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Self-Sustaining Reactions as a Tool to Study Mechanochemical Activation

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Ever since Faraday reported on the reduction of AgCl with Zn and Sn the “dry way,” the study of Mechanically induced Self-propagating Reactions (MSRs) has been an important area within mechanochemistry. An interesting phenomenon is the mutual suppression of ignition in some mixed metal-chalcogen systems, such as in \((1-x)(Sn+Se) + x(Zn+Se)\) powders. Here both the \((Sn+Se)\) and \((Zn+Se)\) mixtures react in a self-sustaining manner after some activation time, but when they are combined, the reaction is gradual in the middle of the concentration scale. Mechanically induced metal-chalcogen combination reactions were studied by Chakurov et al. in the 1980s, using a low-energy vibratory mill. Similar measurements were carried out in our laboratory using the more energetic SPEX 8000 shaker mill. The results show qualitative similarities, but the details are different. It is suggested that the loss of MSR in mixed systems is the consequence of the very different properties of the binary systems, so that either one of the components (Zn) or a product formed gradually without ignition (e.g. SnSe) can act as an inert component relative to the rest of the system. Several examples are presented and the effect of the milling conditions is discussed. Finding new systems with similar behaviour and detailed studies of the activated state are needed to understand MSR in these systems.

Introduction

If a sufficiently exothermic powder mixture (e.g. Al-Fe₂O₃ or Ti-B) is processed in a ball mill, self-sustaining reaction can be induced after some activation time, typically a few minutes to several hours long. This process is called a Mechanically induced Self-sustaining Reaction (MSR). Most of the reaction takes place within a few seconds after ignition and the released reaction heat causes a sudden increase of the mill temperature.

Whether a reaction is exothermic enough to ignite and propagate a self-sustaining process depends mainly on its adiabatic temperature, often simplified to the ratio of the reaction enthalpy to the room temperature heat capacity of the products (\(\Delta H/C\)). But whether an MSR takes place or not depends also on many other factors, like the heat conductivity, activation energy, and the mechanical properties of the powders, as well as the type of the mill and the parameters of operation such as the ball to powder mass ratio.

MSRs occupy a special place in the history of mechanochemistry. Michael Faraday made one of the earliest remarks on a chemical reaction initiated by grinding in 1820. His objective was to decide whether AgCl could be reduced with hydrogen gas. Reacting AgCl with Zn directly was a control experiment. Heating the mixture caused a violently exothermic reaction that produced silver. Faraday also initiated the reaction by grinding. He wrote, “... if dry chloride of silver in powder be triturated in a mortar with zinc filings, the two bodies immediately act, and a heat above that of boiling water is produced.” This statement suggests MSR and a recent attempt to produce the same effect in a SPEX 8000 Mixer Mill indeed resulted in the temperature jump characteristic of ignition. Faraday repeated his experiment with tin causing an even more powerful effect and achieved some reduction of AgCl also with copper and iron.

The first systematic investigation of MSRs was carried out in the 1980s by Chakurov and his co-workers in Bulgaria. They studied combination reactions in dry powder mixtures of a metal, such as Zn, Cd or Sn with the chalcogen elements S, Se or Te affected by grinding in a vibratory mill. Their results were published in a series of five papers that still constitute one of the richest systematic investigations of an MSR system. The first paper provides the earliest example of using the mill temperature to detect the ignition of a self-sustaining reaction. It contains ignition time results for 18 systems, sufficient to look for systematic trends. They observed that inert additives increase the ignition time and in larger quantities make the ignition of MSR impossible.

