number of moles of a substance consumed in a mechanochemical reaction per second of operation of the mill (*i.e.*, the mechanochemical reaction rate) to the energy intensity of the mill; the latter is defined as the energy consumed by 1 kg of powder during 1 s of operation of the mill.[84] The estimates of $G_m$ are as follows: 0.001–0.1 mol $MJ^{-1}$ for the formation of chemisorption sites in oxides; 0.001–0.01 mol $MJ^{-1}$ for the formation of paramagnetic defects; 0.1–1.0 mol $MJ^{-1}$ for solid-phase reactions; and 100 mol $MJ^{-1}$ for polymorphic transformations.

We believe the definition of $G_m$ given above is self-contradictory since the 'yield of reaction' in the form of chemisorption sites or structural defects is placed on a par with the yield of end products or polymorphic transformation. Strictly speaking, the notion $G_m$ is only applicable to the reactions that occur during the act of mechanical activation (impact, friction, shear) and are stopped as the mechanical activation is switched off. As mentioned above, this criterion is met by the slow reaction mode. SHS-type processes, which are only initiated under the action of mechanical factors and then proceed without supply of mechanical energy, do not obey this definition. More recently it was shown that mechanical treatment of a reactive mixture causes accumulation of excess energy. There are a number of carriers of this energy including residual elastic stresses, interfaces and grain boundaries, amorphous domains, regions of supersaturated solid solutions and other metastable structures.[87] Advances in microscopic studies of these structures will be considered below.

At present, the issue concerning forms of stored energy still remains topical. In many studies on mechanical activation it is assumed that a fraction of mechanical energy is accumulated in powders but it is unclear in what form this energy is stored in the activated mixture. For instance, taking into account the results of long-term (up to 20 h) milling of a Ni + Al mixture in a planetary ball mill, it was reported[122] that the total accumulated energy of the grinding balls is more important for the initiation and completion of the reaction than the impact energy of a single ball. The total energy of milling was calculated using the expression[123]

$$E_t = \frac{E_b n_b f_b t}{m_p} \quad (5)$$

where $E_t$ is the total energy of the milling that took the time $t$, $E_b$ is the ball energy per collision, $n_b$ is the number of balls in the milling vial, $t$ is the milling time, $m_p$ is the mass of the powder being treated and $f_b$ is the frequency of impacts calculated using the kinematic model.[93]

Based on these results, it was concluded that a total energy of 200 J $g^{-1}$ is needed to initiate the reaction of

nickel with aluminium, while the completion of the reaction requires a total energy of 550 and 700 J $g^{-1}$ for milling in the steel and tungsten carbide vial, respectively.[122] Further studies of various intermetallic mixtures including Ni + Al, Co + Al, Fe + Al, Mn + Al, Ni + Ti, Co + Fe, Al + Zr, Ni + Mn and Zr + Co revealed that the enthalpy of formation of an intermetallic compound from elements (*i.e.*, $-\Delta H = Q$) is related to the total energy of milling.[123] For certain aluminides the milling energy $E_t$ necessary to initiate the reaction and to form an intermetallic compound linearly decreased with increasing $Q$; this was tentatively explained by a decrease in activation energy.

A dramatic impact of the total milling energy on the properties of activated mixtures was also reported in studies of a thermite mixture CuO + Al.[124, 125] The notion 'activation dose' ($D_a$) was introduced[125] as the product of the specific power density of activator ($J$) and the activation duration. In turn, the power density determined from the rate of increase in the specific surface area upon milling of materials with known properties was estimated at 9.7 W $g^{-1}$ for the Activator-2SL high-energy planetary ball mill.[125] The maximum reactivity of the mixtures (heat of reaction, velocity and the brightness temperature) passed through a maximum at $D_a = 2000$ J $g^{-1}$, which was explained by optimum combination of the concentration of structural defects in the components and by high-quality mixing.[124, 125] Note that the authors of studies[122–125] demonstrated an interrelation between the reactivity of the mixtures and the total mechanical energy consumed by the activator during the treatment process and made an assumption that the reactivity is related to defects in the reactant structure. However, they did not state in explicit form that the mechanical energy is accumulated in the activated substance, thus increasing $Q$, and no superadiabatic combustion regimes were revealed.

Thus, the question remains as to which fraction of mechanical energy can be transformed to the excess energy of crystallite boundaries, vacancies, dislocations and other structural defects that are accumulated in the substance in the course of mechanical treatment. The regularities revealed are in essence empirical, just like the dependences of the heat release intensity on the rotation speed of the mill and on the milling duration obtained for Al + $TiO_2$ + $H_3BO_3$ mixtures using formal methods of regression analysis (it was shown that optimum activation conditions are attained at a vial rotation speed of 340 rpm and a milling duration of 17.43 h).[73]

The influence of the specific contact surface area between reactants, $S$, on the rate of a heterogeneous reaction is obvious. Mechanical treatment not only causes $S$ to increase, but also changes the contact quality, *viz.*, juvenile surfaces are formed that are free from adsorbed molecules and oxide films (the latter were present on the surface of the initial particles). This effect can probably be expressed through the pre-exponent $k_0$ in Eqn (4), but quantitative evaluation is difficult since the physical meaning of $k_0$ for powder mixtures is unclear. The kinetic function $F(\eta)$ for powder mixtures is poorly studied and can take various forms including linear, exponential (with integer or fractional exponent), logarithmic, *etc.*[24, 126, 127] Eventually, the last-mentioned factor in Eqn (4), the Arrhenius exponent, characterizes the dependence of the reaction rate on temperature. The product of four kinetic factors (the first factor, $Q$, can be treated as thermodynamic one) determines the rate of a heterogeneous reaction and is analyzed using various theoretical models.

The most mathematically developed is the macrokinetic theory of mechanical activation and mechanochemical synthesis presented in detail in original communications[128–132] and in monographs.[8, 133] Consider those aspects of this theory that seem to be important for understanding the activation mechanisms. The macrokinetic theory is based on the assumption that mechanical activation causes the activation energy to decrease by a certain value $\varepsilon$

$$E = E_0 - \varepsilon \tag{6}$$

where $E_0$ is the activation energy of the initial mixture before mechanical treatment.

