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Self-sustaining reactions induced by ball milling

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Abstract

Ball milling induces self-sustaining reactions in many sufficiently exothermic powder mixtures. The process begins with an activation period, during which size reduction, mixing, and defect formation take place. The MSR (mechanically induced self-propagating reaction) is ignited when the powder reaches a well defined critical state. Once started, the reaction propagates through the powder charge as a combustion process. In this paper, the current knowledge on MSR is reviewed from both experimental and theoretical points of view. Experimental results on a broad variety of systems are examined and compared. The variation of the ignition time with composition and milling conditions is investigated. Some unusual phenomena, such as the mutual suppression of combustion in mixed metal-chalcogen systems, are discussed. The mechanism of MSRs is extremely complex, with important processes on several length and time scales. The key objective is to understand ignition and the changes during the activation process that lead to ignition. Combining models with systematic empirical studies appears to be the most realistic approach to a detailed understanding of MSR processes. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

1.1. Mechanically-induced self-propagating reactions

Ball milling can induce chemical reactions in a variety of powder mixtures. Mechanochemistry offers direct reaction routes and solvent free, low temperature technologies. The process is called mechanical alloying when applied to metallurgical systems. Ball milling can often produce unique and metastable materials, that cannot be prepared by conventional techniques [1]. A self-sustaining reaction is initiated in many highly exothermic powder mixtures. In the systems of interest here, ignition does not happen at the beginning of the milling process. However, it becomes possible after a certain activation time, as milling reduces the particle size, thoroughly mixes the components, and increases the number of chemically active defect sites.

Mechanically induced self-propagating reactions have been observed in a variety of systems. For example, self-sustaining reactions take place when metal chalcogenides are prepared from their elemental components [2] or a metal oxide is reduced with a more reactive metal [3]. The ignition can be detected by measuring the temperature of the milling vial. The recording shown in Fig. 1 was obtained while reducing magnetite with zirconium metal. The reaction consists of three steps. (i) The first 110 s is the activation period, during which size reduction and mixing take place, chemically active sites are created, but very little product is formed. By the end of the activation period, the powder reaches a critical state. (ii) Ignition occurs between two colliding balls or a ball and the wall of the vial and a combustion front propagates through the powder charge. Compared to the rest of the process, this step is almost instantaneous. Understanding the mechanism of ignition is necessary to relate ignition to the properties of the milled powder. The release of the reaction heat results in an abrupt increase of the temperature. (iii) The reaction is often incomplete immediately after the self-sustaining process. Continued milling is needed to obtain fully reacted product with uniform structure and properties.

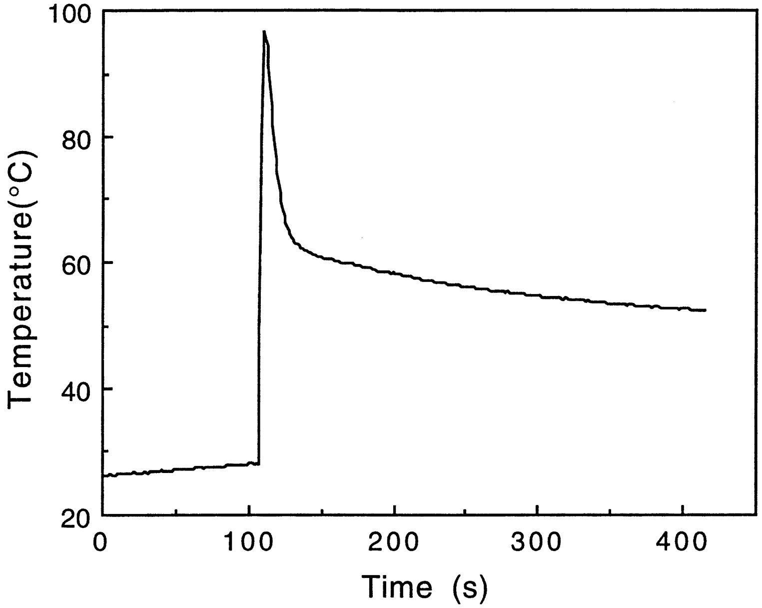

Fig. 1. Temperature of the milling vial during the mechanochemical reduction of Fe_3O_4 with Zr.

The main objective of this paper is to study the activation and ignition steps of the process. The activation time before ignition is usually reproducible to better than 10%, making this simple quantity a valuable parameter; it will be used extensively in this paper. Once a reaction front is established, the process becomes a SHS (self-propagating high-temperature synthesis) reaction which is discussed in excellent reviews elsewhere [4,5]. The effects of milling after combustion are similar to the late stages of any mechanochemical process.

Many different names are used to identify this type of reaction. They are combinations of terms such as ball milling induced, mechanochemical or mechanical alloying with combustive, explosive, self-propagating or self-sustaining. This review advocates using MSR, the acronym for mechanically-induced self-propagating reaction, as proposed by Yen [6]. Investigating MSRs is of interest from several points of view:

1. Applications. The process can be utilized as a tool to produce useful materials, e.g. refractory compounds and ceramic-metal composite powders [7]. The mechanical activation of the reactants, the reaction itself, and the pulverization of the product are performed during a single uninterrupted milling run. Mechanical activation by ball milling can also be used in conjunction with traditional SHS in order to improve product uniformity and lower the ignition temperature [8].
2. Ball milling has been utilized to prepare nanocomposite powders [9,10]. In one variant of the method, the final phases form by an in situ chemical reaction. Grain growth is prevented by the presence of two mutually insoluble product phases. The advantages of the method are lost, if a high temperature reaction takes place and large crystallites form instead of a nanocomposite. In order to prevent this, the conditions of MSR have to be understood and the processing parameters have to be selected to avoid ignition [11]. Preventing ignition is also important when milling energetic materials.
3. Any mechanochemical or mechanical alloying process begins with an induction period. Whether the reaction progresses gradually or a self-propagating process takes place, depends on minor differences in composition and milling conditions. Therefore, investigating mechanical activation and ignition is a possible vehicle to obtain information about the mechanism of mechanochemical processes in general. As Schaffer and McCormick wrote [12]: "These highly exothermic reactions are ideal systems with which to study the kinetics of mechanical alloying, because combustion represents a critical state of the reaction and is a simply determined reference point." The present paper discusses combustive mechanochemical reactions mainly from this point of view.

1.2. Historical survey

Research on mechanically-induced self-propagating reactions (MSRs) is a subfield of mechanochemistry and mechanical alloying. Therefore, it is appropriate to review the history of general mechanochemistry and mechanical alloying before exploring the beginnings of MSR research. The ignition and propagation of self-sustaining reactions is governed by the principles of conventional SHS (self-propagating high-temperature synthesis). Many reactions were studied in both SHS and MSR and the effect of pre-milling on SHS is a subject of current investigations. Consequently, a short summary of the history of SHS is also necessary.

Some simple mechanochemical effects, such as promoting the dissolution of salt by prior grinding or initiating fire by friction have been utilized by mankind since prehistoric times. Even the written history of mechanochemistry goes back to antiquity [13]: Theophrastus of Eresus noted in about 315 B.C. that mercury "... is made when cinnabar (HgS) mixed with vinegar is ground in a copper vessel with a pestle made of copper" [14].

The modern history of mechanochemistry begins with the work of Carey-Lee at the end of the nineteenth century. He showed that the order of the decomposition and sublimation of mercury and silver halides is different upon heating and trituration in a mortar [15]. This study established mechanochemistry as a distinct subject, showing that local heating is not the only possible mechanism of initiating chemical change by mechanical action. Since then, the chemical effects of mechanical treatment have been investigated in a large number of system. Monographs have been published on general aspects of mechanochemistry [16–18], the mechanochemistry of surfaces [19], the application of mechanochemistry to mineral processing [20] and the activation of silicates [21]. More recently, the mechanochemistry of organic compounds [22,23] and fullerenes [24,25] has received attention. Sonochemistry developed as a closely related area of research [26]. Mechanochemical processes are complex and system specific. Although much work has been done on individual reactions, general principles are slow to emerge [27]. Nevertheless, the potential to produce new materials and to develop environment friendly and economical technologies makes mechanochemistry an advancing field.

Although mechanical alloying can be considered a subfield of mechanochemistry, it was developed independently as a means to produce oxide dispersion strengthened superalloys [28,29]. No chemical change was intended in that process, the sole purpose of ball milling was to disperse fine oxide particles in a nickel matrix. Interest in mechanical alloying increased substantially, when the possibility to produce amorphous alloys was demonstrated [30]. That study introduced high energy ball milling as a new tool to achieve both atomic level alloying and the formation of metastable phases. Mechanical alloying was utilized to extend solubility limits and to prepare intermetallic compounds and amorphous alloys [31,32]. Nanocrystalline alloys [33], oxide-metal nanocomposites [34] carbides and silicides [35] were prepared by high energy ball milling. Many other applications can be found in the literature [36] and several conferences were dedicated fully or in part to mechanical alloying [37–39]. A useful overview of mechanical alloying is presented in the recent monograph by Lü and Lai [40] with many useful references to the original literature.

Many features of self-sustaining reactions are independent of whether the reaction is initiated by ball milling (MSR) or local heating (SHS). Therefore, a few words about the history of SHS are appropriate here. The first self-propagating solid state reaction was proposed by Goldschmidt in 1885 [41]. It is the so-called thermite reaction, in which a metal oxide is reduced with aluminium. The process takes place in a mixture of the powders, initiated by either a high temperature reaction or an electrically heated wire. A combustion front develops and propagates across the sample. This is a solid state reaction, no external source of oxygen is needed; neither does the process produce any gaseous product.

Systematic research on SHS was initiated by Merzhanov in 1967, beginning with the investigation of the titanium-boron system [4]. The method was used to prepare refractory compounds, intermetallics, and chalcogenides from mixtures of elemental powders. A variety of thermite-type reactions and some more complex systems have been investigated. Most of these reactions are also of interest for mechanochemical processing. The propagation of the combustion front was modeled theoretically, combining the thermodynamics and kinetics of the reaction with the equations governing macroscopic heat transfer [42]. The current status of research and application is reviewed by Merzhanov [43] and by Moore and Feng [5]. Mechanical activation prior to conventional SHS processing influences the burning velocity and product uniformity. Combined methods taking advantage of this feature create another link between SHS and MSR [44,45].

According to the best of my knowledge, the first systematic investigations on ball milling induced self-propagating reactions — explosive mechanochemical reactions, according to the terminology of the authors — were performed by Chakurov et al. in Bulgaria [2]. They studied the formation of metal chalcogenides from mixtures of the elemental powders. Eighteen reactions were examined between the metals Zn, Cd, In, Sn(II), Sn(IV) and Pb and the chalcogen elements S, Se, and Te. The ignition of a self-sustaining reaction was detected by measuring the abrupt temperature increase inside the mill. Preliminary experiments on the effect of milling conditions and the addition of iodine were reported. This pioneering work was published in 1982, followed by a remarkable series of early papers: a Mössbauer effect study of the reaction kinetics in the Sn–Fe–S system [46]; the only systematic investigation of the effect of inert additives [47] and the loss of combustion in some blends of two combustive mixtures [48]. Sadly, the passing away of Chakurov interrupted this effort.

The first ball milling investigations on thermite-type reactions were performed by Schaffer and McCormick in 1989 [3]. They used Ca to reduce CuO, ZnO and mixtures of the two oxides. This work was extended to a large number oxide–metal and chloride–metal reactions [49]. Similar displacement reactions were soon studied at other laboratories [50–54]. Combination reactions between a transition metal and silicon, carbon or boron attracted attention due to the technological relevance of the products [7, 55–58]. More recently, combustion was induced by ball milling in solid–liquid [59] and solid–gas [60] reactions. Many more investigations on a variety of systems will be reviewed in Section 3 of this paper.

While the amount of empirical knowledge increases steadily, much less has been done to explain the ignition of combustion theoretically. A simple model was proposed by Schaffer and McCormick [61]. They assumed that the powder charge is characterized by an ignition temperature, that decreases with mechanical activation. MSR is set off, when the ignition temperature becomes smaller than the maximum powder temperature between the colliding balls. Although this explanation rationalizes the need for an activation period, it does not attempt to relate the ignition temperature to more fundamental quantities. In order to develop a model with real predictive power, it is necessary to describe the mechanical operation of the mill, calculate the thermochemical properties of the powder as a function of mechanical activation and to describe the chemical kinetics and heat transfer during the ignition and propagation of the combustion front [62]. In spite of much effort in this direction [12,63–65], the problem is far from being solved.

As the theoretical treatment of combustive mechanochemical reactions is extremely complex, there remains a significant emphasis on empirical investigations. Systematic comparison of similar systems can be utilized to identify the relevance of material properties [66]. Processing the same mixture under different milling conditions is useful to study the macroscopic aspects of the process [12,67,68].

A few reactions show unexpected features in their kinetics or the composition dependance of the ignition time. The interrupted combustion effect was first demonstrated by Atzmon in the Ni–Al system [69]; later it was also observed in some thermite reactions [61]. The loss of combustion in blends of two combustive mixtures was first observed by Rusanov and Chakurov [48] and it was investigated in more detail by the author recently [68]. Combustion was ignited and quenched repeatedly in the Zr-S system [70]. The hope is that the knowledge obtained by studying these unusual cases will also be applicable to other MSR processes.

2. Experimental methods

Investigations of MSR processes are performed using a variety of equipment, milling conditions, and characterization methods. The experimental problems and possibilities are discussed in this section. A typical experiment on the reduction of magnetite with aluminium is used as an illustration.

2.1. Milling equipment

A SPEX 8000 Mixer Mill (a high-energy shaker mill manufactured by Spex CertiPrep, Inc., New Jersey, USA) was employed in this experiment. The reactant powder mixture and the milling balls are contained in a cylindrical vial, that is swung back and forth horizontally at the end of an arm, about 15 times per second [65]. The vial also wobbles sideways to make the motion of the balls more random. The main milling action comes from powder being caught between an impacting ball and the end of the vial. Compression and shear between colliding balls contributes as well.

Several different vials are available for the SPEX 8000 mill. This investigation employed a round-ended hardened steel vial. It has the advantage that the milling balls hit every point on the inner surface, there is no dead volume where a fraction of the powder could remain unprocessed. A problem with this vial is that the balls may roll around the end of the vial rather than hitting it, thereby decreasing the milling intensity. The balls may even roll around the inside surface of the vial repeatedly, tracing out a bent 8-shape. This can happen especially easily with only one or two balls and relatively small powder mass. Powder may collect in the eyes of the eight and remain unprocessed there [71]. Another drawback of the round ended vial is its the rather large mass (about 0.8 kg.) The flat-ended vials are 30% lighter, impacts at the ends of the vial dominate the milling action, but some powder may collect at the edges and remain unprocessed. Vials and balls made of other materials (WC, alumina, etc.) are also available for cases where steel contamination is undesirable.

Six hardened steel milling balls, 12.7 mm in diameter, were used in this experiment. The application of smaller balls, e.g. 6.3 or 9.5 mm in diameter, is also customary. Different ball sizes are sometimes mixed to "randomize" the motion of the balls. While the choice of the number and size of the milling balls is somewhat arbitrary, it profoundly effects the products and the reaction kinetics, including the ignition time. Therefore, ignition times from different laboratories can only be compared, if the type and number of the balls and the type of the vial are known. Unfortunately, there are many papers in the literature with incomplete information on the milling conditions.

Mills based on other principles can also be utilized. Vibratory mills consist of a grinding mortar and a single large ball. The mortar is vibrated on a platform, keeping the ball in motion. The milling intensity of vibratory mills is relatively low. Their advantage is the small amplitude of motion that makes measuring and controlling the processing parameters (temperature, pressure) relatively easy. The intensity of small laboratory tumbler mills is too small for most applications in mechanochemistry, due to the small drop height of the balls. This problem is overcome by the planetary mills that place the milling container on a rotating table, using the centrifugal acceleration to obtain an increased effective acceleration of gravity. Stirred ball (attritor) mills are best suited for wet grinding of larger quantities, they are rarely used in MSR experiments.

2.2. Materials

The stoichiometry of the starting powder corresponded to the equation

$$3Fe_3O_4 + 8Al \rightarrow 9Fe + 4Al_2O_3, \tag{1}$$

with 10% excess aluminium. The ignition time is often a sensitive function of the exact composition of the powder charge [51,72]. Therefore, using consistent compositions is important for obtaining reproducible and comparable results.

The reactants were Fe_3O_4 (97%, 325 mesh) and Al (99.5%, 325 mesh) powders. Relatively low grade reactants are usually acceptable, as impurities from the milling tools are hard to avoid anyway. In many publications, only the ball-to-powder ratio is given, implying that the ignition time scales with that parameter, and the mass of the powder and the size and number of the balls are unimportant separately. This is not always the case. Consequently, it is useful to report both the mass of the powder and the number and size of the balls. In our Example, 6 g of powder was milled with six 8.4-g (12.7-mm) balls, corresponding to a ball-to-powder ratio of 8.4:1.

The powder was placed into the vial inside an argon-filled glove box, in order to avoid contamination from the atmosphere. The powder mixture was homogenized in the vial with a spatula, until no agglomerates of either component were observable visually. It may be desirable to pre-mix and homogenize the reactants in a separate step [73]. No organic "process control agent" was added, which is customary practice in mechanical alloying of ductile metals, aimed at obtaining smaller and more uniform particle size. Process control agents also prevent excessive adhesion to the balls and the inner wall of the vial [29,40]. MSR is usually carried out "dry," without any process control agent.

2.3. Monitoring the process

It is easy to detect ignition by recording the temperature of the milling vial. A thermocouple (K type in this experiment) is convenient. Frequent breakage due to the vigorous motion of the vial can be avoided by protecting the thermocouple with plastic tubing, thereby limiting the bending radius.

The main information, in fact, the only parameter of interest in many experiments, is the ignition time. It can be derived from the time-temperature curve accurately, even if the actual temperature values have large systematic errors. The placement of the thermocouple is also unimportant. Fig. 2 shows three time-temperature curves recorded simultaneously with thermocouples attached to different points on the surface of the milling vial. The temperature values were logged every 2 s. The approximate location of the thermocouples is shown on Fig. 3. Although the shapes of the curves are quite different, the times of the sudden temperature increase are within 2 s. The quality of the thermocouple is also immaterial. We often use mechanically sturdy multiwire thermocouple extension cable to reduce further the probability of breakage.