In some mixed systems, such as (Sn-Zn)+S, a remarkable change of behaviour was observed as a function of composition. When an equimolar mixture of Zn and S powders was milled, MSR was initiated after some activation time. The same happened when a mixture of Sn and S powders was milled. Surprisingly, however, the ignition time increased if the two mixtures were mixed, and the (Sn-Zn)+S blends reacted gradually without the ignition of a self-sustaining process in an intermediate concentration interval. Similar behaviour was observed in other (Zn, Sn, Cd) – (S, Se, Te) mixtures. The qualitative explanation is based on the fact that Sn reacts with S much more easily than Zn does, but its reaction heat is much lower. Thus on the Sn-rich side of the composition scale, the relatively inert Zn retards the ignition of the Sn+S reaction. On the Zn-rich side,
some Sn sulphide forms early, but the corresponding reaction heat is not sufficient to ignite the self-sustaining reaction. At a later stage of the process, the SnS (or other tin sulphide) product acts as an inert additive and suppresses ignition. In the middle of the concentration scale neither reaction escalates into a self-sustaining process and the reaction remains gradual. The current paper will look at this phenomenon again, adding new experimental results and looking for more general explanations.

Chakurov’s 1987 paper has an interesting historical significance. Mechanical alloying was invented in 1966 without any knowledge of the rest of mechanochemistry and the two research areas developed independently for over twenty years. The first cross-reference was made by Schaffer and McCormick, who discovered MSR in CuO-metal systems. Although they called the process “combustion synthesis by mechanical alloying” while it was “explosive mechanochemical synthesis” according to Chakurov’s terminology, they realized that the two phenomena were essentially the same and cited the work of Chakurov. This reference is the first connection that broke the separation of the two areas.

The discovery of MSRs in oxide-metal and metal-metalloid systems resulted in significant activity in the 1990s. The study of activation and ignition contributed substantially to our understanding of the mechanism of mechanochemical reactions. Several applications are related to MSRs as well, for example the preparation of some refractory compounds and the synthesis of nanocomposites and free nanoparticles. Knowing how to avoid ignition is necessary to ensure the safe activation of energetic materials such as thermitics. Mechanical activation and ignition are very complex processes. They depend on the chemical and mechanical properties of the powders as well as on the processing conditions. Many open questions remain that keep the investigation of MSRs an active research area.

In this paper, the unique behaviour of the Sn-Zn-S and similar metal-chalcogen systems will be revisited. Some existing results will be summarized and critically analyzed and new measurements will be added to develop better understanding of the phenomenon.

The kinetics of a typical MSR process

Ball milling can turn a highly exothermic reaction into a self-sustaining process in cases like the reduction of a metal oxide with a more reactive metal (e.g. CuO-Al, Fe2O3-Zr), the formation of refractory compounds from a reactive metal and a metalloid (e.g. Mo-Si, Ti-C), and the combination reaction between a metal and a chalcogen element or a pnictide (e.g. Zn-S, Cd-Te, Ni-P). But independent of the chemical nature of the system, the reaction consists of the same three steps. (i) Activation, during which size reduction and mixing take place, chemically active defect sites are created, but little product is formed. (ii) Ignition, that occurs when a critical degree of activation is reached. At this point, the impact of a milling ball initiates a self-sustaining thermal process that propagates through the powder charge as a Self-Propagating High-temperature Synthesis (SHS) reaction. The release of the reaction heat results in an abrupt increase of the mill temperature. (iii) Continued milling brings the reaction to completion and results in a uniform product.

Ignition can be detected by measuring the temperature of the milling vial. The recording shown in Fig. 1 was obtained while milling a (Sn0.7Zn0.3)+Se mixture with a SPEX 8000 Mixer Mill, using round-ended hardened steel vial and 20 small (diameter 6.35 mm) steel balls. The two curves were recorded by thermocouples attached to the opposite end surfaces of the vial. While differences in heat transfer result in minor differences between the two curves, the main features are identical: There is an initial temperature increase due to the dissipation of mechanical energy of milling. As equilibrium is approached between the energy input and the heat loss to the environment, the temperature levels off. At a well-defined moment, in this case 2440 s after starting the mill, an abrupt temperature increase is observed due to the large energy release during the self-sustaining reaction. Observing this sudden jump of the temperature is the clearest indication that an MSR happened. Shortly after the jump, the temperature begins to cool toward a steady-state value and no further release of chemical energy is observed. When Rusanov and Chakurov studied the same reaction using a single-ball vibration mill, they observed ignition after about 6 hours of milling. The difference is a consequence of the much lower intensity of their mill. Many similar measurements have been published in the literature; the detailed shape of the temperature-time curve and the ignition time depend both on the reaction and the milling conditions.