By definition, $\varepsilon$ is the fraction of the excess energy accumulated in the structural defects of reactants, which influences the activation energy of a chemical reaction.[133] In other words, it is assumed that structural defects in reactants (and in the product, if it managed to form) accumulate energy and that a fraction of this energy influences the kinetic parameter, namely, the activation energy. Unfortunately, this theory does not specify the physicochemical nature of the parameter $\varepsilon$ and presents no methods for experimental measurement of $\varepsilon$, which questions the relevance of the model to actual activation mechanisms. Nevertheless, the macrokinetic theory seems to be useful for numerical simulation of the experimentally established dependences of the properties of reactive compositions on the activation modes. It takes account of the diffusion and kinetic regimes of heterogeneous reactions. When the rate of the overall process is limited by the chemical reaction, a linear kinetic law is assumed:

$$F(\eta) = 1 - \eta \tag{7}$$

Diffusion-controlled processes are described using a parabolic law

$$F(\eta) = \eta^{-1} \tag{8}$$

The dynamics of changes in the specific contact surface area between reactants in a binary mixture is given by[134]

$$S = S_0(1 - e^{-bt}) \tag{9}$$

where $S_0$ is the maximum specific surface area of particles that can be achieved in a certain mill and $b$ is a constant characterizing the properties of the material being milled.

The macrokinetic theory was used to calculate the combustion regimes of activated compositions, the structures of combustion waves (dependences of the temperature and conversion on time). The results obtained are in good agreement with the experiment (it should be noted that this was done using a large number of arbitrarily chosen parameters). We believe that a fundamental advance of this theory consists in that it allows one to compare the contributions of the changes in $S$ (an increase) and $E$ (a decrease) to the reaction kinetics of activated compositions under the thermal explosion and combustion regimes.[8]

The authors of many experimental studies reported a decrease in the effective activation energy of reactions owing to preliminary treatment of mixtures in planetary ball mills, but the measured $E$ values are strongly different

even for non-activated mixtures. For instance, a combustion study of non-activated Ni + Al mixtures gave $E = 75$ kJ mol$^{-1}$ from the temperature dependence of the combustion velocity; this value increased to 140 kJ mol$^{-1}$ for the mixtures diluted with an inert product since the combustion temperature became lower than the melting point of nickel.[135] In addition, a high-temperature thermographic study of non-activated Ni + Al mixtures led to $E = 155–159$ kJ mol$^{-1}$.[136] Powders composed of Al–Ni clad particles (1 : 1 mole ratio) were studied by Kissinger's DTA method[137, 138, 139] and $E = 340$ kJ mol$^{-1}$ was obtained. An electrothermal explosion study[140] of identical clad powders gave

| $T$/K | 1113–1250 | 1250–1400 | 1400–1583 |
|---|---|---|---|
| $E$/kJ mol$^{-1}$ | $192 \pm 29$ | $\sim 0$ | $523 \pm 83$ |

According to DSC data, a mechanically activated Ni + Al mixture is characterized by $E = 117 \pm 8$ kJ mol$^{-1}$.[141] The DSC method was also used to establish the dependence of the activation energy on the mechanical milling temperature and to determine the activation energies of different stages of the interaction (DSC traces exhibited up to three exothermic maxima).[77] Milling was carried out in vibratory mills at room temperature and at liquid nitrogen temperature. The activation energy for the first reaction stage was 100 kJ mol$^{-1}$ in the former and 150 kJ mol$^{-1}$ in the latter case. The deeper stages of the reaction were characterized by higher activation energies equal to 200 and 300 kJ mol$^{-1}$ for cryogenic and room-temperature milling, respectively. The DSC traces were also processed[77] not only following Kissinger, but also using a more accurate method by Vyazovkin[142, 143] that gave $E = 75$ kJ mol$^{-1}$ for the first stage of the reaction after cryogenic milling. Studies of mechanically activated clad powders by DSC (Ref. 139) and electrothermal explosion technique[140] led to the same value $E = 104$ kJ mol$^{-1}$. A very large decrease in $E$ was revealed in thermal explosion studies[144, 145] of mechanically activated compositions 3 Ni + Al in AGO-2 planetary ball mill. It was experimentally demonstrated that the effective activation energy decreases with increasing activation time:[144]

| $t$/s | 60 | 90 | >120 |
|---|---|---|---|
| $E$/kJ mol$^{-1}$ | 135 | 38 | 4.4 |

A somewhat higher but still abnormally low value of $9.5 \pm 2$ kJ mol$^{-1}$ was obtained in another study.[145]

Probably, a very large scatter of experimentally measured $E$ values can be explained by different methods used for measurements. The smallest values were obtained from the temperature dependence of combustion velocity (unfortunately, this method still was not applied to mechanically activated mixture Ni + Al). Thermographic methods (DSC, Kissinger's method, *etc.*) give larger values. The highest activation energies were found using thermograms of non-activated compositions obtained in the thermal or electrothermal explosion modes. However, it should be noted that the minimum $E$ values were also determined by processing thermal explosion data, although obtained for activated compositions. It follows that the experimental methods used above give only the effective activation energies of complex processes that can be different from the actual activation energies of elementary (atomic-level) processes, such as diffusion in the crystalline phase or in melt. A large scatter of $E$ values is also observed for other powder mixtures (see, for instance, a review of kinetic parameters of SHS compositions[146]).

In spite of large data scatter, a comparison of the energies $E$ measured by the same methods for activated and non-activated compositions suggests that treatment of powder mixtures in planetary ball mills decreases the effective activation energy of reaction and, consequently, increases the reactivity of these mixtures. Since in the systems in question the reactivity of exothermic mixtures manifests itself through the self-ignition temperature $T_{\rm ign}$, it would be logical to relate the effective activation energy to the self-ignition temperature.

A number of earlier studies[147, 148] were devoted to the problem of thermal explosion (self-ignition) of reacting systems followed by the occurrence of several competing reactions, each being characterized by its own activation energy. It was shown that in this case one can introduce the effective activation energy representing superposition of the activation energies of the competing reactions. Using this approach, a study[66] was carried out of a mechanically activated mixture containing two types of particles, namely, initial non-activated and highly reactive particles with the activation energies $E_1$ and $E_2$ ($E_2 < E_1$). It was shown that such a mixture is characterized by the effective activation energy

$$E_{\rm ef} = E_1 - RT \ln \left\{ 1 + x \left[ \exp \left( \frac{E_1 - E_2}{RT} \right) \right] - 1 \right\} \qquad (10)$$

where $x$ is the fraction of reactive particles in the mixture. The self-ignition temperature of the activated mixture $T_{\rm ign}$ is related to the fraction of reactive particles in the mixture by the equation

$$x = \left\{ \exp \left[ \frac{E_1}{R} \left( \frac{1}{T_{\rm ign}} - \frac{1}{T^0_{\rm ign}} \right) \right] - 1 \right\} \left[ \exp \left( \frac{E_1 - E_2}{RT_{\rm ign}} \right) - 1 \right]^{-1} \qquad (11)$$

where $T^0_{\rm ing}$ is the self-ignition temperature of the initial mixture (before activation).