When the combustion process propagates through the milling vial, a large amount of heat is released and the temperature of the powder increases close to the adiabatic temperature. When magnetite is reduced with aluminium even the resulting alumina melts, as suggested by the spherical shape of the alumina particles after combustion [51]. The reaction heat is quickly absorbed by the milling vial and balls. During the first two minutes after the reaction, there are large temperature differences between different parts of the milling vial, as indicated by the very different time-temperature curves in Fig. 2. The most sensitive and convenient point to measure the vial temperature is in the middle of the top surface (point a). The first curve was measured at this point; the thermocouple was pressed against the surface with a piece of styrofoam. The wall of the vial is the thinnest at this point, resulting in the fastest increase of temperature. After a few seconds the temperature decreases as some heat is conducted into other parts of the vial. Curves "b" and "c" were recorded on the side of the vial, with the thermocouple taped to the surface and covered with a piece of styrofoam. The temperature increase is more sluggish at these points, but it still begins within the same 2-s time interval. After about 2 min, the temperature of the vial is approximately uniform and approaches a steady-state value determined by the balance between the mechanical energy input and the heat loss to the environment.

The temperature increase measured to the maximum temperature depends on the temperature distribution within the vial and the exact placement of the thermocouple. More meaningful results can be obtained by extrapolating the slowly

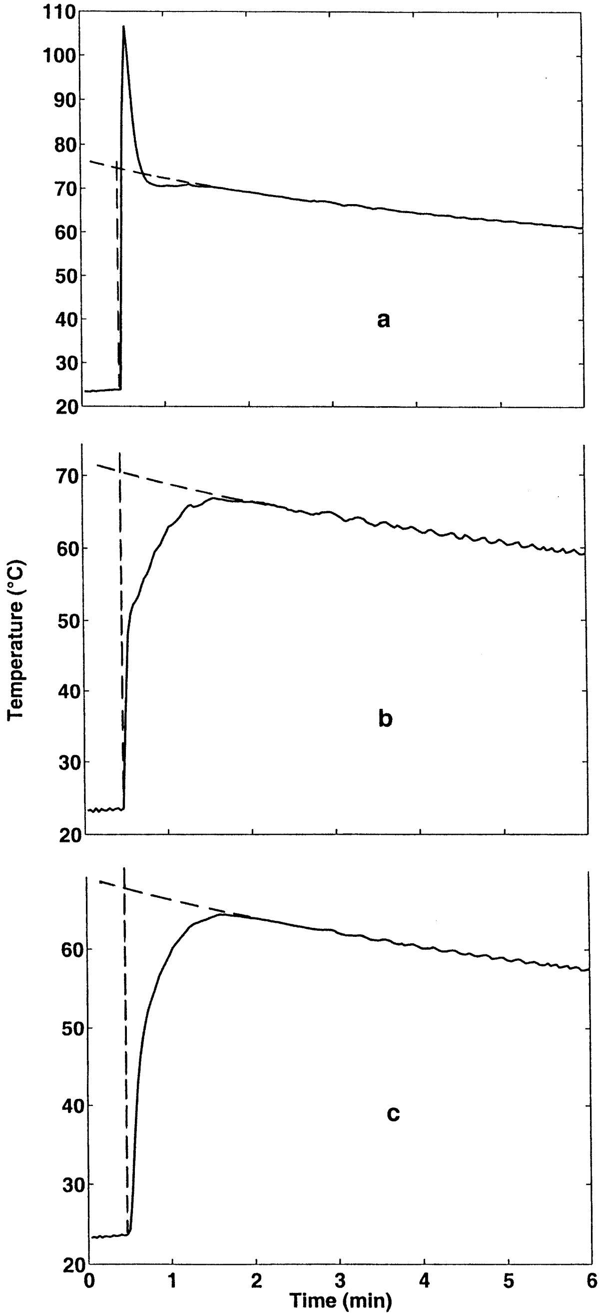

Fig. 2. The temperature of the milling vial as a function of time during the MSR between Fe_3O_4 and Al. Curves a, b, and c were recorded with thermocouples attached to different points of the milling vial as shown in Fig. 3.

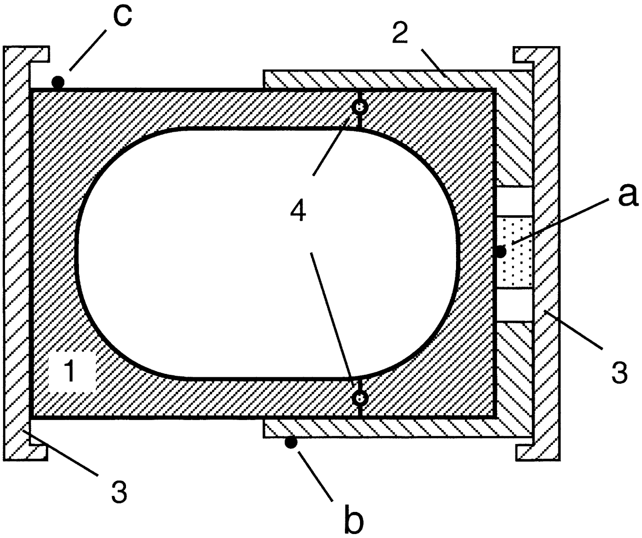

Fig. 3. Schematic cross-section of the round ended milling vial showing (1) the steel body and top, (2) aluminum screw-on cap, (3) holding clamps, and (4) O-ring seal. The thermocouples were attached at points a, b and c.

decreasing portion of the time-temperature curve back to ignition (dashed lines) and measuring the difference between this line and the temperature right before ignition. The resulting value would represent the temperature increase, if all reaction heat increased the temperature of the vial, balls, and reaction products uniformly. The temperature changes obtained from curves a, b, and c are 51, 49, and 47 K, respectively. The temperature increase can also be estimated using the mass and specific heat of the vial and the thermodynamic parameters of the reaction; the result is 51.5 K. This reasonably suggests that the milling vial can be used as a calorimeter, if the heat transfer between the vial and the environment (e.g. the aluminium holding clamps) is controlled. The temperature measurement can also be improved by inserting the thermocouple into a hole drilled in the body of the vial [69]. Little effort is reported on the use the vial as a calorimeter [67], although the method could answer some important questions. For example, a reaction may be incomplete, reaching only an intermediate product, or progressing only through part of the powder charge. Some reaction may take place gradually before ignition, decreasing the amount of heat released during the combustion step.

The vial temperature is not the only parameter that can be utilized to diagnose a MSR process. Chin and Peng measured the pressure in a gas container, that was connected to the milling vial by means of a plastic tube [60,74]. They used this method to investigate the reaction between Ti and N2 gas. The pressure measurement enabled them to calculate the amount of reacted nitrogen, i.e. to determine the reaction kinetics. Pressure measurement could also be used in the case of solid-solid reactions, as the pressure increases due to the temperature increase, even if no gaseous reactant or product is involved. Pressure measurement could also detect unexpected gaseous products.

In most cases, the reaction is accompanied by a noticeable change of the sound of the mill. It is useful as an "alarm," if stopping the mill immediately after the reaction is intended. Mulas et al. recorded and analyzed the sound of the mill, but their intention was to analyze the motion of the milling balls, rather then to test for a reaction [67].

2.4. Safety concerns

The reactions utilized in MSR are inherently highly exothermic. In addition, mechanical activation increases reactivity. Therefore, extreme care has to be exercised when handling the powders. It is not sufficient to consider the desired reaction alone, but all possible processes have to be evaluated carefully both before the milling experiment and before exposing the product to atmospheric oxygen, moisture, or other reagents. A few of the possible problems are mentioned below. However, the experimenter has to be aware that mechanical activation can result in unexpected chemical changes. New systems may present new problems. Careful planning, proper protection, and observing good laboratory practices are essential.

A customary method to study the kinetics of a reaction is to occasionally open the milling vial and remove a small sample for analysis. These intermediate samples are usually more reactive than the final product. For example, one may study the reaction between Ti and B. While the anticipated product, TiB2, is relatively inert, the powder removed before the combustive reaction is a mixture of finely divided and activated Ti and B. Both components are air sensitive, either could self ignite when exposed to air, the mixture of the two certainly will [75]. The same problem exists in many similar systems, such as Zr–C, Mg–S, etc.

Most reactions discussed in this paper are "gasless" combustion reactions, both the reactants and the products are solid. The pressure inside the milling vial increases during the high temperature reaction only due to the change of temperature. About a 10-fold pressure increase is possible for the more exothermic reactions. Although this is a concern, most commercial vials can withstand that pressure. A much larger pressure increase is possible, if the reaction has an unexpected gaseous product or a component of the reaction is in the gas phase during the high temperature reaction. For example, suppose that a halide is reduced by a reactive metal. If the halide is not perfectly anhydrous, the reducing metal may react with the water content, releasing hydrogen. If extra pressure is noticed during opening the cooled-down vial, some gaseous product was formed, whether intended or not. Working with smaller amounts of powder reduces the risk of explosion.

Unintentional reactions may generate poisonous products. For example, AlP is relatively inert in bulk form. However, the fine and activated powder obtained by ball milling is highly moisture sensitive. It produces toxic phosphine gas in humid air and self ignites upon contact with water. This may happen unexpectedly when washing a milling vial. Al_2S_3 is less moisture sensitive, although the characteristic smell of H_2S is noticeable if activated Al_2S_3 is exposed to moist air.

3. Investigations on MSR systems

In this chapter, the literature on MSR systems is reviewed, organized according to the type of the chemical reaction involved. Given the large number of papers published on the subject recently, it is impossible to mention every result here. Nevertheless, an attempt is made to include investigations on most systems and to mention results from most laboratories, that conduct research in this area. The references should be sufficient to guide the reader to further information.

It will be kept in mind that this paper is about understanding ignition and relating it to the properties of the reactants, the thermodynamics of the reaction and the operation of the mill. These aspects will be emphasized throughout this chapter, even if the focus of the original paper is different. The reader is advised to consult the references for more information, especially on the structure and properties of the products.

In selecting reactions that may show the MSR effect, a rule of thumb can be utilized from SHS. It requires that the adiabatic temperature be at least 1800 K for a reaction to become self sustaining [76]. The same criterion is also applicable in our case, although — as with most simple rules — exceptions abound. Instead of the adiabatic temperature, we will use a simplified form, namely the ratio of the reaction heat and the room temperature heat capacity of the product. The value of $-\Delta H^0_{f298}/C_{298}$, written simply as $\Delta H/C$ correlates closely with the true adiabatic temperature [5,77,78]. $\Delta H/C > 2000$ K can be used as a necessary criterion. The main difference between T_{ad} and $\Delta H/C$ is that the latent heats of melting and evaporation are left out. They become important, when the mechanism of the combustion process is investigated. However, when the beginning of the reaction is considered, the very high temperature properties are less relevant.

Highly exothermic solid state reactions are of interest both for SHS in powder compacts and for mechanically induced self-sustaining reactions. Therefore, many systems listed in reviews on SHS [4,5,43] are also of interest for MSR. However, not every SHS reaction can be initiated by ball milling. The main difference is that conventional SHS is performed in a bulk powder compact, with relatively little heat loss to the environment, while the powder in the ball mill is in close contact with the milling tools, heat loss to the vial and the balls may inhibit the formation of a self-sustaining reaction front. SHS can also be promoted by pre-heating the reactants, but MSR is typically performed at room temperature. Consequently, some moderately exothermic SHS systems do not show the MSR effect.

3.1. Combination reactions

3.1.1. Metal–chalcogen systems

The mechanochemistry of chalcogenides, particularly sulfides, is an area of active research, partly due to the importance of sulfide minerals and the application of chalcogenides in technology [79]. The formation of metal chalcogenides is also a very convenient model reaction for MSR studies, with good milling properties, insensitivity to air and impurities, and ignition times from a few minutes to hours.

In their pioneering work, Chakurov and Rusanov investigated a large number of metal chalcogen systems [2]. As they employed a low energy vibratory mill, their ignition times were relatively long, as reproduced in Table 1, $\Delta H/C$ is also given. (Most thermochemical data are taken from Ref. 80, the heat capacity of SnS is from Ref. 81.) Inspection of the data makes it obvious that rules of thumb and simple intuition may be misleading in the area of MSR: (i) $\Delta H/C$ is less than 2000 K for many of these reactions, contrary to the usually accepted criterion. (ii) One would anticipate that the more exothermic reactions ignite after a shorter activation time. This is far from being true. For example, the reactions are more exothermic with Zn than with Cd, yet, the ignition times are shorter for the reactions involving Cd. Clearly, other properties must also be important. The ignition time correlates better with the hardness of the reactants, namely it is shorter for softer metals and harder chalcogens [82]. Hardness data from Ref. 82 are included in Table 1. (iii) The temperature increase due to the reaction should be approximately proportional to the reaction heat. Compared to the temperature changes for the Zn–S, Zn–Se, and Cd–S reactions, most ΔT values are surprisingly small, suggesting that either a large fraction of the reactants combine before ignition or — more likely — the MSR process consumes only part of the reactants.

Table 1
Metal–chalcogen reactions investigated by Chakurov and Rusanov [2]. $\Delta H/C$ (based on data from [80]), the ignition time, t_{ig}, and the amplitude of the temperature increase, ΔT, are given[a]

Reaction	$\Delta H/C$(K)	t_{ig} (min)	ΔT(K)	Microhardness[a]	
				Metal	Chalcogen
Zn + S	4520	365	30	530	290
Zn + Se	3140	312	23	530	450
Zn + Te	2400	300	2	530	500
Cd + S	3070	78	17	290	290
Cd + Se	2920	46	7	290	450
Cd + Te	2020	55	3	290	500
2In + 3S	3010	25	6	100	290
2In + 3Se	2310	20	3	100	450
2In + 3Te	1550	12	2	100	500
Sn + S	2190	110	2	90	290
Sn + Se	1790	42	2	90	450
Sn + Te	1170	22	2	90	500
Sn + 2S	2190	258	3	90	290
Sn + 2Se	1740	21	3	90	450
Sn + 2Te	?	42	1	90	500
Pb + S	1980	40	3	–	290
Pb + Se	1990	12	3	–	450
Pb + Te	1360	14	3	–	500

[a] The microhardness data are from Ref. 82.

Beside obtaining the ignition times, Chakurov and Rusanov also investigated the reaction kinetics using chemical analysis, X-ray diffraction, and Mössbauer spectroscopy [2]. Fig. 4 shows the transformed fraction as a function of milling time for the formation of ZnS, CdS and In_2S_3. Interestingly, significant transformation takes place both before and after the sudden change during combustion, especially for the less exothermic reactions with Cd and In. This behavior is typical of single-ball vibratory mills, the transformation is more abrupt with shaker or planetary mills. (The data in Fig. 4 were derived from analysis of the chemical state of sulfur. The transformed fraction of 10–15% obtained far from ignition may be an artifact of the method. The ignition times deduced from the figure and the values given in Table 1 are different, probably due to different milling intensities.) The kinetics of the Sn + 2S reaction is even more complicated. The Mössbauer line intensities indicate that the sudden formation of SnS_2 is preceded by the gradual formation of SnS (Fig. 5). Further results on metal-chalcogen systems will be discussed in Section 5.

Investigations on metal–chalcogen systems were carried out in several other laboratories. In addition to the systems already mentioned, MSR was observed in Mg–S, Mg–Se, Sb–Se, Bi–Se [83] and Ti–S, Zr–S, Hf–S [66] mixtures, using a SPEX 8000 shaker mill. The ignition times were much shorter, typically of the order of 10 min, due to the more intense milling. Very little product was found in samples milled close to ignition. Balaz et al. used a planetary mill to prepare ZnS from an elemental

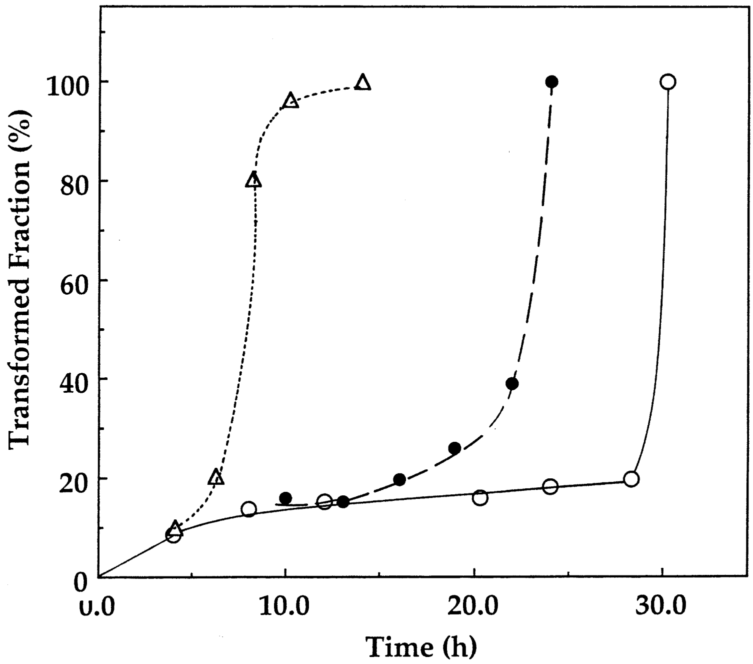

Fig. 4. Transformed fraction as a function of milling time for the mechanochemical synthesis of ZnS (open circles), CdS (filled circles) and In_2S_3 (triangles) based on Ref. [2].

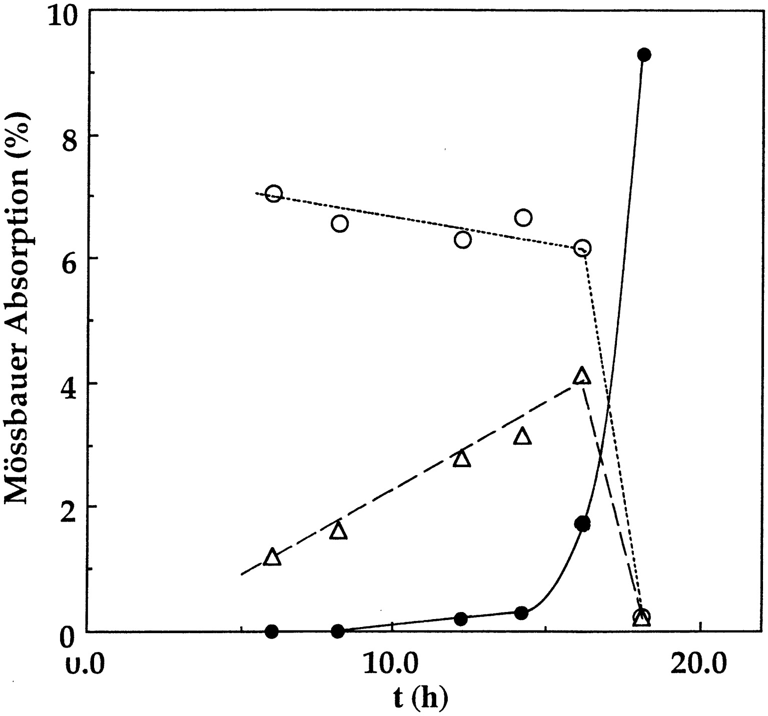

Fig. 5. The kinetics of the mechanochemical reaction in an Sn + 2S powder blend as described by the intensity of the Mössbauer absorption lines for metallic Sn (open circles), SnS (triangles) and SnS_2 (filled circles).

mixture [84]. Although they did not record the mill temperature, the X-ray diffraction patterns suggest that a combustive reaction took place some time between 30 and 50 min of milling. The combustive formation FeS from Fe and S powders was observed recently, using a SPEX mill [85]. This result is interesting as iron was considered an inert component when added to an Sn–S mixture [46].