The effects of inert additives

Adding an inert material to a reactive mixture delays the ignition of MSR and above a certain concentration entirely suppresses ignition. As the behaviour of the quasi-binary metal-chalcogen systems—the main subject of this paper—will be explained using clues from the effects of inert additives, it is necessary to first investigate MSR in mixtures containing additives.

Inert additives, such as an oxide or a polymer, change the conditions in many ways: They make the reaction less exothermic as they contribute to the heat capacity but not to the reaction heat, thereby decreasing ΔH/C. They change the heat conductivity. The inert particles get between the reactants and reduce the contact area. The additives change the mechanical properties of the powder charge; hard particles can accelerate particle size reduction while soft additives reduce the efficiency of milling.

According to Chakurov’s model of mechanochemical reactions, the activation process begins with size reduction, mixing, and the accumulation of lattice defects, followed by the formation of composite aggregates, typically a few tens of microns in diameter. If an agglomerate grows large enough, self-heating by an incipient reaction can overwhelm heat loss at the surface and the reaction extends to its entire volume. Heat transfer to the neighbouring aggregates will ignite further reaction and lead to the propagation of MSR across the powder charge. The critical degree of activation is
characte‌rized by reaching a certain aggregate size. According to this model, the main effect of an inert additive is to inhibit the formation of large aggregates by forming layers that separate one block of the reactant mixture from the other. This is essentially a geometric percolation effect, thus it is natural to characterize it in terms of a critical volume fraction that ensures sufficient fragmentation to prevent ignition. Chakurov determined the critical volume fraction for eleven metal-chalcogen mixtures, using SiO₂ as the inert component⁶. The formation of ZnS was the most exothermic reaction and it required 50 volume % of SiO₂ to prevent its ignition.

In order to establish volume fraction as the most relevant parameter, Chakurov studied the suppression of ignition in equimolar Sn-S mixtures using a polymer, SiO₂, rhyolite, and Fe as inert additives⁷, but the number of experiments was not sufficient to clearly verify a general trend. Also, Fe may react with S rather than behave as an inert additive: in fact, Fe₃S₄ can form from Fe and S powders via MSR in a high-energy mill⁸. Similar experiments have been carried out in a SPEX 8000 Mixer Mill using 5-g powder batches milled in a round-ended hardened steel vial with 5 balls, 12.7 mm in diameter. Both Sn-S and Sn⁺2S compositions were used for the reactive mixture and Al₂O₃, NaCl, and graphite were added as inert materials (Fig. 2). The addition of a small amount of Al₂O₃ left the ignition time practically unchanged, suggesting that the hard oxide particles increased the efficiency of milling, and this effect was sufficient to balance the reduction of ΔH/C up to a point. If more than a few volume percents of Al₂O₃ were added, the reaction was not exothermic enough any more and the reaction became gradual. NaCl could participate in the reaction in some way, as it left the ignition time unchanged or even decreased it with increasing concentration, until ignition became impossible. Only graphite behaved the way usually expected from an inert additive. Similar results have been obtained for the effect of additives on Zn-S mixtures⁹.

In summary, treating the effect of inert additives as a geometric percolation effect is an oversimplification. Nevertheless, it remains true that additives interfere with the ignition of MSR. At low concentration they tend to increase the ignition time and beyond a critical amount they make ignition impossible. In a high-energy mill, the energetic impacts cause significant forced reaction and perhaps local melting, thus ignition can start in the powder caught between the colliding surfaces. The percolation model may apply better to a low-energy mill where the individual impacts transfer relatively little energy to the powder, thus processing causes activation and agglomeration, but the MSR begins with the self-ignition of a free aggregate.