Expressions (10) and (11) allow one to calculate the dependences of the effective activation energy and self-ignition temperature on the fraction of activated particles (Fig. 9). A comparison of Figs 4 *b* and 9 showed reasonable qualitative agreement of the model with the experimental data. Note that the calculated $E_{\rm ef}$ value depends on the temperature specified for the calculations; this is also consistent with certain experimental observations (namely, the activation energy is different for different temperature intervals).

The electrothermal explosion method was used to obtain the dependences of the activation energy on the microstructure of activated mixture Ni + Al.[49] It was shown that $E_{\rm ef}$ varies from 79 to 137 kJ mol$^{-1}$, being a linear function of the specific contact boundary area of reactants inside the composite particle. We believe that this result casts some doubt since the contact surface area between reactants is a macroscopic parameter which more likely should be included in the pre-exponent in the Arrhenius equation for the heterogeneous reaction rather than the exponent. The activation energy of a reaction is determined by elementary processes on the atomic and molecular level rather than

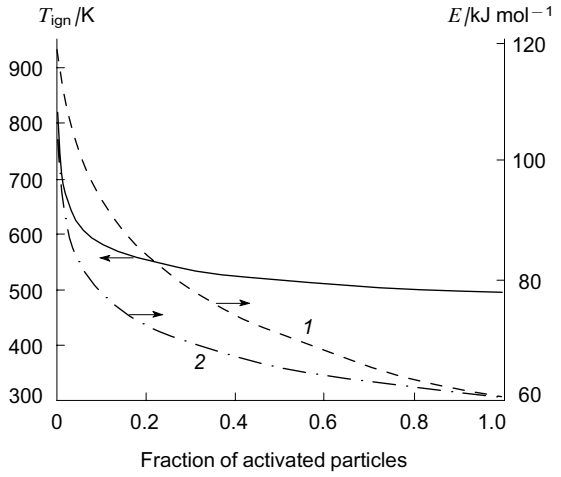



**Figure 9.** Effective activation energy and self-ignition temperature plotted *vs.* fraction of activated particles in the mixture. Calculated using the data taken from Ref. 66 for the Ni + Al mixture; $E_1$ = 120 kJ mol$^{-1}$, $E_2$ = 60 kJ mol$^{-1}$, $T^0_{ign}$ = 930 K, $T$ = 1900 (*1*) and 930 K (*2*).

macroscopic parameters of the mixture. Probably, this dependence can be explained by increasing role of interfacial diffusion that should be characterized by lower activation energy compared to bulk diffusion. In any case, this effect deserves further study.

Thus, the most pronounced effect of mechanical activation manifests itself through a decrease in the effective activation energy of heterogeneous reaction. This assumption serves a basis for theoretical models and does not contradict the experimental data despite a large scatter of the latter. The influence of the specific contact surface area and the kinetic law is less important, although they cannot be ignored. The nature of the influence of mechanical treatment on the activation energy of chemical reaction is tentatively related to structural transformations in the substance being treated.

## 5. Role of structural transformations in the increase in reactivity

Mechanical activation is accompanied by intense plastic deformation of metals and formation of characteristic microstructures (Fig. 10). If a mixture is composed of two highly ductile metals, layered microstructures are formed (see Fig. 10 *a*). Examples are provided by Fe–Al,[46] Ni–Al,[15,27,149] Cu–Al compositions,[80] *etc*. If one has a mixture of a highly ductile metal (*e.g.*, aluminium), and a brittle component (*e.g.*, oxides), the resulting composites represent a metallic matrix containing finely dispersed particles of the brittle phase as inclusions (see Fig. 10 *b*). This was observed for, *e.g.*, thermite compositions Al + $MoO_3$ (Ref. 16) as well as for Ti + C (see Ref. 150) and Ti–Si compositions.[151] If both components of a mixture are brittle (for instance, Si and C), they are milled to submicrometre or nanometre state and then agglomerate to form relatively large (up to tens of micrometres in size) particles containing all initial phases of reactants.[152] In all cases, one deals with abrupt (by 3–4 orders of magnitude and more) increase in the contact area of reactants.

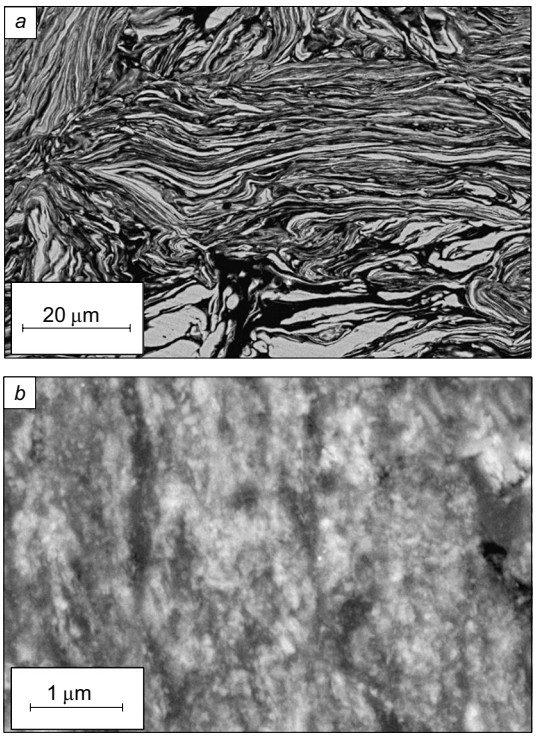



**Figure 10.** SEM images of the microstructures of reaction mixtures treated in a planetary ball mill.
(*a*) Ni + Al composition, bright phase is Ni and dark phase is Al;[88] (*b*) Al + $MoO_3$ composition, bright phase is $MoO_3$ and dark phase is Al.[16]