The behavior of the Al–S system is anomalous: Although $\Delta H/C = 6400$ K, far greater than the usual limit, the mechanosynthesis of Al_2S_3 proceeds gradually, without MSR. The reason for this behavior is not known yet, but it clearly shows that high adiabatic temperature is only a necessary criterion of self-sustaining kinetics.

3.1.2. Metal–metalloid reactions

Interest in the formation of transition metal borides, carbides, and silicides is sustained by the technological importance of the products. Most of these compounds have also been produced by SHS [5]. The product of SHS is typically a porous but hard solid mass that needs to be milled into a fine powder for certain applications. MSR combines the preparation and pulverization into a single step.

The mechanosynthesis of metal carbides was proposed by Matteazzi and Le Caër [86]. They prepared carbides of Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, W, Re, Al, and Si by milling the above elements with graphite powder in either a SPEX

8000 shaker mill or a Fritsch P-7 planetary mill for a fixed amount of time. Although they were not looking for MSR processes, it is very likely that some of their preparations followed that route.

The MSR preparation of TiC from elemental Ti and C powders has been demonstrated by several groups [66,82, 87–89]. ZrC and HfC can also be synthesized the same way [66,90]. Wu et al. investigated the mechanism of the reaction [91]. According to their XRD linewidth analysis, the particle size of Ti decreased to 26 nm and the lattice strain increased to 3.2% during the activation time. Simultaneously, the diffraction lines of carbon disappeared. As the position of the Ti diffraction lines did not change, the dissolution of carbon into the Ti matrix was excluded. A possible explanation is that the carbon was distributed in the grain boundaries of titanium on the nanometer scale. Shifts of the XPS lines suggest that a transitional bonded state between Ti and C formed before ignition, although no trace of TiC was observed. Combustion took place after about 19 h of milling, resulting in a single-phase Ti–C product.

The reaction between Ti and C is highly exothermic, its $\Delta H/C$ value is about 3850 K, almost twice the minimum required for MSR. Consequently, enough heat is produced by the reaction to support combustion even if the composition deviates from stoichiometry [92] or the system is diluted with inert additives. Several variations of the reaction were based on these possibilities. Composites of TiC and either Ni or a Ni–Ti alloy were obtained by adding Ni to the Ti–C mixture [88,93,94]. The reaction between Ni and Ti also contributes to the heat balance, but it would not be sufficient to sustain the MSR process alone. Similar results were obtained when Al was added to the Ti–C mixture [95]. The addition of Mo resulted in a side reaction producing Mo_2C [88]. Many other possibilities can be explored in the future.

The borides of the IVB transition metals are important refractory compounds. As TiB_2 was the very first compound prepared by ordinary SHS [4], it is understandable that the same reaction attracted interest in the ball milling initiated process as well. Radev produced TiB_2 by milling Ti and B powders in a Fritsch P-5 planetary mill [75]. The self-sustaining reaction ignited after 80 minutes of activation; the product was single phase with 0.86 μm mean particle size. The particle size of TiB_2 prepared by SHS in the same laboratory was 40–60 μm [96]. Park et al. prepared both TiB_2 and ZrB_2 using a low energy vibratory mill [58]. Rather long activation time (about 100 h, varying with the ball size) was required to ignite the reaction between Ti and B. No MSR took place at all when milling a Zr–B mixture. Given the highly exothermic nature of the reactions ($\Delta H/C$ is 7110 K for TiB_2 and 6660 K for ZrB_2) the very long ignition time in the Ti–B mixture and the lack of ignition in the Zr–B system is surprising. MSR was easily observed in Ti–B, Zr–B, and Hf–B mixtures when using a SPEX shaker mill, 3 g of powder, and five 3.5-g balls [66]. XRD results on the Zr–B system are presented on Fig. 6. After about 90% of the ignition time, only the broadened diffraction peaks of Zr are visible. (The shoulder at about 32.4° is probably an impurity. The boron content could be amorphized or distributed in the grain boundaries of Zr. No traces of ZrB_2 are seen.) Ignition took place after 2760 s of milling. The sample taken after the reaction is almost pure ZrB_2.

The interest in silicides, particularly $MoSi_2$, is driven by their applications in high temperature heating elements and as coating materials. The formation of this

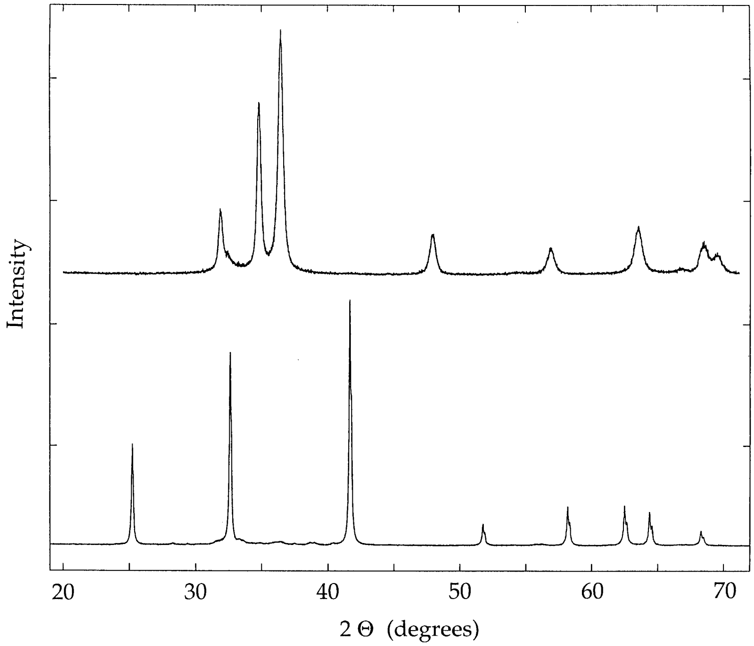

Fig. 6. X-ray powder diffractograms taken immediately before (upper curve) and after (lower curve) the self-sustaining reaction between Zr and B. All lines of the upper curve are from unreacted Zr (except the shoulder at 32.4°) and the main lines of the lower curve are all from hexagonal ZrB_2.

compound is moderately exothermic, $\Delta H/C = 2060$ K, making the reaction between Mo and Si a borderline case. In fact, both gradual and MSR formation of $MoSi_2$ has been observed, the type of kinetics depended on the milling intensity [97]. (The formation of the other molybdenum silicides is less exothermic, the kinetics is always gradual [6].) The formation of $MoSi_2$ is gradual even with a SPEX mill, if a very low ball-to-powder ratio is used [98]. Higher milling intensity resulted in combustive reaction [6,99,100]. The reaction product is the tetragonal, room temperature form of $MoSi_2$ [99]. Interestingly, the same form is preferred, when gradual reaction is induced in a planetary mill and milling is performed with large balls. Lower energy milling with smaller balls produces the hexagonal, high temperature form [97].

The formation of several other silicides takes places via MSR. $NbSi_2$ and $ZrSi_2$ were prepared by Yen [101]. Lou et al. observed that the formation of $NbSi_2$ is self-propagating, but only upon uninterrupted milling; gradual reaction is observed, if the mill is stopped to cool after every 5 min of processing [102]. The monosilicides of Ti, Zr, and Hf [66] and several Zr silicides with different stoichiometries were obtained by MRS [90].

3.1.3. Other combination reactions

The combination of Ni and Al powders to form NiAl is the only metal–metal system in which MSR has been demonstrated. In Atzmon's experiment [69], ignition was not obtained upon continuous milling. However, it could be achieved by interrupting the

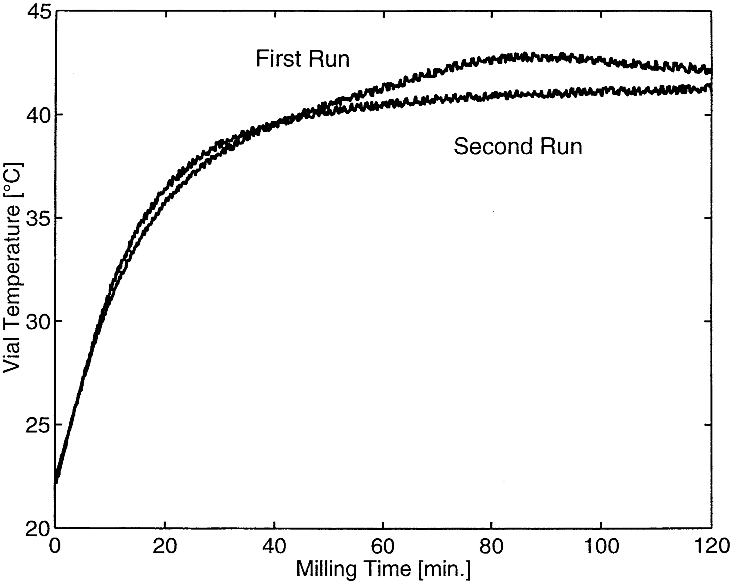

Fig. 7. The temperature of the milling vial as a function of time while milling 4.5 g of equimolar Al–P mixture by three 12.7-mm and eight 9.5-mm balls.

milling process for a half hour cooling period. After that, ignition occurred in less than a minute as milling was resumed. This "interrupted combustion effect" will be discussed further in Section 5. Liu et al. observed combustion upon continuous milling in the same system [103]. The two groups used identical mills (SPEX 8000) but slightly different ball-to-powder ratios (6:1 versus 10:1.) MSR was preserved even if a few percents of Al was replaced with Ti or Fe.

Most metal–metal systems are not exothermic enough to make MSR possible. $\Delta H/C = 2980$ K for $CaAl_2$, but an attempt to induce combustion in this system failed, probably due to the softness and good heat conductivity of both components [104].

The mechanochemistry of phosphides is largely unexplored. Gradual reaction by ball milling is one of the methods used to prepare amorphous Ni–P and Co–P alloys [105]. MSR has been demonstrated in the $Ni_{1-x}P_x$ system for $0.25 \leqslant x \leqslant 0.4$ [106]. The reaction products are mixtures of Ni_3P, $Ni_{12}P_5$ and Ni_2P.

The combination reaction between equal amounts of elemental Al and P powders took place as a gradual process [106]. MSR could not be achieved, although the reaction is obviously exothermic enough, $\Delta H/C = 3910$ K. Traditional SHS is a standard method to prepare AlP [107]. Several different ball-powder mass combinations were explored unsuccessfully. Fig. 7 shows the temperature as a function of milling time while milling 4.5 g of stoichiometric Al–P powder blend with three 8.4-g and eight 3.5-g balls. The curve marked "first run" shows that the temperature of the vial varied smoothly during the milling process; the abrupt temperature increase, that would signal ignition, did not happen. However, when the curve is compared to a "baseline" obtained by milling the already reacted powder for a second time under identical conditions, the presence of an excess heat effect becomes evident between about 50 and 80 min. As confirmed by XRD, most of the reaction takes place in this time interval. The first 50 min is an induction period, no product is formed yet. After that time, the reaction progresses quickly, although it does not become self-sustaining.

The only solid halogen element is iodine. Its reactions with the reactive metals are quite exothermic, self-sustaining reaction may be expected in a number of systems. Yet, no previous experiment attempted to prepare iodides by MSR. The reaction between Al and I was investigated as an exploratory experiment. The temperature of the milling vial as a function of milling time is shown in Fig. 8, compared to a second milling run for baseline. Much of the reaction takes place in two MSR-like steps as indicated by the temperature jumps. A probable explanation is that iodine sublimes from the vicinity of the initial reaction site, so that the reaction does not extend to the entire volume of the vial during the first event. It seems that investigating reactions involving iodine can uncover a number of interesting phenomena.

3.2. Displacement reactions

3.2.1. Oxide–metal systems

Thermite reactions between aluminium powder and the oxide of a less reactive metal were the first solid state combustion reactions [41]. Therefore, it is not surprising that analogous reactions are probably the most widely investigated processes in MSR.

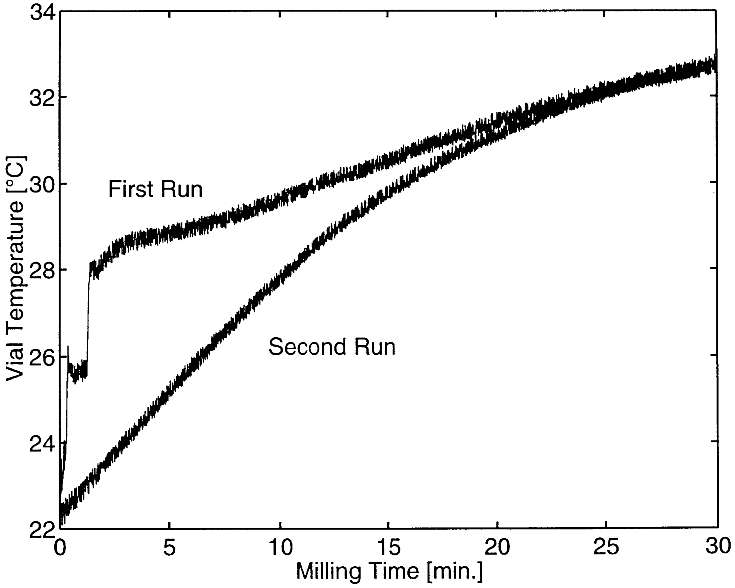

Fig. 8. The temperature of the milling vial as a function of time while milling 5 g of equimolar Al–I mixture by seven 9.5-mm balls.

The general equation representing an oxide–metal displacement reaction is

$$A_xO + yB \rightarrow xA + B_yO, \tag{2}$$

where x and y are not necessarily integers. The reaction is thermodynamically favored in the indicated direction, if the heat of formation (per oxygen atom) is larger for the oxide of B than for the oxide of A. Table 2 presents the heat of formation for a number of oxides in decreasing order. (The thermochemical data are from Ref. 80.) The reducing metal, B, must be above A on this list, in order to make the reaction exothermic. The reaction may progress as a MSR process if the reaction heat is large, i.e. the appropriate oxides are far from each other on the heat-of-formation scale. Of course, this is only a necessary condition. Whether MSR actually takes place or not also depends on the specific heat of the products, the mechanical properties of the powder, the milling conditions, etc.

The number of possible MSR systems is well over one hundred even if only the metals in Table 2 are included. In fact, the heat of formation varies in such a broad range that the metals in the middle of the table can serve as the reducing metal in

Table 2
Heat of formation of some oxides in order of decreasing heat of formation per oxygen[a]

Oxide	$-\Delta H$ per formula (kJ/mol)	$-\Delta H$ per oxygen (kJ/mol)
CaO	634.9	634.9
MgO	601.6	601.6
HfO_2	1117.5	558.8
Al_2O_3	1675.7	558.6
ZrO_2	1100.8	550.4
TiO	542.7	542.7
TiO_2	944.0	472.0
SiO_2	910.9	455.5
B_2O_3	1263.5	421.2
MnO	384.9	384.9
Nb_2O_5	1899.5	379.9
ZnO	350.5	350.5
V_2O_5	1550.2	310.0
WO_3	842.7	280.9
Fe_3O_4	1108.8	277.2
Fe_2O_3	823.4	274.5
FeO	263.0	263.0
CdO	258.4	258.4
MoO_3	745.2	248.4
NiO	239.7	239.7
PbO	219.4	219.4
CO_2	393.5	196.8
Cu_2O	173.2	173.2
CuO	161.9	161.9
Ag_2O	31.1	31.1

[a] The data are taken from Kubaschewski [80].

one MSR process and the reduction of the oxide of the same metal by metals close to the top of the reactivity scale is also self sustained. For example, Fe was involved both ways in the MSR processes

$$4CuO + 3Fe \rightarrow 4Cu + Fe_3O_4 \tag{3}$$

$$Fe_3O_4 + 2Ti \rightarrow 3Fe + 2TiO_2 \tag{4}$$

In the following, the peculiarities of some oxide–metal displacement reactions are discussed.

The forerunner of combustive displacement reactions is the investigation of Schaffer and McCormick on the reduction of CuO with Ca. Milling was performed in a SPEX mill with 4 ml toluene added to the CuO–Ca charge as lubricant [108]. Although the reaction kinetics was gradual due to the presence of toluene, the temperature of the milling vial exhibited a broad maximum due to the large reaction heat (Fig. 9). The first MSR studies on oxide-metal systems were natural extensions of this work. The lubricant inhibits the reaction both by decreasing direct contact between the particles and by conducting the reaction heat away from the reaction site. Therefore, in order to initiate MSRs, the powder charge has to be milled without any lubricant. CuO was reduced with Ca, Mg, Al, Ti, Mn, and Fe [109]. Some ignition time data are reproduced in Table 3, based on the results presented in Ref. 109. Both the true adiabatic temperature and the value of $\Delta H/C$ are given. The data show that T_{ad} and $\Delta H/C$ indeed correlate very closely, either is appropriate to characterize exothermicity. Both depend on the stoichiometry of the reaction, as the higher valency of the metal (Al or Ti) results in smaller heat capacity of the product. As a result, high-valency metals can exhibit MSR more easily than ΔH alone would suggest. The ignition time correlates very weakly with the adiabatic temperature. In particular, the very short ignition time in the case of Ti is hard to explain. (It is not an experimental artifact. Even shorter ignition time, 60 s, was obtained under somewhat more energetic conditions [66].) The small difference between the ignition times when using Mg and Mn

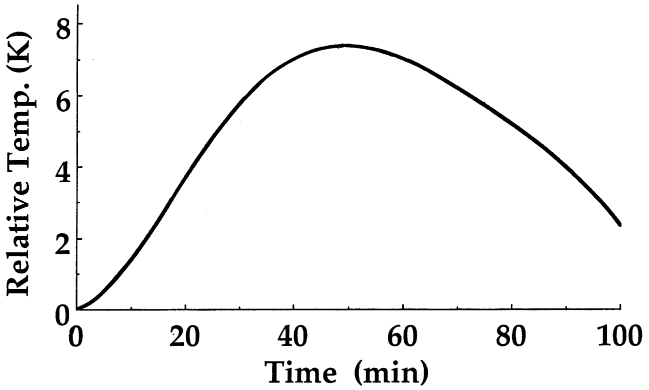

Fig. 9. Relative temperature of the vial during the reduction of CuO by Ca in toluene [108].