**Suppression of MSR in quasi-binary metal chalcogen systems**

In a few cases, a surprising phenomenon happens when two reactive powder mixtures are blended together. It is possible that MSR occurs in either of the two mixtures, but when they are mixed together in different proportions, the ignition time increases and at some compositions MSR is not ignited at all. This phenomenon was first observed by Rusanov and Chakurov⁷ in some (M₁-M₂)+Ch systems, where M₁ and M₂ represent Zn, Cd, or Sn and Ch is a chalcogen element. A broad composition interval with no MSR was found in the (Zn-Cd)+Te and (Sn-Zn)+Te systems, ignition was suppressed only in a narrow composition range in (Sn-Zn)+S and (Sn-Zn)+Se, and only an increase of the ignition time relative to the binary systems and a cusp in the concentration dependence were observed in (Zn-Cd)+S.

The explanation given by Chakurov considered this behaviour a percolation phenomenon, similar to the effect of inert additives, but here the main components of the powder charge were assumed to play the role of the additives⁷. A key feature of these systems is that the reactivity of the two metals is always very different, as indicated by the very different ignition times of the M₁+Ch and M₂+Ch mixtures. Thus one reaction occurs much more easily than the other. When the more reactive metal (the one with shorter ignition time) is the main component, the less reactive metal acts as an inert additive. When the less reactive metal is the main component, some chalcogenide of the more reactive metal forms gradually before ignition and acts as an inert additive later. The presence of an inert component holds back the reaction either way, thus the ignition time increases at both ends of the concentration scale. Also, there are critical amounts of the inert components, above which the reactions become gradual. Depending on the relative position of the two critical compositions, a region with no MSR or a cusp in the concentration dependence of the ignition time can be observed.

**Fig. 3** Concentration dependence of the ignition time in (1-x)Sn⁺xZn+S mixtures as measured in a low-energy vibratory mill (squares) and in a SPEX 8000 shaker mill (5 g powder, five 12.7-mm balls; circles). The data obtained with a vibratory mill are multiplied by 15 to aid comparison.
Investigations on the same systems using a SPEX 8000 Mixer Mill showed that although some qualitative features are the same, the details are very different. Fig. 3 shows the concentration dependence of the ignition time for the (Sn-Zn)+S system. The two vertical dashed lines show the postulated critical concentrations. While the results obtained with the vibratory mill clearly show the “percolation phenomenon,” the ignition time obtained with the SPEX mill varies smoothly, not even a cusp is visible. Nevertheless, the ignition time increases from either end of the concentration scale, thus there remains some similarity between the two behaviours.

The (Sn-Zn)+Se system shows the opposite relationship, shown by the ignition times presented in Fig. 4. The system is more reactive – the ignition times are about a factor of 2 shorter – thus larger critical concentrations are expected; in fact, they are expected to cross over so that only a cusp should remain in the concentration dependence, but no MSR-free concentration range should exist. The results obtained using low-energy mill exhibit such behaviour. If similar mixtures are processed in a SPEX 8000 mill using mild conditions (10 small balls, 6.35 mm diameter each) the ignition time varies in a similar way, although a rounded maximum is obtained instead of a sharp cusp. But if milling is carried out with five 12.7-mm balls, providing higher impact energy and larger ball-to-powder mass ratio, a rather broad concentration range, from at least 65 at.% to 75 at.%, is found where no MSR is ignited. The results show that the ignition time always increases compared to the binary systems, but the suppression of ignition depends on the milling conditions as well. (The reaction in the binary Sn+S mixture happens as soon as the mill is started and only the substitution of some Zn for Sn makes the ignition time finite.)