The development of methods for 3D reconstruction of microstructures made it possible to construct 3D models for activated compositions (Fig. 11).[50,52] To this end, composite particles formed after mechanical treatment were sectioned using ion beam etching. Two-dimensional images of the microstructure were taken after etching of each layer. The 3D reconstruction was performed using a set of nearly 500 2D images of the microstructure and software devel-

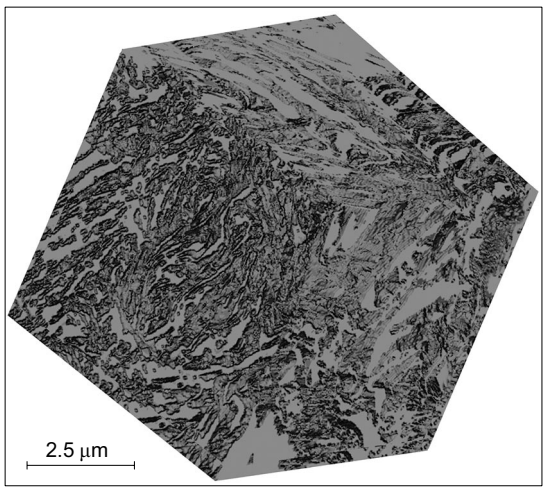



**Figure 11.** Reconstructed 3D microstructure of Ni/Al reactive composite particle.[50]

oped at Thermo Fisher Scientific (USA). An analysis of the model showed that the specific contact surface area in the Ni/Al composite particles can be as large as 0.012 $nm^{-1}$, which corresponds to an effective particle size of 80 nm at the initial particle size ranging from 3 to 15 nm.[50] Mixtures of ductile metals also exhibit cold welding areas at the contact boundaries between reactants; this reinforces the layered particles and cleans the contact boundaries from oxide films and other contaminants.

The essence of cold welding consists in that intense deformation stretches the metal surface, the oxide film breaks down and its fragments are immersed in the metal, while the fresh exposed metal surfaces are brought together to a bonding distance.[153] In non-activated exothermic compositions a direct contact between metallic particles occurs at certain spots, *viz.*, protrusions on the surface, while other surface spots at the contact area are separated by distances of the order of a few tens of nanometres.[154] Cold welding becomes possible when the microscopic surface inhomogeneities are smoothed and a rather large direct (atom–atom) contact surface area is formed. In this case, both the mechanical strain and the temperature at the contact spot are of great importance.

As shown above (see Section 2), the impact force of a ball against the wall reaches a value of $10^3$ N within a very short time interval while the compression force at ball contact points in a planetary ball mill can be as high as $10^2$ N. The yield point of aluminium is 20–30 MPa, that of annealed nickel is 80 MPa and that of pure titanium is in the range of 100–300 MPa.[155] It follows that the impact stress necessary for plastic deformation of a metal can be achieved for a rather large contact surface area ranging from 3 to 50 $mm^2$; however, the action time of such a stress is short ($\sim$1 ms or shorter). For surface friction of stagnant balls in a planetary ball mill this surface area is tenfold smaller, but in this case the action time of the compression and shear stress is a few orders of magnitude longer. In both cases the mechanical stress is high enough to smooth microscopic inhomogeneities as well as for plastic deformation of reactants and for cold welding of the surfaces formed.

In mixtures of ductile metals prolonged action is provided by sticking the deformed mixture to the surface of steel grinding balls; therefore, the mixture experiences a continuous mechanical deformation in both pulsed mode through each impact and continuous mode through friction of balls with one another and with the vial wall. Experiments with the Ni–Al system treated in a high-energy planetary ball mill for 5 min showed that the thickness and microstructure of the stuck layer depend on the gas atmosphere inside the milling vial.[67] Activation in argon atmosphere led to formation of a continuous layer $\sim$200 μm thick that covered the whole surface of the grinding balls (Fig. 12 *a*). The layer had an inhomogeneous microstructure, namely, the inner regions (bottom part in Fig. 12 *a*) near the surface ball were much less deformed compared to the outer layer (upper part in Fig. 12 *a*) of thickness 10–30 μm.

Probably, intense cold welding in inert atmosphere causes the formation of a thick bimetallic layer on the surface of grinding balls within a few seconds after the start of the activation process, so only the outer surface of this layer then experiences the most intense deformation. Cold welding in air under identical activation conditions is

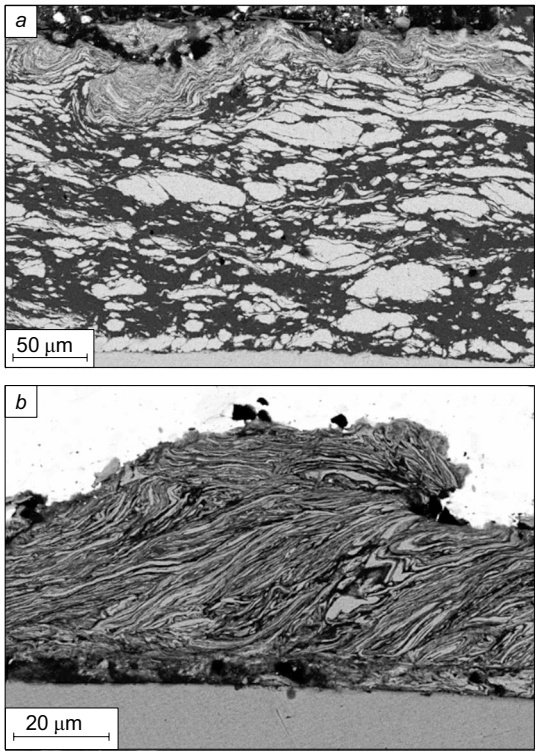



**Figure 12.** Layers of activated Ni + Al mixture formed on the surface of grinding balls (bottom).[67]
Activation: in Ar atmosphere (*a*) and in air (*b*).

less intense (probably, due to fast oxidation of the metal surfaces); therefore, the stuck layer is only 40–50 μm thick (see Fig. 12 *b*). Its microstructure is homogeneous over the entire thickness and is very similar to the microstructure of activated particles (see Fig. 10 *a*). Taking account of this fact, one can conclude that activated two-phase particles and agglomerates represent fragments of bimetallic layers formed on the surface of grinding balls.