Table 3
The reaction heat, $-\Delta H$, adiabatic temperature, T_{ad}, $\Delta H/C$, and the ignition time, t_{ig}, for the reduction of CuO with a few metals after Ref. 109

Reaction	$-\Delta H$/oxygen (kJ)	T_{ad} (K)	$\Delta H/C$(K)	t_{ig} (s)
$3CuO + 2Al \rightarrow 3Cu + Al_2O_3$	396.7	5151	7810	930
$CuO + Ca \rightarrow Cu + CaO$	473.0	4716	7100	1126
$CuO + Mg \rightarrow Cu + MgO$	439.7	4531	7120	2039
$2CuO + Ti \rightarrow 2Cu + TiO_2$	310.1	4175	5960	167
$CuO + Mn \rightarrow Cu + MnO$	223.0	2227	3220	2580
$4CuO + 3Fe \rightarrow 4Cu + Fe_3O_4$	115.3	1668	1850	9205
$CuO + Ni \rightarrow Cu + NiO$	77.8	1288	1130	–

as the reducing agents is also unexpected, given the large difference between the thermochemical parameters of the reactions. This result clearly shows that the adiabatic temperature is only a useful first guide. The more exothermic reaction is not necessarily faster, the ignition time is also sensitive to other parameters. According to T_{ad} and $\Delta H/C$, the reaction with Ni is not sufficiently exothermic for MSR. Indeed, CuO and Ni react gradually, no ignition is observed.

The reduction of CuO with Al was also investigated by Zhang and Richmond, using a SPEX 8000 mill and the extremely low ball-to-powder ratio of 1:1.2 [110]. Due to the very exothermic nature of the reaction, ignition was obtained after activation times between 1.5 and 2 min. Only Cu and Al_2O_3 phases were found immediately after the MSR process. As deduced from the microstructure, Al_2O_3 melted and at least part of Cu evaporated during the reaction. The shape of the product particles was also analyzed by Schaffer and McCormick, to identify which product phase melted during combustion. Such investigations give upper and/or lower limits of the actual temperature of the powder during the reaction [111].

The adiabatic temperature is slightly below the usually accepted limit of 1800 K for the CuO–Fe system. Indeed, the kinetics of this reaction was found to be gradual or self-sustaining, depending on the exact conditions. MSR was observed by Schaffer and McCormick, who milled an 8-g powder charge with three 8-g balls. The ignition time was 9205 s [109]. The same ignition time was obtained in our laboratory when using identical conditions. The deviation was only about 5%, showing that reproducing the ignition time is possible even in sensitive systems, if the conditions are known exactly. Forrester and Schaffer milled 12 g of powder with fifteen 8-g balls. This unusually large charge resulted in the much shorter ignition time of about 2200 s [112]. Gradual reaction was observed when 6 g of powder was milled with 6 balls of the same size [113]. The product of the reaction was a nanocomposite. Each experiment above used a SPEX 8000 mill and round-ended hardened steel vial. Shen et al. observed MSR in the same reaction by employing a planetary mill [50, 114]. The ignition time was 7740 s, unusually short for a moderately exothermic reaction and not very energetic milling device. The authors also pointed out that Cu_2O was an important intermediate phase. No iron oxide other than magnetite was found by either group.

Attritors are rarely used in studies of MSR due to their low energy concentration. The study of the very highly exothermic reaction between CuO and Al by Shengqui et al. is an exception [115]. In a stoichiometric mixture, ignition occurred after about 2 hours of activation. Cu and Al_2O_3 formed as expected. Excess Al suppressed combustion and a mixture of $CuAl_2$ and Al_2O_3 formed with gradual kinetics.

The heat of formation of Cu_2O is close to that of CuO. Consequently, the reaction heats for the reduction of Cu_2O and CuO with the same reactive metal are similar. However, the extra Cu atom increases the heat capacity and proportionately lowers the adiabatic temperature. As a result, the ignition times for the reduction of Cu_2O are about an order of magnitude longer than the analogous values with CuO [66]. MSR was observed when reducing Cu_2O with Ti, Zr, Hf [116], and Mg [117].

The interest of the author in the Fe_3O_4–Al system was originally motivated by the intention to make magnetic nanocomposites consisting of Fe and Al_2O_3 phases. This goal could be achieved only by adding inert material (Al_2O_3) to the powder charge [118]. If Fe_3O_4 is milled with a stoichiometric amount of Al, MSR is ignited [51]. The reaction remains combustive even if the composition of the powder mixture deviates from stoichiometry. A deficit in Al results in partial reduction of magnetite and the formation of $FeAl_2O_4$. If excess aluminium is present, it alloys into the freshly formed iron and a disordered Fe(Al) solid solution is obtained. The microstructure of the reaction products contains spherical Al_2O_3 particles, indicating that the temperature exceeded the melting point of Al_2O_3 (2325 K), at least in some parts of the milling vial. Given the high adiabatic temperature of the reaction ($\Delta H/C = 6220$ K), this is expected.

Once the ignition time of a reaction is known, it is possible to mill a charge to within a few percents of ignition. XRD phase analysis on a sample taken immediately before ignition revealed the presence of the reactants, Fe_3O_4 and Al only. As in most MSR processes, very little chemical change preceded ignition. Samples taken soon after combustion were also investigated. As very high temperature was reached inside the vial during combustion, only the final products were anticipated. Surprisingly, this was not the case. Traces of the reactants and a significant amount of $FeAl_2O_4$ were found in a sample milled for 5 min after combustion (Fig. 10). Reaching the final state containing only Fe and Al_2O_3 required a substantial amount of milling after MRS [51]. Fe_3O_4 has been reduced by other reactive metals. The IVB metals [66,116] and Mg [72] were used successfully.

Similar results were obtained when hematite, Fe_2O_3 was reduced with Al [119]. The stoichiometric powder mixture was diluted with 25 wt.% Al_2O_3 to reduce the reaction temperature. MSR was observed only for very energetic milling conditions — using eight 8-mm and eight 10-mm steel balls to mill 5 g of powder in a SPEX mill. The product immediately after combustion contained the intermediate oxide $FeAl_2O_4$ and some Al was dissolved into the bcc Fe phase. The final state was achieved after several hours of additional milling.

Osso et al. reduced several mixtures of Cr_2O_3, Fe_2O_3, and NiO with Al in a P-5 planetary mill [120]. Self sustaining reaction was not observed in the Cr_2O_3 rich systems and the ignition time became shorter with increasing NiO fraction. This behavior is a direct consequence of the different heats of formation for the three component oxides.

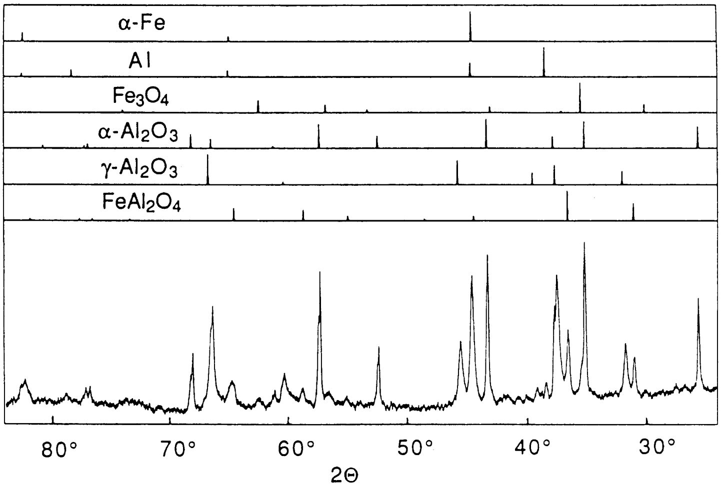

Fig. 10. X-ray diffraction pattern of a magnetite–aluminum powder that was milled for an additional 5 min after the thermite reaction.

XRD and Mössbauer spectroscopy were used to analyze the reaction products. A number of mixed oxide and alloy phases were identified.

The heat of formation of V_2O_5 is quite large (Table 2). Consequently, only the most reactive metals are capable of reducing it in an MSR process. Self-sustaining reactions with Al, Mg, and Ti were induced successfully [121]. The reduction of ZnO is even less exothermic. Its reactions with Ca and Ti show the interrupted combustion effect, while the reduction with Mg follows the usual course of MSR [122]. The most stable oxide that has been reduced with a reactive metal in an MSR process this far is Nb_2O_5. Al, Zr and Al_2Zr intermetallic compound was used as the reducing agent [123].

The reaction heats of the displacement reactions involving Si are almost as large as the reaction heats of the similar reactions of Ti. Both elements are tetravalent. Consequently, Si is about as strong a reducing agent as Ti. For the reduction of CuO with Si, $\Delta H/C = 6280\text{K}$, actually higher than the corresponding value for the reduction of CuO with Ti. Yet, gradual kinetics was observed when CuO was milled with Si in an attritor [124]. MSR was observed in the PbO–Si system, when it was processed in a high energy planetary mill. However, the ignition time of 68 min is quite long for such a highly exothermic reaction [125]. As both components are brittle, it is difficult to develop intimate contact between the particles, the usual process of distributing the brittle oxide particles in the ductile metal matrix does not operate. More systematic studies comparing thermochemically similar ductile and brittle reactants milled under identical conditions would be beneficial.

3.2.2. Displacement reactions involving sulfides and halides

The heats of formation of sulfides are much smaller than the corresponding values for oxides (Table 4) Consequently, the displacement reaction between a sulfide and a more reactive metal is less exothermic than the analogous reaction

Table 4
Heat of formation, $-\Delta H_{298}$ in kJ/mol per nonmetal atom for some typical metal oxides, sulfides and chlorides[a]

Metal	Oxide	Sulfide	Chloride
Ca(II)	635	473	398
Mg(II)	602	346	321
Al(III)	559	241	235
Zr(IV)	550	289	245
Ta(V)	409	177	172
Sn(IV)	289	77	132
Fe(III)	274	38	133
Ni(II)	240	88	152
Cu(II)	162	52	108

[a] The data are from Ref. 80.

between the corresponding oxide and the same metal. Nevertheless, the reaction heats are high enough to permit MSR. Milling a mixture of SnS_2 powder with a stoichiometric amount of Ca shot (3 g total mass milled with three 8-g balls) lead to combustion in just 8.4 min [104]. The reduction of CuS with Ti, Zr, and Hf is also self sustaining. The temperature of the milling vial as a function of milling time is presented in Fig. 11. It is interesting to note that the ignition time is much shorter for Zr than for either Ti or Hf, a trend that is also observed in oxide-metal displacement reactions [66,116]. Analogous reactions involving selenides or tellurides have not been investigated.

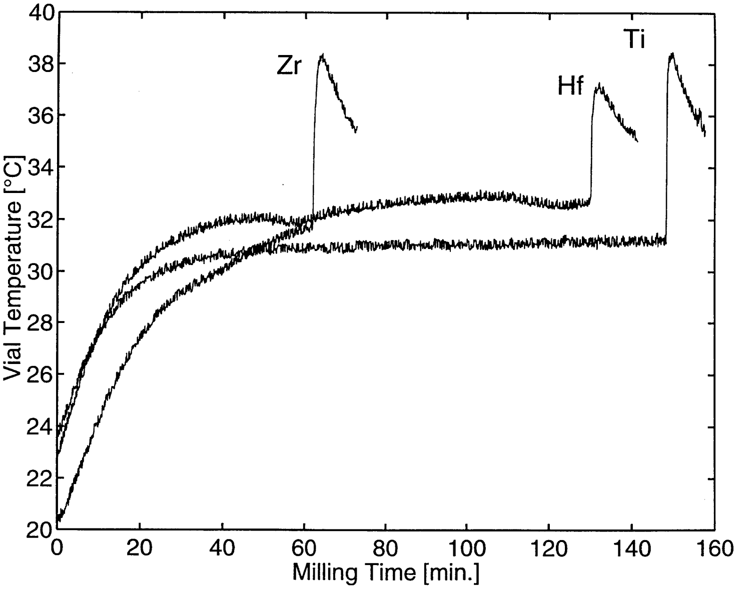

Fig. 11. The temperature of the milling vial as a function of time during the MSR between CuS and a IVB metal. Three grams of powder was milled with three 12.7-mm balls.

As it is suggested by the heat of formation of chlorides (Table 4) displacement reactions with MSR kinetics are also possible between a halogenide and a more reactive metal. The possibility has been demonstrated for the case of $TaCl_5$ reduced with Mg [126]. Given the rather low (true) adiabatic temperature of 1616 K, surprisingly short ignition times were found. For example, when 5 g of powder was milled with ten 9.5-mm balls, ignition took place after only 5 min of milling. The reason for the fast reaction may be the low melting point of the reactants. A useful property of the halides is their solubility in water. Ultrafine powders of Cu [127] and Ni [54] were prepared by reducing the chlorides with Mg and washing away the $MgCl_2$ product with water. The data in Table 4 suggest that many other reactions involving chlorides may be self sustaining. The similar reactions with fluorides are more exothermic, this suggests that MSR must be possible in a variety of fluoride-metal systems.

3.3. More complex reactions

3.3.1. Reactions between oxides

The mechanochemical synthesis of complex oxides from simple oxides has been demonstrated by Boldyrev [128]. The investigated systems can be divided into two groups: (i) Both reactants are the most stable oxides of the respective element. The combination of CaO and MoO_3 to form $CaMoO_4$ is a typical example. SHS was possible in such reactions, but no self-sustaining reaction could be induced during ball milling. (ii) The reaction heat is higher between an oxygen rich and an oxygen deficient oxide. MSR was successfully initiated in a few systems of this kind. The reactions in this group can be considered the combination of two consecutive steps, the displacement of oxygen to form more stable simple oxides and their combination to form the final product. For example, the reaction between PbO_2 and SiO can be divided into two steps

$$PbO_2 + SiO \rightarrow PbO + SiO_2 \rightarrow PbSiO_3. \tag{5}$$

The heat of the entire reaction is 460 kJ/mol, of which only 50 kJ/mol is associated with the second step. We observed instant ignition for the reaction

$$2KO_2 + 3SiO \rightarrow K_2Si_3O_7. \tag{6}$$

This is not surprising, given the very large reaction heat — about 1500 kJ/mol. Approximately 1200 kJ/mol can be attributed to the oxidation-reduction step forming K_2O and SiO_2 [129]. The reaction between the superoxide BaO_2 and a reactive metal, e.g. Ti yields a mixed oxide in a similar manner

$$2BaO_2 + Ti \rightarrow 2BaO + TiO_2 \rightarrow Ba_2TiO_4. \tag{7}$$

This reaction is complete in 5 min upon ball milling, suggesting an MSR process [130].

The combustive combination of two oxides is possible even if both are the most stable oxides of the respective elements. Sufficiently large reaction heats occur between a strongly acid forming and a base forming oxide. Phosphates of Mg and Ca were obtained by milling mixtures of MgO or CaO with P_2O_5. It was difficult to obtain reproducible ignition times due to the moisture sensitivity of P_2O_5 [129].

3.3.2. Systems with two chemically independent reactions

Zhou et al. observed MSR in both the Ni + Al and Ti + C systems, the ignition times were 95 and 182 min under identical milling conditions. They also milled a mixture of the two systems, attempting to produce a NiAl–TiC composite with 6:1 molar ratio. Combustion was observed, with an ignition time of 105 min [131], a value close to the weighted average of the ignition times of the two binary reactions.

Very similar results were obtained by Fan et al. in the Nb–Si–Ti–C system [132]. The heat of formation of the possible reaction products favors the formation of a mixture of $NbSi_2$ and TiC. That is indeed observed and the ignition time in the four-component system is between the ignition times of the Nb + 2Si and Ti + C reactions. Similarly, a composite of $NbSi_2$ and NbC was obtained from a Nb–Si–C mixture.

3.3.3. Systems with two coupled reactions

It is possible to design two-step processes, using the product of the first reaction as a reactant for the second. For example, the reactions taking place in the B_2O_3–Mg–Ti system are

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \quad \text{and} \tag{8}$$

$$2B + Ti \rightarrow Ti_2B. \tag{9}$$

Both steps are highly exothermic, an MSR process is observed. WC, W_2C, and SiC were obtained in a very similar way by milling WO_3–Mg–C or SiO_2–Mg–C mixtures [52].

Sm_2Co_{17} particles were prepared by milling an appropriate mixture of Sm_2O_3 and CoO with Ca. (Some CaO was also added to reduce the combustion temperature.) Ca reduces the two oxides simultaneously; the resulting Sm and Co combine to form the desired intermetallic compound. Hard magnetic Sm_2Co_{17} particles were obtained after washing off the CaO by product [133].

One can also design reactions where the excess of the reducing metal reacts with the product of the first reaction. For example, the reaction

$$3P_2O_5 + 16Al \rightarrow 5Al_2O_3 + 6AlP \tag{10}$$

starts with an ordinary thermite reaction. The elemental P product then reacts with the excess Al to form AlP. Both steps are highly exothermic, the combined value of $\Delta H/C$ is 7470 K. Yet, ignition took place only after 27 min of activation with an 18:1 ball-to-powder ratio. This is an unexpectedly long activation time, probably related to the lack of ignition in the Al + P system [129].

In a similar reaction, NiO was reduced with Al according to the equation

$$3NiO + 5Al \rightarrow 3NiAl + Al_2O_3. \tag{11}$$

Three grams of powder was milled with three 8.4-g balls in this experiment. The analogous reaction with CuO was also studied. Replacing NiO by CuO brings about two competing changes: it is easier to reduce CuO than NiO due to its lower enthalpy of formation, but the reaction between Ni and Al generates 118.4 kJ/mol extra heat, while the enthalpy of formation of CuAl is only about 20 kJ/mol. The second difference is the larger one, making the total reaction heat almost 5% larger for the reaction with NiO. Yet, the MSR process involving CuO turns self sustaining after only 10 s of milling, while ignition required 17 min of activation in the NiO–Al mixture. This comparison suggests that ignition depends on the first step of the reaction and not the reaction heat of the entire process [129].