Recall that the temperature of grinding balls after activation in argon was higher than after activation in air.[67] The character of deformation of nickel and aluminium lamellae (see Fig. 10 *a* and 12) is indicative of intense shear stress. This confirms the assumption of predominant role of dry friction compared with impacts in the activation of reactive compositions. A molecular dynamics simulation (MDS) of dry friction in Ni + Al mixture (friction pairs Ni/Al, Al/Ni and NiAl/NiAl) showed that the temperature of the rubbing surfaces can be as high as 600–700 K[156] and that sliding can occur either at constant velocity or in the stick–slip regime.[157] An MDS for the friction pairs Cu/Fe and Cu/Ag gave an even higher temperature of the friction surface, namely, up to 2000 K.[158] However, these calculations were carried out assuming a rather high relative sliding velocity of the surfaces (150–1000 m $s^{-1}$).

The friction velocity of the grinding ball surfaces in planetary ball mills has almost not been studied as yet. Based on the available data for the motion velocities of the grinding ball centres and the vial wall, it seems logical to assume that it is at most tens of metres per second. Nevertheless, even a moderate increase in temperature should favour cold welding of reactants. The possibility of local melting of powders under impact in a vibratory mill was

demonstrated for a low-melting mixture Bi + Te.[159] Consolidation of metal particles abruptly increases if their temperature becomes higher than half the melting point (so-called homologous temperature).[153] That of aluminium is 465 K and can be achieved locally at the point of contact between rubbing or colliding balls. Note that the introduction of even a small amount of liquid (water, ethanol, heptane, *etc.*) into the milling vial not only makes cold welding of reactants impossible, but also causes dispersion of metallic layers stuck on the grinding balls. This effect is used to clean the balls and walls of milling vials.

These transformations of the microstructure provide an explanation for an increase in the specific contact surface area between reactants as a result of mechanical activation; however, they give no idea why the activation energy of the reaction decreases. Usually, this is attributed to an increase in the concentration of vacancies and in the specific surface area of grain boundaries as a result of multiple plastic deformation events and milling of crystallites. Indeed, the authors of almost all experimental studies involving X-ray powder diffraction investigations of activated compositions reported a considerable broadening of diffraction peaks due to a decrease in the crystallite size (dimensions of coherent scattering domains) and accumulation of microstresses up to complete amorphization of mixture components. For instance, the size of the coherent scattering domain of Al in a Ni + Al mixture decreased from 1000 to 100 nm after treatment in a planetary ball mill, while the microstresses in Al and Ni increased to 150 and 500 MPa, respectively.[160] A study[161] of Ti + Si mixture revealed a decrease in the crystallite size from 1500 to 300 nm only for silicon; this was accompanied by an increase in the microstresses to 700 MPa; the size of titanium crystallites remained unchanged, and the diffraction peaks broadened due to the increase in the microstresses to 550 MPa owing to accumulation of structural defects.

Similar (either qualitative or quantitative) results derived from X-ray powder diffraction data were also obtained for other systems.[30, 80, 150, 151, 162] Published data on broadening of the diffraction peaks of components of exothermic mixtures are not accompanied by information on their shifts as a result of accumulation of numerous structural defects (*e.g.*, vacancies or impurity atoms) or correlations between the concentrations of various defects and the mechanical activation modes. Clearly, elucidation of the role of structural defects in activation of reactive compositions requires additional studies; however, certain approximate estimates can be made using the results obtained.

The energy of formation of a vacancy in the crystal structure of a metal is $\sim$1 eV, or 50%–65% of the activation energy of solid-phase diffusion.[163] Correspondingly, the equilibrium concentration of vacancies is $10^{-19}$ at room temperature; it exponentially increases with temperature and can be as high as $10^{-4}$–$10^{-3}$ at the melting point. It follows that the excess energy accumulated in vacancies is negligible ($10^{-14}$ J mol$^{-1}$) at room temperature and increases to 10–100 J mol$^{-1}$ at the melting point. The most probable defects to appear under intense plastic deformation are dislocations that can store up to 1–2 kJ mol$^{-1}$ of excess energy.[164, 165] The maximum energy that can be stored in $SiO_2$ as component of copper concentrate was estimated at 8.4–9.6 kJ mol$^{-1}$.[10] It was obtained using X-ray powder diffraction data assuming that the energy accumulated during mechanical activation is proportional to the change in the unit cell volume; however, the applicability of these data to exothermic compositions is not obvious. The energy of crystallite boundaries can be estimated at 0.5 J m$^{-2}$ (the model treats the boundary as supercooled liquid).[166] Assuming that the size of mechanically activated crystallite falls in the range of 10 to 100 nm (specific boundary surface area is $10^{-8}$–$10^{-7}$ m$^{-1}$), one gets for, *e.g.*, titanium the following estimate of the energy stored by the boundaries: 50–500 J mol$^{-1}$.

These estimates demonstrate that the excess energy stored in various structural defects is negligible compared to the energy (heat) of exothermic reactions, which is of the order of a few hundreds of kJ mol$^{-1}$ for the systems studied in this review. This conclusion is consistent with those reported in Refs 167 and 168 and with the experimental data presented above (see Section 2). However, they are in poor agreement with the estimates made using the notions 'energy yield of mechanochemical reaction' and 'mechanical activation dose', which relate the energy gained by the substance to the energy consumed by the mill activator. For instance, it was stated[169] that the 'mechanical energy dose $D$ transferred to the powder material can be as high as $D = It \approx 10^2$–$10^3$ J g$^{-1}$' (here $I$ is the specific power of the mill and $t$ is the treatment duration). For comparison, the exothermic effect of formation of NiAl and TiC phases from corresponding elements is 1.37 and 3.85 kJ g$^{-1}$, respectively, and the temperature of the reaction products reaches a value of 1912 and 3290 K, respectively. It is easy to imagine what happens if an energy of about $10^6$ J g$^{-1}$ will be actually transferred to the powder mixture, *viz.*, the mixture will evaporate or turn into plasma.

We believe this apparent contradiction consists in that almost all power of a mechanical activator is consumed for heating balls and the device itself (through friction and inelastic collisions), while the released heat is removed using by a coolant (liquid or gas). Only a small fraction of consumed energy is accumulated in the crystal structure and in the microstructure of reactive mixtures. An increase in the concentration defects and specific boundary surface area can lead to significant increase in mass transfer coefficients owing to solid-phase diffusion by the vacancy mechanism and crystallite boundary diffusion.[166] Accumulation of defects can also be followed by amorphization of metals and intermetallic compounds.[170, 171] The enthalpy of amorphous metal is usually at least 5 kJ mol$^{-1}$ higher than that of corresponding crystalline metal.[165] For instance, the enthalpy of intermetallic phase $Ni_3Al$ increases by 21 kJ mol$^{-1}$ after long-term (> 15 h) milling.[171]

Obtaining experimental proofs of local increase in diffusion coefficients and decrease in activation energy of diffusion owing to an increase in the concentrations of structural defects and amorphization of preactivated reactants seems to be a topical avenue of nearest-future research. Direct microscopic observations of the structure of atomic-crystalline defects in mechanically activated systems carried out using modern methods of investigation should help to relate information on macroscopic properties of activated reactive compositions to the kinetic theory of mechanochemical transformations,[87, 169] which is based on the kinetics of atom–atom bond dissociation under deformation and breakup developed by Prof S.N.Zhurkov and his scientific school.[172]

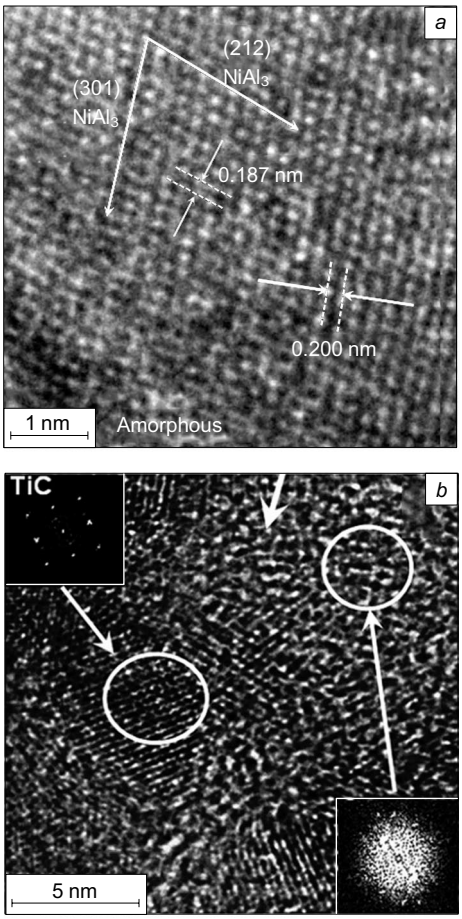



**Figure 13.** TEM images of amorphous phase and nanocrystalline clusters in mechanically activated mixtures Ni + Al (*a*)[66] and Ti + C (*b*).[150]
(*b*) Fast Fourier transform which shows an ordered (upper left corner) and disordered (lower right corner) atomic arrangement.

Interesting results were obtained using HR TEM.[66,150] It was found that activated mixtures Ti + C and Ni + Al contain not only amorphous phases, but also nanoclusters of crystalline reaction products (Fig. 13). These clusters are so small that give no diffraction reflections and thus cannot be detected by single-crystal and powder X-ray diffraction. However, they can serve as seeds of new phases and thus reduce the potential barrier to initiation of exothermic reaction. It was assumed[66] that these clusters represent metastable phases that undergo transition to the crystalline state accompanied by heat release and thus initiate an exothermic reaction at abnormally low temperatures. To confirm this assumption, it was experimentally shown that low-temperature annealing of activated mixture Ni + Al at 400–500 K produces a crystalline phase $NiAl_3$ that could not have formed as a result of diffusion at so low temperatures; the self-ignition temperature of the annealed mixture was found to increase. A qualitative mechanism proposed for the formation of metastable clusters involves trapping of nickel atoms and clusters by plastically deformable aluminium at the interface between the rubbing layers of these metals.[66]

The results of recent high-resolution electron microscopy studies are in good agreement with the two-stage scheme of solid-phase mechanochemical reactions.[87] According to this scheme, the first stage involves deformation mixing followed by accumulation of the excess energy and formation of various metastable structures (supersaturated solid solutions, amorphous domains, *etc.*). In the second stage, relaxation occurs, *viz.*, the accumulated energy is released, the structure of the reactive mixture is ordered and crystalline product phases are formed. It seems likely that nanocrystalline clusters (see Fig. 13) appear as a result of such a relaxation process.

Thus, unusually high reactivity of powder reactive mixtures, which manifests itself in abnormally low reaction initiation temperature, can be explained by transformations of the microstructure and crystal structure resulting from multiple intense plastic deformation of metallic reactants. At present, this field is poorly studied and new experimental data on the interrelations between the reactivity, diffusion coefficients, microstructure and atomic structure are required. Solving this problem is important for developing efficient methods for controlling the properties of preactivated reactive compositions and those of products and materials fabricated using mechanical activation.

## 6. Application of mechanical activation to synthesis of materials

Problems and prospects for application of mechanical activation in the synthesis of materials are widely discussed in the literature (see, *e.g.*, reviews,[3,173] a monograph,[9] *etc.*). In addition to examples of successful practical application of mechanical activation and mechanochemistry, mention was made of difficulties arising on going from laboratory-scale experiments to industrial technologies.[3] The scaling conditions for materials production using mechanical milling are also discussed and simulated (see, *e.g.*, Ref. 174). In this Section we present certain recent results.

Most publications are devoted to the synthesis of various powders. Nanocrystalline and amorphous intermetallics belong to key products of mechanochemical synthesis since the pioneering studies by Koch and co-workers;[171,175,176] various intermetallic systems were analyzed in a review.[177] Two technological approaches were used, *viz.*, the synthesis from elemental powders by milling (emphasize that milling continued after the formation of intermetallic product) and milling of an intermetallic phase. More recent R&D activity was mainly aimed at optimizing the milling modes in order to synthesize nanocrystalline NiAl,[122] at combining mechanical and electrical activation (synthesis of $TiAl_3$)[178] and even at stimulating mechanical activation by the influence of $\gamma$-quanta.[179] A modern trend is to synthesize multicomponent and composite powders. For instance, composites were synthesized from the intermetallic matrix $Fe_3Al$ reinforced by submicrometre TiC particles[180] and from the multicomponent matrix Cu–Fe–Co–Ni containing hexagonal boron nitride inclusions.[181] Cubic boron nitride was synthesized by mechanical activation in a planetary ball mill followed by shock load.[182] Powders of amorphous alloys in the system Ti–Cu–Fe–Al were also synthesized from mixtures of elemental powders using a planetary ball mill.[183]

There has been rapid progress in mechanochemical synthesis of so-called high-entropy alloys[184] that are composed of five and more metals taken in nearly equal concentrations. These systems are synthesized from elemental pow-

ders immediately during mechanical treatment in planetary ball mills. Examples are provided by the synthesis of five-component alloys FeCoNiCrMn,[185] AlFeCrNiMn,[186] NiCoCrFeTi,[187] *etc*. One can assume that the process is accompanied by exothermic reaction since many high-entropy alloys contain such pairs of metals as Ni–Al, Ti–Al and Ni–Ti that can react with considerable heat release. To date, this area has been very poorly studied.