Hector and Parkin used metathesis reactions between Na_3P and halides of some transition and main group metals to produce phosphides. They found that mixtures of $FeCl_3$, $TaCl_5$, $MoCl_5$, WCl_4 or $NbCl_5$ with Na_3P self-ignite on light grinding with a pestle and mortar [134]. Clearly, many similar reactions can be of interest for ball milling investigations.

Many more variations are reviewed by Moore and Feng in connection with SHS [5]. The more exothermic ones are also candidates for MSR investigations.

3.4. Solid–liquid and solid–gas reactions

The investigations of MSRs can be extended to solid–liquid and solid–gas reactions. Although there are relatively few examples at the moment, comparing them to solid-solid reactions contributes to developing better understanding of the process.

Mulas et al. investigated the reaction between calcium hydride and hexachlorobenzene [65,67]. Two reactions are possible,

$$6CaH_2 + C_6Cl_6 \rightarrow 6CaHCl + C_6H_6 \tag{12}$$

$$3CaH_2 + C_6Cl_6 \rightarrow 3CaCl_2 + C_6H_6. \tag{13}$$

Both reactions are highly exothermic, making a MSR possible. The reaction kinetics was investigated as a function of the composition of the starting mixture. Interestingly, combustion was observed, if the CaH_2/C_6Cl_6 molar ratio was between 4 and 15. This is very different from the molar ratio interval — 3 to 6 — defined by reactions (12) and (13) above.

The formation of TiN during ball milling of Ti in nitrogen atmosphere was investigated by Chin and Perng [60,74]. A SPEX shaker mill was employed, with the milling vial connected to a volumetric nitrogen gas container by means of a plastic tube. The reaction was monitored by measuring the pressure in the gas container. By knowing the volume of the system and the mass of the Ti powder, the pressure values could be used to derive the nitrogen content of the Ti powder (Fig. 12). In this way, the reaction kinetics was obtained. The nitrogen content of the powder increased gradually to about 33 at.%. Ignition took place only at this point, as signaled by a sudden

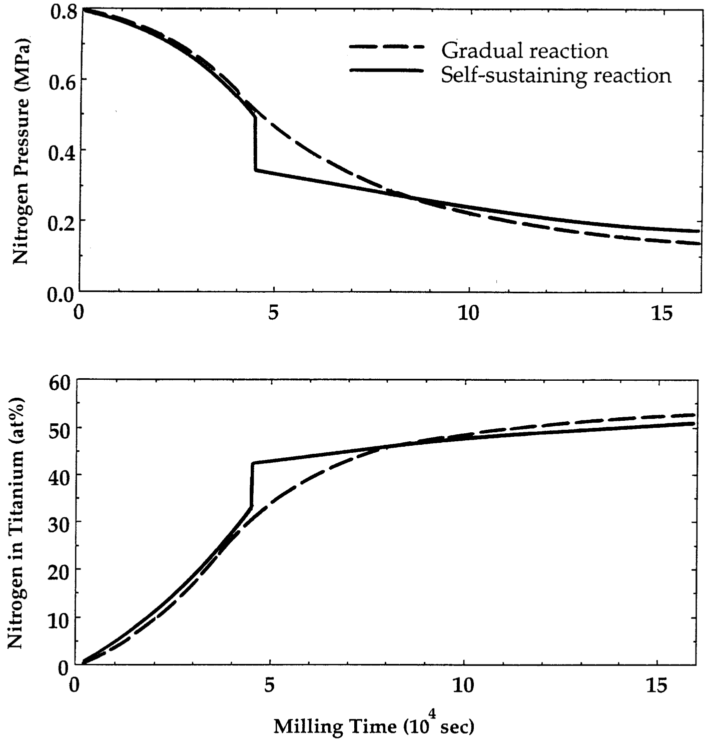

Fig. 12. Kinetics of TiN formation during ball milling of Ti powder in nitrogen gas [60]. Upper figure: pressure change, lower figure: nitrogen content of titanium.

decrease of the gas pressure. The final pressure corresponded to 50 at.% nitrogen, i.e. the formation of stoichiometric TiN compound. It is surprising that about 2/3 of the nitrogen gas was absorbed before ignition. XRD shows a large quantity of gradually formed TiN as well as peak shift of the Ti phase due to absorbed nitrogen [74]. It would be interesting to compare these results with the formation of TiC under similar conditions.

The atmosphere may play a direct role in solid–solid reactions. For example, Wang et al. milled a powder charge of 60 at.% Ni and 40 at.% Ti [135]. Milling in inert atmosphere resulted in gradual alloy formation. However, if milling was performed in oxygen, the oxidation of Ti produced sufficient heat to ignite a MSR process between Ni and Ti. Ni_3Ti was produced by the reaction. Similar results were obtained in a study on Ti rich mixtures, the product phases are Ti_2Ni, TiNi, and an amorphous phase. The amorphization probably took place by rapid quenching from the melt close to the surface of the milling tools [136].

3.5. Mechanically activated SHS

In a compacted pellet of a reactive powder mixture, combustion reaction can be initiated in two different ways: (i) the whole sample is heated uniformly, until the ignition temperature is reached (simultaneous combustion mode) or (ii) the reaction is ignited locally and a reaction front propagates through the sample (propagating mode) [5]. Both the ignition temperature and the propagation velocity of the reaction front can be influenced by prior mechanical activation.

For example, the thermal reaction between Cr_2O_3 and Al takes place at about 1000 K, between molten Al and solid oxide. Mechanical activation reduces the ignition temperature to below the melting point of Al [137]. TiO_2 and Al react to form a composite of $TiAl_3$ and Al_2O_3. The ignition temperature of this reaction can also be lowered to below the melting point of Al by ball milling [138]. Similarly, the ignition temperature of a Mo–Si mixture was reduced from 1200 to 800°C. Beside the obvious reduction of energy and equipment cost, the grain size of the product is finer and more uniform [139]. Significant decrease of the ignition temperature was achieved in the carbothermic reduction of ilmenite. An Fe–TiC composite is obtained as the product of that reaction [140]. Thermal analysis of milled powder mixtures show the same shift of the reaction temperature [99,141]. Such investigations are very useful in order to relate MSR processes to the more conventional forms of self-sustaining reactions.

Likewise, mechanical activation increases the propagation velocity of the reaction front in SHS reactions. It also improves the uniformity of the product. Mechanical activations combined with SHS (MASHS) was applied to Ti–C based systems [44]. A very active program on MASHS is currently under way in France. Combination reactions have been investigated in several systems, including Fe–Al [142], Mo–Si [143], and Nb–Al [144]. As the heat of formation of Ni_3Si is relatively low, SHS preparation of this compound usually requires pre-heating. Mechanical activation provides sufficient increase in reactivity that the reaction between Ni and Si ignites at ambient temperature [145].

4. Models of MSR

4.1. A model based on ignition temperature

A simple explanation of the ignition of MSR was proposed by Schaffer and McCormick [61]. They characterized the powder with its ignition temperature, T_{ig}, the temperature at which a self-sustaining reaction would start upon heating. On the other hand, when two balls collide or a ball hits the wall of the vial, much of the kinetic energy is used to increase the temperature of the powder caught between the colliding surfaces. The highest temperature achieved due to the impact is T_m. The ignition of combustion during ball milling can be understood by comparing T_{ig} with T_m (Fig. 13). If $T_{ig} < T_m$ from the beginning, the reaction starts upon the first collision. We are not dealing with such extremely sensitive materials (e.g. high explosives) here. For a typical MSR system, $T_{ig} > T_m$ at the beginning, hence ignition does not occur immediately. However, T_{ig} decreases upon milling. Several factors contribute to that: the particle size decreases, the reactants mix on a increasingly fine scale, chemically active defect sites form, newly created dislocations and interfaces provide fast diffusion pathways, etc. T_m may also change, although this is probably

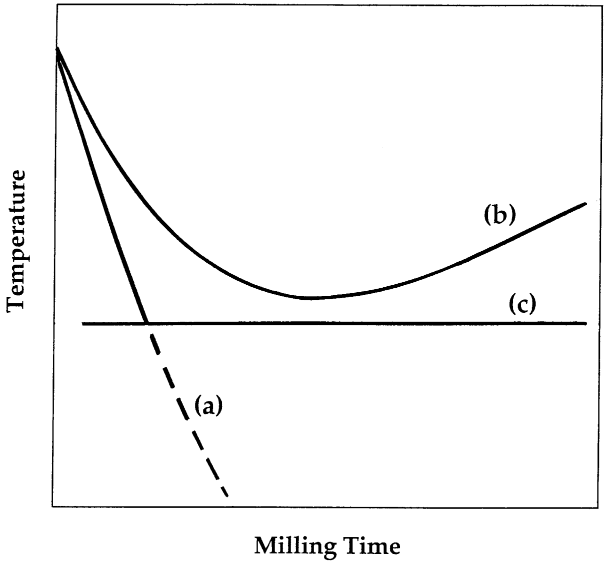

Fig. 13. Schematic illustration of the ignition temperature (T_{ig}) for a sample in which MSR occurs (a) and does not occur (b). Line (c) shows the maximum local powder temperature (T_m) during collision (after Ref. [61]).

a secondary effect. For example, T_m depends on how the balls become covered with a compacted layer of powder [146]. For sake of simplicity, we ignore the variation of T_m here. Two different kinetics are possible. Curve "a" represents a MSR, ignition occurs when T_{ig} falls below T_m. Curve "b" corresponds to a gradual reaction as T_{ig} has a minimum and begins to increase before reaching T_m. The increase of T_{ig} is caused by the small amount of reaction product that forms non-combustively and inhibits ignition like an inert additive. If the self sustaining reaction does not start before the minimum of T_{ig}, it cannot happen later either and the reaction progresses gradually.

This model rationalizes why a certain activation time is needed before ignition and explains that both gradual and combustive kinetics are possible. It also relates MSR to calorimetric investigations and the study of thermally induced self-sustaining reactions. The decrease and even the minimum of T_{ig} has been observed experimentally. Maric et al. observed that T_{ig} was decreasing with increasing milling time in Ni–Al and some related systems [141]. Some of their heating curves are reproduced in Fig. 14. Similar results were obtained in Ti–C, a metal-metalloid system [91]. Even the minimum of T_{ig} was observed for the displacement reaction between CuO and Fe [12]. Clearly, the model must reflect some important aspects of MSR, in spite of its simplicity.

Of course, T_{ig} is a complex quantity itself. Yet, it helps us divide the problem of predicting the ignition time to three simpler, more manageable tasks: (i) the determination of the maximum temperature encountered by the powder between the colliding balls; (ii) relating the ignition temperature to more fundamental properties of the powder and (iii) estimating how the properties of the powder change due to mechanical activation.

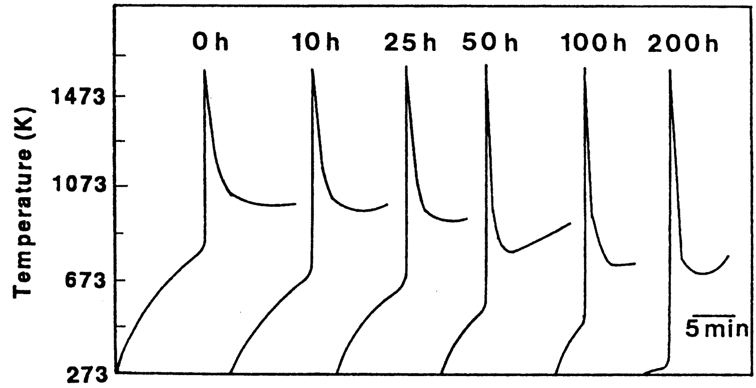

Fig. 14. Heating curves of Al–Ni powder mixtures pre-milled for the indicated durations [141].

Strictly speaking, the reaction kinetics cannot be characterized by a single ignition temperature. As the temperature of the powder increases, the reaction rate increases gradually. The point at which the reaction can be considered self-accelerating also depends on the heating rate and the heat transfer between the sample and its environment. Describing the thermal effect of a collision with a single maximum temperature can also be objected. The powder temperature in the miniforging volume is nonuniform. Even if its average temperature is insufficient to initiate the self sustaining reaction, it may contain "hot spots" with temperatures much higher than the average [147]. The situation is similar to the initiation of explosives by impact, where the existence and nature of hot spots is an important problem [148,149].

Skeptics may argue that any realistic model should consider the above and many more complexities simultaneously, rendering any useful theoretical treatment virtually hopeless. It is indeed unlikely that a theory capable of predicting the ignition time from first principles would develop. However, it is possible to investigate the different aspects of the problem separately. Deeper understanding can emerge from connecting theoretical results with guided empiricism. In that effort, the ignition temperature is a useful organizing principle.

4.2. Some questions and approaches

Mechanical activation and the ignition of a self-sustaining reaction are very complex processes. In order to gain full understanding, questions have to be addressed on several length and time scales. The mechanical operation of the mill, the mechanics of the individual collisions, chemical processes, structural changes, and defect formation have to be investigated. These are not different approaches to the same problem; all of them have to be developed and connected into a coherent picture. The elements of the necessary research topics and their relationships are shown on Fig. 15 in a block diagram form. Similar diagrams have been presented for mechanical alloying of ductile-ductile materials [150,151]. Our task is more complicated due to the broader variety of materials and the incorporation of highly exothermic reactions and ignition.

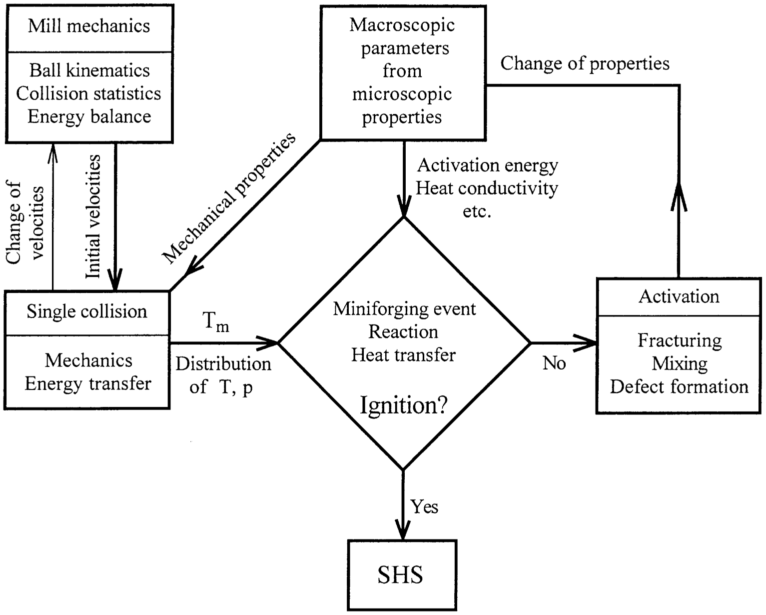

Fig. 15. Schematic representation of the research approaches and their relationships that can be combined into a complete model of the MSR process.

The central problem is to describe the "miniforging event," the compression of the powder between the colliding milling tools and its thermal and chemical consequences. The criterion of ignition has to be developed in that part of the theory. This problem will be discussed in the next section. The other aspects of the problem will be discussed below. Theoretical work is needed that (i) supplies parameters for the study of the miniforging event and (ii) investigates how a single collision can affect the later course of the process. On the "input" side, the mechanics of the mill has to be studied. It is also necessary to know the properties of the powder that is being compressed between the tools. The miniforging event has two possible outcomes. If ignition takes place, the process becomes an SHS reaction. If not, it contributes to the activation of the powder.

The mechanical description of the milling process is an important component of any modeling effort. Two related subjects have to be investigated: the global motion of the balls inside the milling container and the mechanics of an individual collision including the elastic and plastic deformation of the powder. Much research along these lines was performed in connection with modeling the mechanical alloying process. As excellent summaries are available in the literature [40,63], little detail will be given here.

The first step is to describe the mechanics of the mill, starting with the kinematics of a single ball in an otherwise empty vial. This problem was considered by several groups for the planetary mill [152,153]. The ball motion is complicated by the fact that the balls are not point particles, their rotation and slip during collision with the wall need to be considered and the viscoelastic properties of the collisions have to be accounted for [153,154]. Collisions between balls and the viscous resistance due to the floating powder have to be taken into consideration. The collisions are influenced by the powder layer coating the balls [146]. The kinematics of rod mills [155], tumbler mills [156], vibratory mills [157] and shaker mills [65] was considered. The global modeling of the milling process requires information on the frequency of collisions with specific relative velocities and impact parameters.

The actual processing of the powder takes place during the collisions between two balls or a ball and the wall of the milling vial. Several groups investigated the details of the collisions [153,158,159]. From the point of view of MSR, a particularly important question is the temperature increase during collision. The possible approaches were reviewed by Koch [160]. Depending on the model, rather different estimates of the temperature increase were obtained. For example, when Nb powder was impacted by an 8-mm steel ball at 6 m/s, the bulk temperature increase was estimated to be 48 K [161] or 130 K [162], depending on the assumptions of the model. Those temperatures are too low to achieve ignition in most systems. However, much larger temperature increase — about 350 K — is predicted for the contact surface [163]. The mechanical properties of the powder coating and their variation with activation have to be known for a complete evaluation of the collisions.

For evaluation of the chemical effects of the miniforging event, many properties of the powder have to be known. The heat capacity, the latent heat of phase transformations, the heat conductivity, and the parameters describing the reaction kinetics are needed. This is a very complicated issue. Even if these properties are known for the pure phases, the macroscopic properties of the powder depend on microstructure, e.g. the particle size and porosity. The compression of the powder during the collision changes the properties. They also change as a function of the mechanical activation. Describing this variation is an important objective of MSR research. More will be said about this problem in the next section.

A miniforging event can result in ignition or activation. If ignition occurs, the methods of SHS can be applied to analyze the propagation of the reaction front [5, 42]. The reaction starts in a single agglomerate or in the powder layer coating a milling ball or the wall of the vial. Once the reaction front propagates into other parts of the powder, the situation becomes very complicated. This part of the process is outside the scope of this paper.

If ignition does not happen, the collision contributes to the mechanical activation of the powder. Comminution, mixing, and defect formation take place. The appropriate sections of the existing mechanical alloying models are useful to describe these processes. Courtney considered the development and refinement of a layer structure as the key component of mechanical alloying of ductile metals [159,162]. Schwarz based his model on dislocation kinetics and diffusion along dislocations. The model can account for the incorporation of the faster-diffusing component into the other one before true alloying takes place [164]. Much more has to be done along these lines, as the activation steps are responsible for the gradual change of the macroscopic powder properties that eventually bring about ignition. Describing the gradual effects of ball milling is a problem shared with ordinary mechanical alloying and mechanochemistry. In fact, an important objective of studying MSR is to stimulate research in this direction and to provide a sensitive test for newly developed theories.