Pioneering studies on mechanochemical synthesis of cermets (solid alloys based on tungsten carbide) with high-entropy binders, for instance, WC–AlFeCoNiCrTi (Ref. 188) and WC–FeCoCrNi (Ref. 189) have been reported. A seven-component alloy $Zr_{54}Cu_{19}Ni_8Al_8Si_5.Ti_5O_1$ synthesized in a vibratory mill appeared to be a bulk amorphous material (metallic glass) with very high degree of supercooling.[190] The binary alloy $Cu_{50}Ti_{50}$ obtained in a planetary ball mill also exhibited the properties of a metallic glass.[191] Mention should be made of the mechanochemical synthesis of so-called pseudo-alloys, *i.e*., alloys of immiscible metals, *e.g*., Cu–Bi or Fe–Bi.[192] They represent amorphous metallic matrices containing nano-sized inclusions (clusters) of other metal which forms neither chemical compounds nor stable solid solutions with the first metal. The Cu–Cr pseudoalloy exhibited unusual electrical properties and increased resistance to vacuum discharge, which makes it a promising material for high-power vacuum interrupters.[193–195] Although pseudoalloys are characterized by positive enthalpy of mixing (they are formed with endothermic effect), they can be treated as mechanically activated systems. In addition to the fact that methods for mechanical activation of such systems are essentially the same as those applied to exothermic compositions, mechanical treatment of mixtures of immiscible metals leads to formation of metastable supersaturated solid solutions and to unusually high concentration of phase boundaries,[192] which can accumulate excess energy. Multicomponent alloys, pseudoalloys and metallic glasses synthesized by mechanical treatment have been poorly studied and one can expect, in the nearest future, a rapid increase in the number of publications devoted to these systems.

Ceramic powders and materials are obtained using preactivation of reactive mixtures followed by the combustion synthesis and by the synthesis immediately in the course of milling in the milling vial. Both approaches were used to prepare so-called MAX-phases[§] and compositions based on them. Systems obtained from elements immediately in the activator include $Ti_3AlC_2$ with[196] and without[197] tin additives, as well as two-phase ceramics $Ti_3AlC_2–Al_2O_3$ (in this case, $TiO_2$ was used in addition to Al and C powders).[198] Treatment of preactivated mixtures in the combustion mode (SHS) resulted in $Ti_2AlC$,[199] $Ti_3AlC_2$,[200] and composites $Ti_5Si_3C_x$–TiC (see Ref. 201) and $Ti_3AlC_2–Al_2O_3$.[202]

Recently, there has been interest in ultra-refractory, extreme melting point ceramics that can be used in aerospace components. High-energy milling of carbides TaC, HfC and WC followed by hot pressing resulted in the compound $Ta_4HfC_5$ with a tentative melting point of 4215 K.[203] Ultrahigh-temperature carbide (Ta,Zr)C was synthesized from a mechanically activated mixture of elemental powders in the combustion mode.[35]

Silicon carbide cannot be obtained by SHS from elements owing to low exothermicity of this mixture (thermal, chemical or mechanical activation is required to initiate the reaction). Initially, a joint activation by long-term (from 2 to 16 h) milling of Si + C mixture with $NH_4Cl$ additive was proposed to initiate a self-propagating reaction in air.[204] Then, a series of studies[152,205–207] showed that 15-min high-energy treatment in a ball mill is sufficient to initiate a SHS reaction resulting in submicrometre and nanocrystalline particles of SiC powder containing no additives. This powder was used to prepare dense ceramics with good mechanical properties. The Si–SiC composite was synthesized by SHS from a mixture of natural sand, carbon and magnesium mechanically activated in a planetary ball mill.[208]

Various materials with useful magnetic and catalytic properties were obtained by combining mechanical activation of oxide-containing systems with SHS. In particular, hexaferrites $BaCo_{2-x}Zn_xFe_{16}O_{27}$ were synthesizeds[209] from an activated mixture of different oxides in the combustion mode while activation dose dependent treatment of NiO + Al mixture gave powders with controlled magnetic and catalytic properties.[210] Concluding our review of powder products, mention should be made of the formation of single-phase $AlB_2$ from mechanically activated mixture of elemental powders in the thermal explosion mode.[211]

Often, modern technologies require consolidated materials rather than powder products; therefore, it is of great importance to combine mechanical activation with various consolidation techniques. Undoubtedly, spark plasma sintering (SPS) ranks first in the number of publications in this field and in the volume of results obtained. The method is as follows: a mould is loaded with powder stock material and pressed with dies, then short electrical current pulses are passed through the mould and the stock material is heated to the sintering temperature. Simultaneously, pressure is applied to the powder through the dies to obtain a non-porous consolidated material. Unlike hot pressing with d.c. heating, pulsed heating in the SPS regime allows one to reduce the temperature and to shorten the consolidation time and thus to favour fabrication of fine-grained and nanocrystalline materials.