Some features of the activation process can also be investigated experimentally. The decrease of the grain size was determined from XRD in many laboratories [12,112,165]. Investigating the defect structure is more difficult. An indirect approach is to perform thermal analysis after mechanically activating the powder for different lengths of time. Forrester and Schaffer found that the activation energy of the reaction between CuO and Fe decreased from 575 to 199 kJ/mol upon milling, suggesting a change from intrinsic diffusion to diffusion along defects [112]. The accumulation of lattice strain is another measure of defect formation. The strain accumulation of graphite in a Ti–C mixture is shown as a function of milling time on Fig. 16 [89]. The different mass of the balls resulted in markedly different strain accumulation rates.

The activation of the powder can be characterized by the mechanical dose (the absorbed energy per unit mass) received over a large number of collisions. Therefore, activation can be investigated by evaluating the energy balance of the milling process. That approach was followed by Magini et al. [64,166,167]. The total energy input to the mill was related to the energy required for the activation of the powder. The energy considerations also provide a test for the kinematic model of ball motion. Clear understanding of energy transport/distribution is important as the effects of milling depend both on the total amount of energy transferred to the powder (activation) and the energy involved in the individual collisions (ignition).

4.3. Models of ignition

As a first step, the ignition of a self-sustaining reaction will be discussed in terms of a simple analytical approach. This model was put forward by Rusanov and Chakurov to explain their findings on metal-chalcogen combination reactions [168].

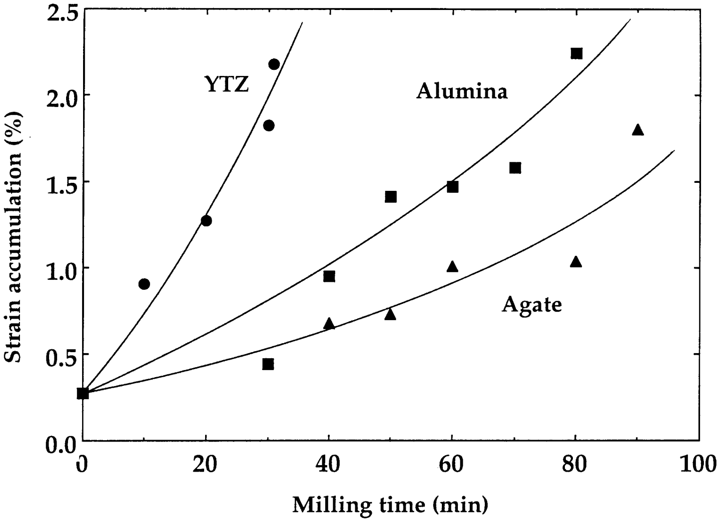

Fig. 16. Strain accumulation in the graphite component of a Ti–C powder as a function of milling time, using zirconia (YTZ), alumina, and agate balls.

Although the model cannot include the complexities of the problem, it gives the ignition criterion in a closed mathematical form.

It was assumed that after a period of comminution, mixing, and activation, agglomerates begin to form and increase in size. The combustive reaction starts with self-ignition in the largest agglomerates. To quantify this idea, a mathematical model was adopted, that was originally developed to obtain explosion limits for a reactive gas [169,170]. The gas is contained in a vessel that has a significant geometric dimension r. In the present application, the size of the agglomerate stands for the size of the vessel. The reaction kinetics is described by an Arrhenius law. The reaction heat is transferred to the walls of the vessel according to the equation

$$\frac{\mathrm{d}^2\Theta}{\mathrm{d}z^2}+\frac{k}{z}\frac{\mathrm{d}\Theta}{\mathrm{d}z}=-\delta\exp(\Theta) \tag{14}$$

Here z is a dimensionless coordinate, $z = x/r$, and Θ is the dimensionless temperature, defined as

$$\Theta=\left(E/RT_0^2\right)(T-T_0) \tag{15}$$

with E being the activation energy, R the gas constant, T the temperature of the gas, and T_0 the temperature of the wall. k is a geometry-dependent constant, $k=0$, 1, or 2 for plane, cylindrical, or spherical vessels, respectively. Several parameters are collected in δ:

$$\delta=\left[\frac{Q}{\lambda}\frac{E}{RT_0^2}r^2ca\ \exp(-E/RT_0)\right] \tag{16}$$

where Q is the reaction heat, c is the concentration of the reactants, and a is the frequency factor of the Arrhenius law, λ is the heat conductivity.

It turns out that — independent of the geometry — Eq. (14) can only have a stable solution, if δ is smaller than a critical value, e.g. 3.32 for a spherical vessel [170]. If δ is larger than that value, the solution is unstable, corresponding to a run-away reaction. As expected, δ is large, if the reaction heat, the frequency factor, and the concentration are large. Better heat conductivity results in smaller δ and less likely ignition. This is expected, as larger λ results in increased heat loss, that works against ignition. The exponential is large for small activation energy and hot container walls. T_0 can be identified with the ignition temperature, T_{ig} of Section 4.1. The most important result is that δ depends on the square of characteristic size of the vessel. Reworded for the current application, δ is a square function of the agglomerate size. If we assume that ignition takes place in the coating layer over the balls or the wall, rather than in free agglomerates, the thickness of the layer is the characteristic dimension. Larger agglomerates and thicker coating promote ignition.

The above approach is clearly oversimplified in order to make an analytical approach possible. A somewhat more detailed numerical model of ignition was proposed recently [62]. It is considered an illustration, rather than a model with real predicting ability. More complete and realistic equations from the theory of SHS could be applied to this case [5,171,172].

It is assumed that ignition takes place in the miniforging volume, represented here by a thin, flat disk of reactant powder mixture. It can be attached to the surface of a milling ball or the inner wall of the container. When this layer is hit by a ball, part of the kinetic energy is transferred to the powder as heat, increasing its temperature. The initial temperature distribution is determined by the deformation mechanics of the collision. The radius of the affected area is of the order of the Hertzian radius, typically about 0.1 mm [173]. This is much smaller than the radius of the balls thus, assuming a flat layer is acceptable. The resulting temperature distribution changes according to an energy balance equation. In polar coordinates, neglecting the temperature variation across the thickness of the layer and assuming azimuthal symmetry, the temperature distribution *T(r,t)* is determined by the equation:

$$\rho c\frac{\partial T}{\partial \mathrm{t}}=k\left(\frac{\partial^2 T}{\partial \mathrm{r}^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-\rho(-\Delta H)\frac{\partial \eta}{\partial t}-h(T-T_0) \tag{17}$$

where ρ, c, k_r are defined and discussed below.

Although this model is oversimplified, it helps us to identify some quantities of importance.

The left side describes the amount of heat absorbed by the material. No phase transformations are included, although they are important as they limit the temperature increase. Phase changes were incorporated into modeling SHS reactions [172,174]. Temperature-enthalpy plots are useful tools to present the necessary thermodynamic information [5,78]. If side reactions and branching are possible, the thermodynamics of the process can become quite complex. The density and the specific heat (ρ and c) depend on the porosity and they incorporate the layer thickness.

The first term on the right side of Eq. (17) describes heat conduction within the powder, k is the heat conductivity. It depends on the porosity and microstructure, consequently it changes as the powder gets compressed during collision. The problem of relating heat conductivity to microstructure is shared with SHS theory [175]. Heat transfer by radiation and by conduction through the gas phase inside pores have to be included.

The second term represents the heat from the chemical reaction, $-\Delta H$ and η are the reaction heat and the fraction of unreacted powder. A simple Arrhenius equation with activation energy E and pre-exponential factor is assumed for the reaction rate:

$$\frac{\partial \eta}{\partial t}=-K\eta e^{-\frac{E}{RT}} \tag{18}$$

The typical situation is clearly more complicated. The reaction takes place at interfaces, its rate depends on the specific interface area. Interdiffusion is a possible reaction mechanism, but the situation is seriously complicated by the mechanical activation. Transport along defects can short-circuit intrinsic diffusion, drastically increasing the reaction rate [112]. Fresh surfaces are created and brought together repeatedly, making nucleation and growth mechanisms possible. Matter transport by gaseous components can be important [176].

The last term describes the heat loss to the milling tool — ball or container wall — in contact with the powder. The heat transfer to the atmosphere also contributes to this term. Heat loss is rarely critical in conventional SHS [177]. However, the geometry of ball milling is essentially different: Instead of a bulky compact, ignition is considered in a thin layer of powder, that is in contact with the surface of a large, good heat conductor object, namely a ball or the wall of the vial. The estimation of heat transfer to the milling tools is a difficult problem. Direct interaction between the powder and the tools exists at certain contact points only, the actual contact area is hard to estimate. At other points of the interface, heat transfer takes place by conduction across a thin layer of gas and by radiation [178]. The heat contact changes when the surfaces are pressed together during collision.

Temperature profiles as a function of time after collision are shown on Fig. 17. The parameters were chosen to give the expected behavior, with little reference to realistic material properties. Impact is represented by an initial temperature increase close to the center of the powder disc. In the case shown, the local temperature increase due to the reaction heat is sufficient to initiate a typical combustion front. The fast cooling behind the front is due to the heat loss to the environment. Conversion of the reactant is close to 100%. A situation where the combustion front quenches can be obtained by slightly changing the model parameters, e.g. increasing the coefficient of heat transfer to the environment. Even if the reaction front is quenched by heat loss, substantial amount of conversion can take place. Quenched

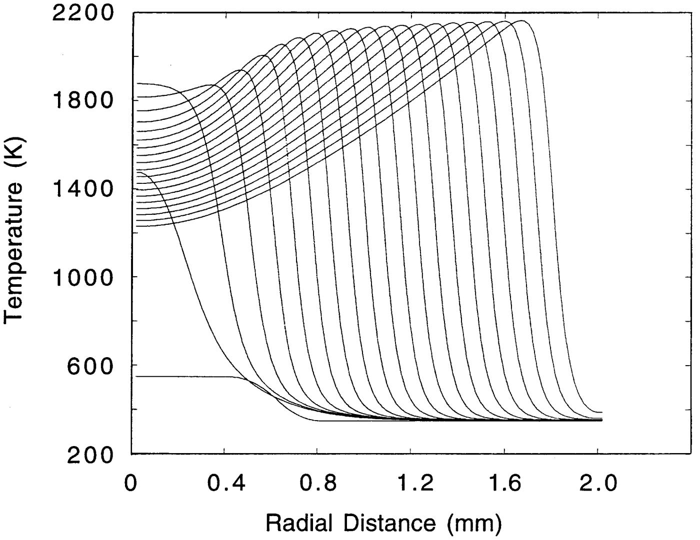

Fig. 17. Temperature distribution around an impact site as a function of time, showing the formation and propagation of a reaction front.

local combustion events like that were suggested as the mechanism of — seemingly — gradual mechanochemical reactions [179].

Mechanical activation affects most parameters in Eqs. (17) and (18). It has the most important effect on K and E. At the beginning of the milling process, the parameters are such that the model predicts quenched reaction with negligible transformation. Ignition is achieved when the parameters change sufficiently to obtain a propagating reaction front. The macroscopic parameters in Eqs. (17) and (18) have to be calculated based on the microscopic structure and properties of the powder, taking into account the changes due to mechanical activation. This is a difficult task, but it may be attempted for each property separately. It is also possible to fill some gaps with empirical information.

More detailed description of the collision is possible. Urakaev and Boldyrev determined both the temperature and the pressure as a function of time and distance from the point of contact [180,181]. If the thermochemical properties of the powder are known, the chemical consequences of the collision can be evaluated.

The above models considered uniform powder and described it with average macroscopic properties. On the microscopic scale, the powder in the miniforging volume is nonuniform, it consists of particles, agglomerates, and pores of different sizes. Considering the reactions and the heat transfer processes in the complicated structure of a powder mixture is an extremely difficult task, but it is also very important for both MSR and SHS. The effect of pores on the propagation velocity was investigated by Bhattacharya [175]. The geometry is manageable in the case of self sustained reactions in multilayers [182–184]. Qualitative trends observed there can be related to MSR observations.

The nonuniformity of the powder is already important when the effect of compressing and sheering the powder between two colliding surfaces is considered. The stresses inside the powder are not uniform, but concentrate at a few points. The result is the formation of hot spots, where the reaction can start even if the average temperature of the powder in the miniforging volume is not sufficient to initiate a reaction front [147]. This hot spot formation and the chemical kinetics should be considered simultaneously.

It was implicitly assumed that any chemical reaction is initiated thermally. The kinetic energy of the colliding balls results in local temperature increase, and it is the high temperature alone that brings about the chemical change. This is not necessarily the case. The mechanical action of the mill may induce chemical changes directly. These "true" mechanochemical reactions may be different from the usual thermochemical ones. Investigating this possibility is a fundamental question in mechanochemistry [27]. Clear understanding of what can be explained by thermochemical principles alone is needed to answer this question.

5. Systematic studies of the ignition time

The kinetics of mechanochemical reactions is sensitive to the properties of the powder charge and it also depends on the conditions of the milling process. Yet, relatively few publications report on systematic investigations of the reaction kinetics as a function of composition and milling conditions. In particular, few groups investigated the effects of experimental conditions on the ignition time, although the utility of such studies is obvious. As was discussed in the previous chapter, the weakest link in the theoretical study of ball milling processes is understanding the changes during the activation phase. This is where the investigation of the ignition time can provide information that is valuable beyond MSR. Ignition can be used as a marker, changes of the ignition time reflect changes in the rate of activation.

5.1. Balls and powder mass

When setting up a milling experiment, one has to select the number and size of the milling balls and the total mass of the powder. Many investigators choose a ball-to-powder ratio of about 10:1 for the SPEX 8000 mill or a somewhat larger value for a planetary mill. The typical mass of the powder is a few grams. Such conditions work well in most cases. If the same conditions are maintained as a standard protocol, consistent results can be obtained on other aspects of the problem.

There have been few attempts to investigate the effect of the milling conditions on the ignition time. Already Chakurov compared the ignition time at two different milling intensities of his vibratory mill [2]. The ignition time was about 2.6 times longer with the lower intensity, but the temperature increase was about twice as large as the one with the higher intensity. Unfortunately, they did not follow up on this result. Vibratory and planetary mills would be very suitable for studies of the ignition time as a function of milling intensity, as the frequency of the vibration or rotation can be varied easily. Unfortunately, few ignition time measurements used these types of mills. The frequency of the shaker mills is usually fixed.

There is a general consensus among practitioners of ball milling that the milling intensity is adequately characterized by the ball-to-powder (charge) ratio, the number, material, and size of the balls and the mass of the processed powder are not particularly important separately, at least not within reasonable limits. As the charge ratio is proportional to the rate of specific energy input, assuming that the ignition time is a function of the charge ratio is equivalent to assuming that ignition takes place when the powder has received a certain amount of a mechanical dose [67]. In other words, the degree of mechanical activation is characterized by the amount of absorbed mechanical energy. Whenever the powder is sufficiently activated, there is always a hot spot where ignition is possible. This is a very strong statement, making the ignition time a direct measure of the rate of activation.

The inverse proportionality between the charge ratio and the ignition time was confirmed by Schaffer and McCormick for the reduction of CuO with Fe [12]. They used three different ball sizes, the number of balls varied from 3 to 21, the mass of the powder charge was between 3 and 36 g. The formation of TiC from the elemental powders and the reaction between CuO and Fe was studied by Schaffer and Forrester [89]. The purpose of this study was to eliminate any artifact that could originate from the different ball size. Therefore, milling balls made of different materials were used, their density varied from 5.7 g cm^{-3} for zirconia to 16.4 g cm^{-3}

for WC–Co. The diameter of the balls was 10 mm. The ignition time is shown on Fig. 18 as a function of the charge ratio. The correlation is quite reasonable. Mulas et al. milled about 8.8 g of C_6Cl_6–CaH_2 mixture with a single ball of several different sizes [67]. Ignition always took place after a certain amount of mechanical dose was received by the powder. As the dose rate is approximately proportional to the mass of the ball, the constancy of the dose is equivalent to an inverse relationship with the ball mass and — due to the constant powder mass — the charge ratio.

Not every result is that simple. When Ti–C powder was milled with light balls made of alumina or agate at the very large charge ratio of 40:1, the reaction remained gradual [89]. Obviously, the idea that ignition takes place whenever the powder reaches a certain level of dose accumulation, does not apply in this case. At least three explanations are possible: (i) The impacts are too weak, the temperature increase is not sufficient to start the reaction even at the hottest spots. This is unlikely, as the only moderately heavier zirconia balls could create sufficient hot spots at

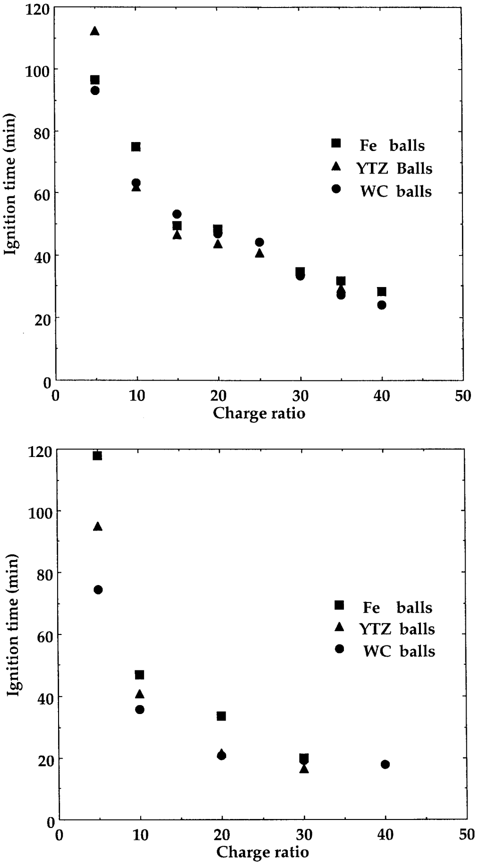

Fig. 18. The effect of the charge ratio on the ignition time for the synthesis of TiC (upper figure) and the reduction of CuO by Fe (lower figure) according to Ref. [89].

much smaller charge ratios, i. e. in much thicker layers of powder. (ii) It is possible that the reaction front gets extinguished by heat loss to the balls. An argument against this possibility is the low heat conductivity of these balls. An experiment with a lower charge ratio would decide this problem, if the thicker powder layer resulted in ignition. (iii) It is possible that a collision contributes to the activation of the powder only if its stress exceeds the yield stress of the reactants. The slower strain accumulation with light balls speaks for this possibility [89]. On the other hand, some Sn–Zn–S mixtures show MSR when milled with aluminium balls, but not when milled with steel balls of the same number and size [68]. As aluminium balls have smaller mass and better heat conductivity, this result argues against both options (ii) and (iii). This question clearly requires further studies.

It is usually difficult to initiate self-sustaining reaction if the amount of powder is very small. This is consistent with the simple analytical result described at the beginning of Section 4.3, as a smaller quantity of powder results in thinner coating on the surfaces. MSR did not happen in the CuO–Fe system for 1–3 g samples although it was observed with larger quantities [12]. Gradual reaction was observed in this system even with 6 g of powder in our laboratory [113]. No MSR was observed when milling 1.88 g of the more exothermic Fe_2O_3–Al mixture with three 12.7-mm balls [185]. The charge ratio was about 13:1 in that study, not unusually large.

The ignition time in the Cu_2O-Al system is shown on Fig. 19 as a function of powder mass [62]. Milling was carried out in a SPEX mill with three 12.7-mm balls. Very short ignition times were observed for the larger quantities of powder and a constant 10 min ignition time was measured between 1.5 and 3 g. Clearly, these ignition times do not scale with the charge ratio, they suggest different controlling mechanisms for small and large masses. Beside the fact that the easier ignition took place with large powder quantities again, the behavior is unique, it needs both confirmation and explanation.

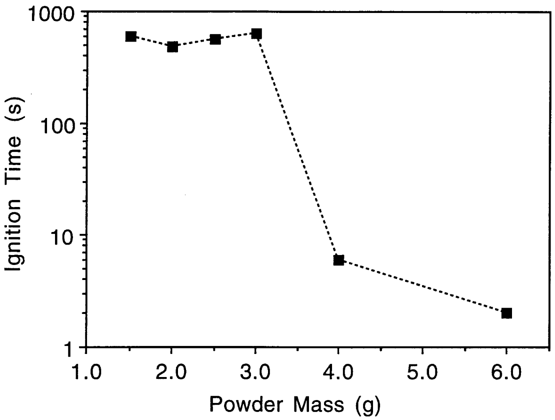

Fig. 19. Ignition time as a function of powder mass for the reduction of Cu_2O by Al. Three 12.7-mm balls were used in every run.

5.2. Inert additives and off-stoichiometry

Adding an inert material to the mixture of reactant powders has uses in both MSR and SHS. For example, the reaction temperature during the simultaneous reduction of Sm_2O_3 and CoO with Ca was decreased by adding CaO, one of the products of the reaction [133]. The lower temperature resulted in smaller particle size of the product. The addition of about 25% Al_2O_3 to a stoichiometric Fe_2O_3–Al mixture either decreased the reaction temperature during combustion or suppressed ignition entirely, depending on the milling conditions [119]. The addition of Al_2O_3 or SiO_2 to Fe_3O_4–Al was used to obtain a nanocomposite product by keeping the reaction gradual [118,186]. Inert additives are also used to tame very exothermic SHS reactions [5,187]. None of these MSR studies investigated the effect of inert additives systematically as a function of type and amount. If more than one composition was tried, it was done to optimize the process, e.g. to avoid the high temperature reaction with the smallest possible amount of dilution.

It is intuitive that the addition of an inert material should increase the ignition time or suppress ignition entirely, when used in larger quantities. There are at least two obvious mechanisms: (i) An inert additive increases the heat capacity without contributing to the reaction heat. Therefore, it decreases T_{ad} and $\Delta H/C$. If the other conditions are similar, a less exothermic reaction requires longer activation time before ignition. A large amount of additive decreases the adiabatic temperature to below the minimum required for MSR. (ii) The additive gets in between the reactant particles, decreasing the contact surface and consequently the overall reaction rate. Of course, additives change the conditions in many other way: they influence the mechanical properties of the powder, change the way the powder coats the balls and the wall of the vial, change the heat conductivity, etc. Separating these factors is a difficult task.

The only extensive study of the effect of inert additives was performed by Chakurov et al. [47]. A polymer, SiO_2, rhyolite, and Fe were added to an equimolar mixture of Sn and S. As the amount of the additive was increased, the ignition time increased monotonously. When the amount exceeded a critical value, the reaction became gradual. If expressed in volume fraction, x_c, this critical amount is approximately independent of the nature of the additive. For the formation of SnS, $x_c = 0.13 \pm 0.03$. Critical volume fractions were determined for a number of metal chalcogen reactions using SiO_2 as the additive (Fig. 20). The reasonably good correlation between the critical volume and the reaction heat is obvious. That correlation is much better than the relationship between the ignition time of the additive-free mixtures and the reaction heat (Table 1). It seems that any metal-chalcogen reaction becomes gradual, if the volume fraction of the additive exceeds 0.5. The authors suggest that ignition originates from agglomerates that are larger than a critical size and the additives delay or prevent ignition by hindering agglomeration. Much more work is needed to clarify these points and to investigate the effects of different additives on other reactions and under different conditions.

A related problem is how deviation from the stoichiometry of the anticipated reaction affects the kinetics. In most investigations, the composition of the starting

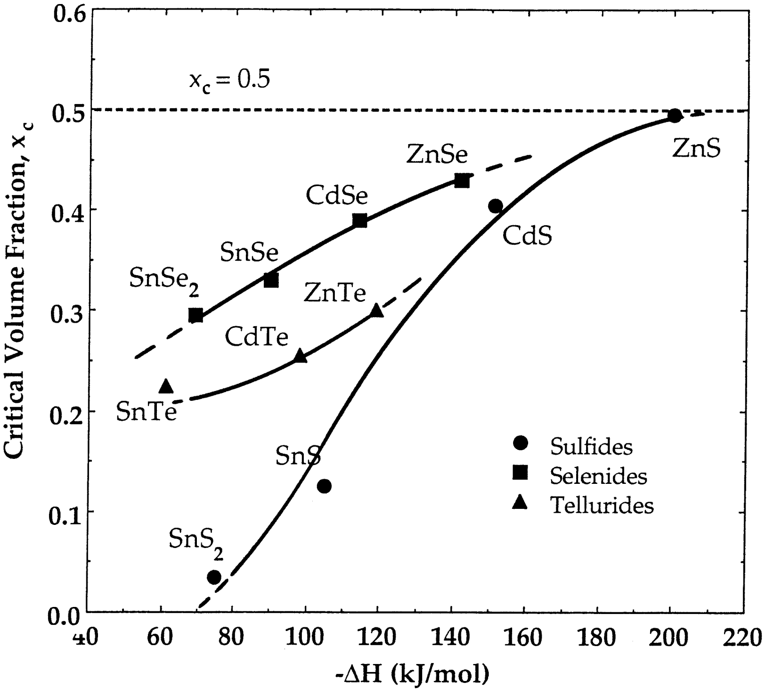

Fig. 20. Critical volume fraction, x_c, needed to suppress ignition during the mechanochemical reaction between a metal and a chalcogen element as a function of the reaction heat, $-\Delta H$.

mixture corresponds to the stoichiometry of the desired reaction. This is a natural choice. One may assume that the stoichiometric powder composition represents an optimum, the excess of either component acts like an inert additive, increasing the heat capacity without increasing the reaction heat. Experiments on several different systems show that this is not the case.

The ignition time for the reaction in $Zn + yS$ mixtures is shown on Fig. 21 [72]. The total mass of the powder was kept constant at 5 g. Chemically, this is a very simple case, as ZnS is the only possible product. However, the shortest ignition time is obtained at $y = 0.5$, i.e. at a strongly S deficient composition. When the S concentration is decreased further, the ignition time increases slightly and the kinetics becomes gradual at about $y = 0.3$ abruptly. The ignition time increases to a much larger value before becoming gradual upon increasing the S concentration. The ignition time is also shown for $Sn + yS$ mixtures. Three sulfides of tin could form, SnS, Sn_2S_3, and SnS_2, but the ignition time curve is smooth at these compositions. $\Delta H/C$ is practically the same for the three sulfides, but the ignition time varies from its lowest value at $y = 1$ to more than twice longer at $y = 2$. No MSR is observed for $y < 0.9$, a composition close to that of the fastest ignition. This is obviously a complicated behavior that cannot be fully explained by considering $\Delta H/C$ alone. Differences in the coating of the balls' surface, the variation of the average density, the change of heat conductivity and other properties can be important. The ignition time depends on

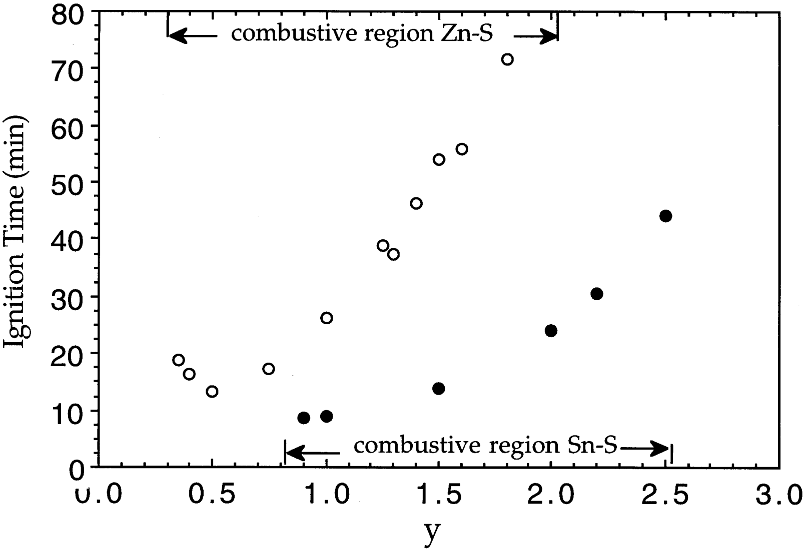

Fig. 21. Ignition time as a function of composition in Sn + yS (full symbols) and Zn + yS (empty symbols) mixtures.

the composition of the starting powder, but not the stoichiometry of the products. This can be explained considering that the reaction starts at an interface, where the reaction is controlled by diffusion rates, not the overall composition.

When Fe_3O_4 is milled with Mg, the strong cold welding tendency of Mg prevents efficient mixing. As a result the ignition time increases with increasing Mg content from about half the stoichiometric quantity [72]. On the other hand, a slight excess of Al promotes the reaction between Fe_3O_4 and Al [51]. Decreasing the C concentration shortens the ignition time in the Ti–C system, probably due to faster mixing of the powders [188]. The reaction between C_6Cl_6 and CaH_2 is similar to the formation of Sn sulfides, in that it also has two possible stoichiometric compositions as described by Eqs. (12) and (13), but the composition dependence of the ignition time has no relationship to those compositions [67]. The ignition time is shown for this system on Fig. 22.

It is necessary to mention that while a number of very different systems have been explored and many different behaviors have been observed, the underlying mechanism are not understood. Further investigations are necessary, both on the empirical behavior of the ignition time and on the structure of the powders as a function of milling time.

5.3. Comparing similar systems

Investigating the mechanism and product of a single MSR is interesting and useful, but little can be learned from the ignition time of one reaction alone. The ignition time becomes a more powerful tool, when values for a set of systematically selected reactions are compared.

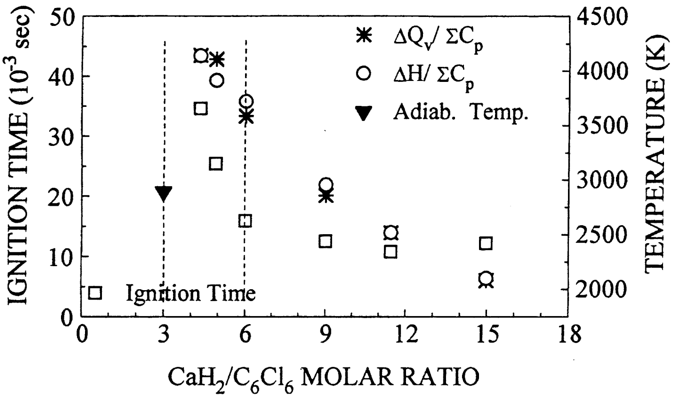

Fig. 22. The ignition time (open squares) compared to $\Delta H/\Sigma C_p$ (same as $\Delta H/C$ in the text) and its experimental value determined from the temperature increase of the milling vial, $\Delta Q_v/\Sigma C_p$, for the reaction between hexachlorobenzene and calcium hydride, after Mulas et al. [67].

The most important material property concerning MSRs is the adiabatic temperature or its "simplified form" $\Delta H/C$. Intuition suggests that the more exothermic reactions, i.e. the ones with higher T_{ad} and $\Delta H/C$, become self-sustaining after a shorter activation time. A number of examples have been mentioned in the previous section, some supporting this expectation, others showing a different trend. A few examples are mentioned here, without repeating the details.

The ignition times of the metal-chalcogen reactions (Table 1) have little relationship to the adiabatic temperature [2]. However, they do correlate with hardness, emphasizing the importance of understanding the mechanics of the collisions and their chemical consequences [82]. Data for a few reactions, in which CuO is reduced with several different metals, were given in Table 3 [109]. There seems to be a loose correlation between T_{ad} and the ignition time. The main deviations are the unexpectedly short ignition times for Ti and Mn. The reason may be the faster oxygen transport in these multivalent metals. Mg particles have a strong cold-welding tendency, probably resulting in less efficient milling and, consequently, longer-than-expected activation times [72].

Better correlation between the adiabatic temperature and the ignition time can be obtained, if the metal reactant is kept constant and the oxide is varied. Fig. 23 presents data for the reduction of CuO, NiO, Fe_3O_4, Cu_2O, and ZnO with Ti, Zr, and Hf [66]. The correlation is particularly convincing if the data for each metal are considered separately. The ignition times vary in a broad range, from about 15 s to 100 min.

Several analogous reactions were investigated between Ti, Zr, and Hf and an oxide or a light element. The properties of these metals, especially Zr and Hf, are very similar. Not only the reaction heats and adiabatic temperatures are close, but the crystal structures, the mechanical properties, the phase diagrams, and even the properties of the compounds and alloys of Zr, Hf, and — to a lesser extent — Ti are very similar. Consequently, it is surprising to find any major difference in the chemical behavior of

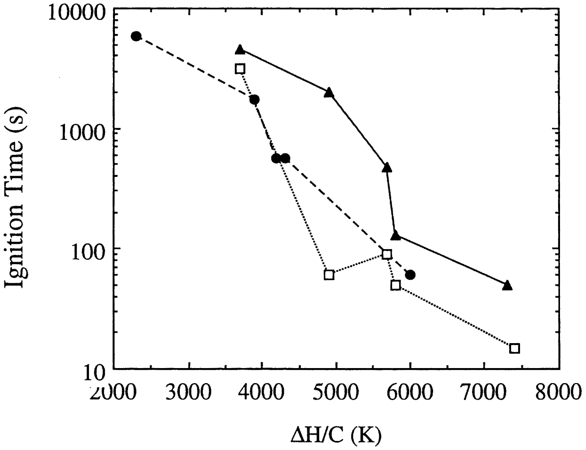

Fig. 23. Ignition time as a function of $\Delta H/C$ for the reduction of some metal oxides with Ti (circles), Zr (squares) and Hf (triangles).

these elements. The results in Table 5 constitute a rare example [62,66]. A number of displacement and combination reactions have been initiated in a SPEX 8000 mill. Three grams of powder was milled in a round-ended steel vial with either three 12.7-mm or five 9.5-mm balls. Whenever oxygen or sulfur is involved, the ignition time is shorter with Zr than with either Ti or Hf. In some cases, the difference is more than an order of magnitude. (The case of sulfide formation from the elements is a special case that will be discussed further in Section 5.6. A series of small exothermic steps are observed when Zr or Hf is the metal reactant, the times here are the activation times before the first of those steps. The reaction with Ti happens in one large step as usual. Consequently, the data for sulfide formation are not quite comparable.) On the other hand, the variation of ignition time from Ti to Zr and Hf is monotonous

Table 5
Activation time before the ignition of combustion, T_{ig}, for several reactions with Ti, Zr, and Hf

Reaction	T_{ig} (s)		
	M = Ti	M = Zr	M = Hf
$2CuO + M \rightarrow 2Cu + MO_2$	60	15	50
$2NiO + M \rightarrow 2Ni + MO_2$	570	90	470
$Fe_3O_4 + M \rightarrow 3Fe + 2MO_2$	570	50	130
$2Cu_2O + M \rightarrow 4Cu + MO_2$	1730	60	1980
$2ZnO + M \rightarrow 2Zn + MO_2$	5860	3160	4500
$2CuS + M \rightarrow 2Cu + MS_2$	8900	3720	7800
$M + 2S \rightarrow MS_2$	8820	17	250
$M + 2B \rightarrow MB_2$	3600	2760	1850
$M + C \rightarrow MC$	3120	2570	2180
$M + Si \rightarrow Msi$	1620	840	1030

for boride and carbide formation and the small minimum for silicide formation can be attributed to thermodynamic reasons.

The explanation of this behavior has to include a process that (a) distinguishes Zr from Ti and Hf and (b) promotes its fast reaction with oxides and sulfides or sulfur, but not with B, C, and Si. Such a process is the diffusion of the nonmetal in the product phase. The diffusion coefficient of oxygen is anomalously large in ZrO_2 and very likely sulfur diffuses relatively easily in ZrS_2. On the other hand, the diffusion coefficients of B in borides and C in carbides are close for Ti and Zr compounds. (Some measured diffusion coefficients are collected in Ref. 62.) The difference in diffusion properties can be rationalized by analyzing the atomic structure of the relevant compounds. It is found that the structure of Zr oxides and sulfides is more "open" than the structure of the similar Ti and Hf compounds, i.e. the atomic volume of the nonmetal is larger in ZrO_2 and ZrS_2 than in the corresponding Ti and Hf compounds. This difference is in addition to the larger atomic volume of Zr than Ti and Hf. There is no similar trend in the case of borides, carbides, and silicides [66].

5.4. Mutual suppression of ignition

One may argue that the most astonishing phenomenon in MSR research is the mutual suppression of ignition in some mixed metal–chalcogen systems, first reported by Rusanov and Chakurov [48] and investigated further by the present author [68,189]. The phenomenon is the following: when an equimolar mixture of Zn and S powders is ball milled, MSR is initiated after some activation time. The same happens when a mixture of Sn and S powders is milled, except for the complications due to the existence of several tin sulfides. Surprisingly, however, some mixtures of the Zn–S and Sn–S blends react gradually, when processed under identical conditions.