There are three routes to consolidation materials involving mechanical activation. One of them consists in that milling is accompanied by exothermic synthesis of the target products (phases) in the form of a powder that is used as raw material for SPS. This procedure was used to prepare $Al_2O_3$–NiAl composites.[212,213] The second route involves preliminary activation of the reactive mixture followed by SHS in reactors or furnaces and subsequent consolidation of the product by SPS (some cases, additional milling of the SHS product is required). It was used to obtain composites $Ti_5Si_3–Ti_2Ni$ and $Ti_5Si_3–TiC–Ti_2Ni$,[214] as well as ceramics based on $Ti_5Si_3$ (Ref. 215) and $TaSi_2$–SiC.[216] Eventually, the third route assumes preliminary mechanical activation of the reactive mixture that is then transferred to a mould and exposed to SPS. The reaction is initiated immediately by heating in the mould and the synthesis and consolidation of material occur simultaneously. This procedure was used to synthesize ceramics and cermet such as

§ MAX phases are ternary compounds $M_{n+1}AX_n$, where M is a transition metal, A is a Group IIIA or Group IVA element and X is carbon or nitrogen. The MAX phases have a layered structure and their mechanical properties are unusual for ceramics.

$B_4C-TiB_2$,[217,218] $B_4C-Al$,[217] $TiB_2-B_4C$,[217] $HfB_2-SiC$,[217] $Al_2O_3-NiAl$ (coating on cast iron),[219] and $TiN_{0.3}-Ti_5Si_3-TiN$.[220]

Certain materials, *e.g.*, SiC (Refs 206 and 207) or $B_4C$ (Ref. 221) were obtained using two or even all three routes.

The SPS is not the one and only method for consolidation of mechanically activated materials. In particular, solid alloys based on titanium carbide with nickel binder were obtained by hot quasi-isostatic SHS pressing using Ti + C + Ni mixtures activated in a planetary ball mill.[38] The synthesis and consolidation of the material occurred simultaneously. It was found that by activating all three components or only two of them in different combinations (Ti + C, Ti + Ni or Ni + C) and adding the third non-activated component immediately prior to the synthesis, one can obtain different microstructures of the material. A $TiB_2-Cu$ composite with a porosity of less than 2% was synthesized following the second route using high-velocity quasi-dynamic pressing that represented high-speed extrusion of a bar.[222] Probably, in the nearest future one can expect progress in the existing and development of new production methods combining mechanical activation, synthesis and consolidation of powder materials.

In conclusion we will dwell on the application of mechanical activation to the synthesis of functional energy-rich materials. A number of mechanically activated thermite compositions were considered above.[20,124,125] Of particular interest are fully dense (almost zero-porosity) thermite composites ($CuO-Al$, $MoO_3-Al$, $Bi_2O_3-Al$, *etc.*).[223,224] The strength of such materials is high enough to fabricate various articles and parts of devices; however, when initiated, they burn with considerable heat release. This offers great prospects for application of these materials in rocket technology, pyrotechnics and other fields. Powder-like reactive mechanocomposites can be used as additives to various metallized fuels, *e.g.*, $Al(Mg)-MoO_3-$poly(tetrafluoroethylene)[225] or Al(Mg)–solid propellant.[226]

A new application field is associated with the use of mechanically activated powder reactive composites in modern 3D technologies, such as selective laser sintering and selective laser melting. Replacement of conventional powdered metals and alloys by reactive nanocomposites enables local initiation of reactions in the particles being sintered under laser beam. The heat of reaction is added to the heat flux from the laser and refractory intermetallic phases formed in the reaction increase the number of materials for 3D printing. Additive technologies often require that powders behave as highly ductile materials; therefore, fabrication of mechanocomposites with round-shaped particles is topical. This problem can be solved by choosing appropriate operating modes of planetary ball mills.[15,227] Recently, the first successful results were obtained for a mixture of Ti + Al with Ni + Al.[228] Note that ferrite nanopowders with spherical particles were prepared earlier by mechanical activation of salt systems.[229]

## 7. Conclusion

The material presented in this review shows that mechanical activation of exothermic powder compositions is undergoing rapid development. New experimental results urge to take a fresh look at the process of activation and at the reasons for structural transformations that lead to an increase in the reactivity of powder mixtures. In addition to investigations of 'classical' mechanochemical reactions that proceed only under the action of mechanical factors and require continuous supply of mechanical energy, research has expanded into self-sustained reactions for which mechanical activation plays the role of preliminary treatment changing the properties of the reactive mixture or the role of a trigger pulse initiating a spontaneous reaction proceeding without supply of mechanical energy.

The results obtained clearly demonstrated an increase in the sensitivity of mechanically treated mixtures, which manifests itself in a decrease in the initiation temperature (self-ignition temperature) for all systems studied. Data on the influence of mechanical activation on the combustion velocity reported by different authors are contradictory. This can be explained by the fact that the combustion velocity of SHS compositions is limited by heat transfer between particles of the reactive mixture, which depends on the shape, size and properties of inter-particle contacts. Different modes of mechanical treatment lead to formation of reactive composite particles of different shape and size and therefore the linear combustion velocity can either increase or decrease after mechanical activation. The increase in the combustion temperature was observed only for compositions characterized by incomplete combustion and can be explained by the fact that grinding of reactant particles in the course of mechanical treatment leads to an increase in combustion efficiency. For all systems studied to date, the measured combustion temperature is lower than the adiabatic value corresponding to a 100% conversion. This indicates that the excess energy accumulated in the mixture is low compared to the chemical heat of reaction.

Considerable progress has been made in the experimental studies of mechanical activation *per se* and of the nature of structural transformations induced in the reactive mixtures. In particular, it was shown that sliding friction and friction-induced shear deformation and cold welding rather than direct impacts play a decisive role for mechanical activation of exothermic powder mixtures (SHS compositions). This points to a fundamental relation between mechanical activation and seminal works of P.W.Bridgman and Academician N.S.Enikolopov on the influence of pressure and shear deformation on physicochemical processes. Electron microscopy data confirm the conclusions drawn using the two-stage mechanism of mechanochemical reactions 'deformation mixing–relaxation' proposed by P.Yu.Butyagin. Recently discovered nanoclusters represent seeds of product phases and favour a decrease in the energy barrier to initiation of the reaction. Further development of this approach should relate the experimental microscopic data to the kinetic theory of strength in order to explain the key regularities of mechanical activation of reactive mixtures.

The application of mechanical activation in the synthesis of various materials considerably increased in the last decade. A promising technological area has been formed, namely, a combination of mechanical activation and SPS for fabrication of non-porous (dense) materials. However, there are numerous questions and technological issues that require further R&D in the title field. We believe that research activity aimed to solve these issues will be based on direct experimental observations of processes occurring in mill activators including self-propagating exothermic

reactions and on studies of the dynamics of structural transformations in reactive mixtures.

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