This phenomenon can be explained as follows: The properties of the Sn–S and Zn–S reactions are quite different. The reaction between Zn and S is much more exothermic, $\Delta H/C$ is about twice as large as the formation of the tin sulfides (SnS, Sn_2S_3, SnS_2). In spite of this, the ignition times are about the same for the formation of ZnS and SnS_2 and it is almost three times shorter for the formation of SnS [68]. Therefore, the difference in exothermicity must be compensated by some other feature that makes the initiation of the reaction between Sn and S easier. If this hypothesis is valid, ignition is controlled by different criteria in the cases of Zn and Sn. One possibility is the following: when Zn is processed with S in the ball mill, the decisive process is the initiation of a primary reaction. Once that happens, the reaction front propagates through the vial easily due to the large self-heating. In the case of Sn, local reactions occur during the collisions quite easily, but the reaction gets extinguished until the degree of activation reaches a critical state. Consistent with this explanation, XRD finds little ZnS but a few percents of Sn sulfides in samples milled until immediately before ignition.

On the Sn-rich side of the $(1-x)(\mathrm{Sn}+2\mathrm{S})+x(\mathrm{Zn}+\mathrm{S})$ systems, Zn behaves like an inert additive, as the temperature increase associated with the formation of Sn sulfides is too small to initiate the sulfidation of Zn. As the Zn content increases, the ignition time increases and the reaction becomes gradual. Sn participates in the reaction on the Zn-rich side, but as the sulfidation of Sn is less exothermic than the sulfidation of Zn, the reaction heat decreases with increasing Sn concentration, increasing the ignition time. The combination of the two effects results in the gradual kinetics for intermediate compositions.

Even though this explanation is very tentative, investigations of the phenomenon as a function of composition and milling conditions gave some useful results. The ignition time multiplied by the ball-to-powder ratio, i.e. normalized by the mechanical dose, is presented on Fig. 24 for $(1-x)(\mathrm{Sn}+2\mathrm{S})+x(\mathrm{Zn}+\mathrm{S})$ mixtures. Four different combinations of powder mass and ball number and size were used. Points on the top frame of the figure indicate the absence of MSR. Wherever ignition is observed, the normalized ignition times for the different ball-powder combinations agree within experimental error, lending strong support to using the mechanical dose as the measure of activation.

The concentration interval, where the reaction remains gradual, becomes broader when decreasing the mass of the powder. This trend is quite counterintuitive, as a smaller amount of powder translates to more intense milling. The explanation depends on the thickness of the powder layer in the miniforging volume. Smaller amount of powder results in a thinner layer between the impacting surfaces. The energy of the collision is dissipated in a small amount of powder, very high temperature results and probably some sulfide forms. However, the powder is not capable of propagating

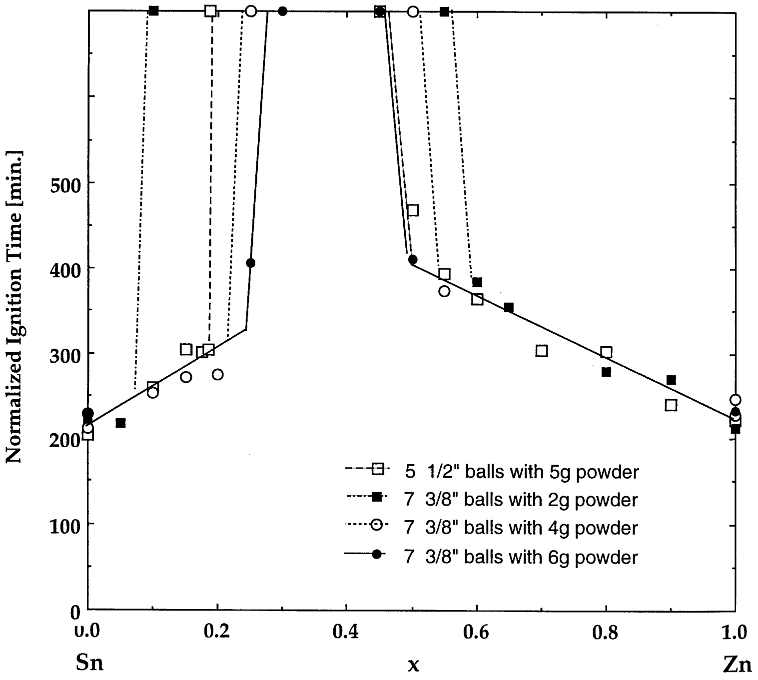

Fig. 24. Ignition time multiplied by the ball-to-powder ration for the MSR process in $(1-x)(\mathrm{Sn}+2\mathrm{S})+x(\mathrm{Zn}+\mathrm{S})$ mixtures as a function of composition for several ball–sample mass combinations.

the reaction front across the vial due to the proportionately large heat loss to the milling tools. Ignition does not happen, but an increasing amount of product phase is produced. These reaction products act as inert additives later, hindering the ignition of a self sustaining process. In experiments performed with aluminium balls, the ignition time for Zn rich mixtures was longer than anticipated, probably due to a minimum stress needed to induce defects. The interval with gradual kinetics becomes narrower for the lighter balls, again suggesting less pre-ignition reaction.

In the first publication on this phenomenon, Rusanov and Chakurov reported gradual kinetics in the $(1-x)(\mathrm{Sn}+\mathrm{S})+x(\mathrm{Zn}+\mathrm{S})$ system in the narrow concentration range of $0.35<x<0.4$ [48]. (The difference between this and the previous system is the expected tin sulfide product.) Their experiments were performed using a low energy vibratory mill. The result could not be reproduced using a SPEX mill. For typical milling conditions, only a shallow maximum of the ignition time was observed at about $x=0.8$ [68,189]. Gradual reaction was obtained only when the amount of the powder charge was decreased to 1 g. However, the reason why ignition did not happen was primarily the proportionately strong heat loss to the milling tools. The concentration interval with gradual reaction is not in the middle of the composition range but includes binary Sn–S. More energetic milling conditions resulted in broader interval with gradual reaction, as already anticipated.

One may wonder, whether this phenomenon is an exclusive property of the metal-chalcogen combination reactions. The loss of ignition in the middle of the composition range has not been observed in any other system. However, the ignition time is a nonlinear function of the composition in a few mixed systems. A maximum of the ignition time was observed in $\mathrm{Ni}_{50}\mathrm{Al}_{50-x}\mathrm{Ti}_x$ mixtures by Liu et al. [190]. Relative to the binary Ni–Al mixture, the ignition time increased by about 30% at $x=0.08$. Further increase of the Ti concentration decreased the ignition time, and the reaction suddenly turned gradual for $x>0.16$. Competing changes in thermochemical properties and milling efficiency may explain this behavior.

Two distinct reactions could “get into each other’s way” in the simultaneous preparation of NiAl and TiC from a four-component $43(\mathrm{Ni}+\mathrm{Al})+7(\mathrm{Ti}+\mathrm{C})$ mixture [131]. The measured ignition time was within two percents of the weighted average of the ignition times in the separate Ni–Al and Ti–C systems. A slight nonlinearity was is found in the behavior of the ignition time in $80(\mathrm{Nb}+2\mathrm{Si})+20(\mathrm{Ti}+\mathrm{C})$ and $80(\mathrm{Nb}+2\mathrm{Si})+20(\mathrm{Nb}+\mathrm{C})$ mixtures [132]. The ignition times are slightly longer for the three- and four-component systems than the weighted averages of the ignition times of the corresponding binary systems (see inset of Fig. 25). Whether the silicide and the carbide phases are both formed with Nb or the carbide forms with Ti does not seem to make any difference in the behavior of the ignition time. As the mixtures are close to one end of the concentration scale, further investigations are needed to clarify the nature of this case.

5.5. Milling with interruption

Interruption and room temperature aging can significantly alter the kinetics of some mechanochemical reactions. This “interrupted combustion effect” was

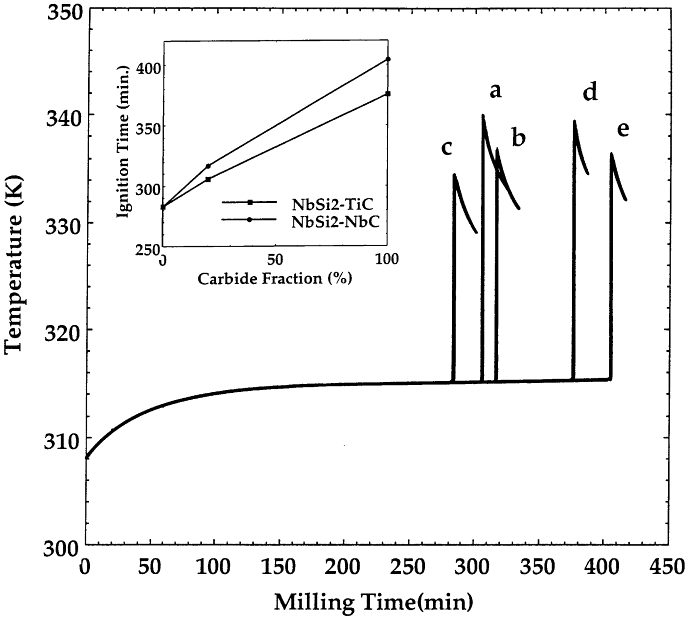

Fig. 25. Thermal history of $(NbSi_2)_{80}(TiC)_{20}$ (a), $(NbSi_2)_{80}(NbC)_{20}$ (b), $Nb_{33}Si_{67}$ (c), $Ti_{50}C_{50}$ (d), and $Nb_{50}C_{50}$ (e) based on the results of Fan et al. [132]. The inset shows the ignition time as a function of composition for the $(NbSi_2)$–(TiC) and $(NbSi_2)$–(NbC) mixtures.

observed by Atzmon in one of the earliest MSR experiments [69] on Ni–Al. The result was later reproduced by Maric et al. [191]. If an equimolar mixture of Ni and Al powders was milled continuously, NiAl formed in a gradual process, no abrupt temperature increase was observed. However, if milling was interrupted after two hours and the sample was aged at room temperature for 30 min, a self sustaining reaction ignited within one minute upon resumed milling. The same phenomenon was also observed by Schaffer and McCormick when reducing ZnO with Ti [61]. In other oxide-metal systems, e.g. the reduction of CuO with Mg or Fe, MSR took place also upon continuous milling, but the total activation time was shortened, if the mill was stopped and then re-started after an interval of room temperature aging [61]. Park et al. investigated the formation of titanium silicides in a low energy mill [192]. MSR was observed only at the Ti-40 at.% Si composition and only when milling was interrupted after 60 h, resumed after 48 h of aging and continued for an additional 32.5 h. The mechanism of this process may be different, as suggested by the long secondary milling time.

The interrupted combustion effect is very sensitive to the milling conditions. As implied earlier, Liu et al. did observe MSR in the Ni-Al system upon continuous milling [190]. Both Atzmon and Liu processed their powder in a SPEX 8000 mill, the ball-to-powder ratios were similar, 6:1 [69] and 10:1 [190], in the two experiments. Unfortunately, not enough experimental detail is given to decide if that was the only difference between the two investigations.

The interrupted combustion effect relates to atomic level changes during room temperature ageing. A tentative explanation was proposed relating the effect to the formation and growth of nuclei [62]. When high temperature is obtained between the colliding milling balls, nucleation of the product phase takes place. The critical size of a stable nucleus is relatively large at this temperature. Consequently, most of the nuclei dissolve during the same or a later collision. If the mill is stopped, the temperature of the powder remains close to room temperature, where the critical size of a nucleus is much smaller. Therefore, these nuclei will grow, aided by the high mobility along defects. By the time the mill is re-started, many stable nuclei are available, leading to high reaction rate and easy ignition. A somewhat different explanation was given by Schwarz, who assumed that mixing by diffusion along dislocations was the process that made the self sustaining process possible after aging [164]. The two explanations share a key point: The enhanced diffusion due to the mechanical activation plays an important role in room temperature aging.

Interrupting the milling process is not always "beneficial." In most cases, no significant change of the total activation time is observed. When NbSi2 was prepared from the elements by milling in a SPEX 8000 mill, MSR was observed after 65–70 min of continuous activation. If milling was interrupted every 5 min, gradual reaction took place [102]. In another experiment, $NiCl_2$ was reduced with Mg [54]. Interruption and ageing increased rather than decreased the total activation time needed to ignite a MSR process.

5.6. Multiple combustion effect

Once a self-sustaining reactions is ignited, it usually spreads through most of the powder charge. If any chemical change takes place upon continued milling, it is gradual, as already enough reaction product is present to make another self-sustaining reaction impossible. The time temperature curves for Zr–S mixtures (Fig. 26) show an unusual case [70], Hf–S mixtures behave similarly. The small temperature jumps signal a series of reactions, each restricted to a small fraction of the sample. These little jumps happen at rather unpredictable times. The last, much larger temperature effect ends the series of events. About 70% of the reaction heat is released during this step. A possible explanation of the phenomenon is that sulfur evaporates from around the reaction zone, removing one of the reactants and stopping the reaction. The sulfur vapor condenses in a cooler part of the milling vial and it is blended back into the mixture by further milling. Soon, the conditions are ripe for the next ignition, in spite of the small amount of inert product in the mixture. As one little burst of self-sustaining reaction takes place after the other, the amount of the product phase increases. Finally, the presence of this inert material decreases the reaction temperature sufficiently to make a "regular" self-sustaining reaction possible.

A similar series of incomplete reactions has been observed in mixtures of Al and I (Fig. 8), except for the lack of a final, more energetic reactions. The sublimation of iodine may play a role analogous to the evaporation of S.

It has been proposed that highly exothermic mechanochemical reactions always occur via self sustaining events, even if the series of many localized reactions is

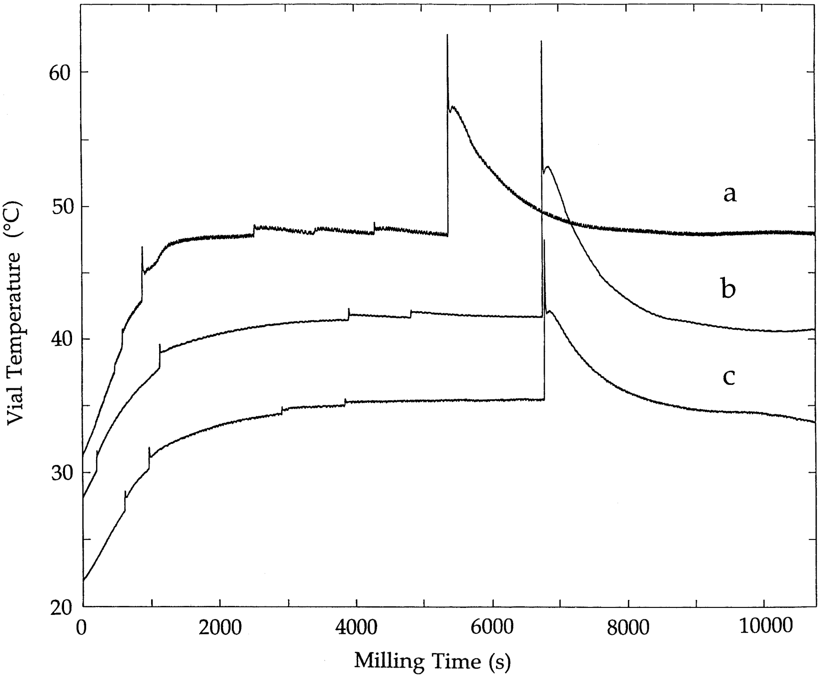

Fig. 26. The temperature of the vial while milling Zr + 2S powder mixtures. The ball-to-powder ratio was 6:1, 3 g (a), 4.2 g (b) and 6 g (c) charges were milled with 9.5-mm balls.

perceived as a gradual process macroscopically [69]. It is tempting to use the result on the Zr–S system to support that idea. However, this is a very different case. The formation of ZrS_2 is an extremely exothermic reaction, $\Delta H/C = 8400$ K. The local combustion could not be stopped by the heat loss to the tools alone. Many "mini" combustions are a more plausible explanation, if a relatively small amount of powder is processed and/or the systems is close to the $\Delta H/C = 2000$ K limit.

6. Conclusions

The current state of knowledge on mechanically-induced self-propagating reactions (MSR) has been reviewed. The key questions of how ignition happens and why does it happen after a certain amount of mechanical activation have been investigated both from the experimental and theoretical points of view.

MSR processes begin with a period of mechanical activation. During that time, particle size reduction, mixing of the reactants on an increasingly fine scale, and the formation of chemically active defect sites take place. At some point, a self-sustaining reaction is ignited. The key objective of MSR research is to understand ignition and the conditions that make ignition possible after the activation period. Once started, the reaction propagates as an SHS (self propagating high-temperature synthesis) reaction.

The ignition time can be measured easily, its variation from system to system and as a function of milling conditions have been used to learn about the mechanism of the MSR process. Many model reactions have been studied, for example combination reactions in metal–chalcogen and transition metal–metalloid systems and displacement reactions between a metal oxide and a more reactive metal. It was concluded that mechanical activation can be characterized adequately by the mechanical dose received by the powder charge; ignition usually occurs when a certain amount of total dose is received. However, there are many exceptions: The ignition time is longer than expected or the reaction is gradual, if the milling intensity is too low. No MSR is observed if the amount of the powder is too small, due to heat loss to the milling tools. In some metal chalcogen systems, gradual reaction is observed when blending binary powder mixtures that both show the MSR effect when processed separately.

The product of some MSRs is technologically important. For example, fine powders of TiC, $MoSi_2$, and other refractory materials can be prepared in a single step, in a closed reactor, without externally heating the sample. Ultrafine metal powders, composites, and inorganic compounds can be prepared. Mechanical activation can be used in combination with thermally induced SHS. It lowers the ignition temperature and improves the uniformity of the product.

Theoretical investigations are needed on several length and time scales, from atomic level events at the interface between two reactant grains, to the macroscopic operation of the mill. A particularly important objective is to relate the macroscopic properties of the reactant powder to its microstructure and the properties of the individual components. These issues are also important for other areas of mechanochemistry and SHS. A feature unique to MSR is its focus on ignition and on deriving the properties of the powder that characterize the critical state, where the ignition and propagation of a self-sustaining reaction become possible.

Further progress in MSR studies is needed in several directions. Experimentally, further systematic investigations have to be performed as a function of powder composition and milling conditions, including the effects of inert additives. New types of reactions and phenomena can be explored. The structure and properties of pre-milled powders have to be investigated to gain more insight into the nature of mechanical activation. The theoretical work has to combine modeling with empirical findings. Many problems are shared with other areas of mechanochemistry, mechanical alloying, and SHS. Close cooperation with those areas is mutually beneficial.

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