Beside the monosulphide and -selenide discussed above, Sn can also form disulphide (SnS2) and diselenide (SnSe2). (In fact, mixed-valence compounds such as Sn2S5 exist also, but we did not investigate reactions with the corresponding stoichiometry.) The ignition times for (1-x)(Sn+2S)+x(Zn+S) mixtures and their Se analogues are shown in Fig. 5. The ignition time increases starting from either end of the concentration scale and broad MSR-free concentration interval is observed in both cases. (Notice that the reactions with selenium were initiated at relatively mild milling conditions, using 20 balls, 6.35 mm in diameter. MSR is ignited over the entire composition range, if milling is carried out with 5 balls of 12.7 mm. These systems were not investigated by Chakurov’s group.)

The cessation of ignition is very different when approaching the MSR-free middle region from the two ends of the concentration scale. On the Sn-rich side, the ignition time increases moderately, to about 34 and 20 min in the sulphur- and selenium-containing systems, respectively, but if the Zn concentration is increased further, ignition is lost abruptly. On the Zn-rich side (x decreasing from 100%), the ignition time increases much farther, to at least 60 min, before the reaction turns gradual. The difference may be explained the following way: It seems that the activation process is not held back by the increasing Zn content on the Sn-rich side, but at some point the reaction is no longer exothermic enough to ignite the MSR. (Zn is not involved, as it is not activated enough at that point.) On the other side, the increasing Sn content results in an increasing amount of gradually formed tin sulphide and the milling efficiency decreases due to the presence of soft Sn, but the reaction remains quite exothermic. Thus the ignition time increases substantially before the ignition of MSR becomes impossible. The effect of inert additives shows similar differences, e.g. little increase of the ignition time is observed before the loss of ignition, if the additive is a hard oxide, but the ignition time increases substantially before the reaction turns gradual with the addition of graphite (Fig. 2). Similar asymmetry is observed in off-stoichiometric Sn-S and Zn-S mixtures between the S-rich and S-lean compositions. The ability to describe such fine details is a sensitive test of the validity of any future model of the ignition process.

When using a SPEX mill to process (Zn-Cd)+S and (Zn-Cd)+Se powder mixtures, MSR was observed at any composition. The ignition time was a smooth monotonous function of concentration, without any cusp. It is possible that gradual reaction or a transition between MSR and gradual kinetics could be obtained by using substantially different milling conditions. The use of more energetic milling conditions, such as larger milling balls as in the case of (Sn-Zn)+Se (Fig. 4) or small amount of powder like in (Sn-Zn)+S, may change the kinetics to gradual for all compositions or just in a restricted concentration interval. The reason may be that the reaction is initiated between the colliding surfaces before the conditions become favorable for the propagation of the reaction across the entire powder charge. It may be self-sustaining in the small volume of powder involved in the collision, but it seems gradual on the macroscopic scale. It is also possible that milder conditions result in
gradual reaction; after all, a cusp in the concentration dependence of the ignition time was observed in this system when it was processed in a low-energy mill.\textsuperscript{7}

Qualitative explanation of the observed behaviour

Whether the effect of inert additives is indeed a simple percolation phenomenon or more complex changes, such as the reduction of the adiabatic temperature and the change of the milling efficiency are at work, it remains true that an additive suppresses the ignition of MSR above a critical amount, and this is usually preceded by an increase of the ignition time. Thus the main question is whether Zn on one side and gradually produced Sn (or Cd) sulphide or selenide on the other can indeed be considered an inert component.

The most important property of a self-sustaining reaction is its adiabatic temperature, or its simplified form, the ratio of the reaction enthalpy to the room temperature heat capacity of the products (\(\Delta H/C\))\textsuperscript{10,21}. For MSR (and SHS) this quantity is the primary measure of the exothermicity of the reaction. A large enough value means that the degree of self-heating is sufficient to propagate the reaction. In an oxide-metal or a metal-metalloid mixture, MSR is usually possible if \(\Delta H/C\) is at least 2000 K\textsuperscript{21}; smaller values can be sufficient for metal-chalcogen and metal-halide systems. The relevant parameters of the reactions considered in this paper are listed in Table 1. Notice that the formation of the Zn compounds is much more exothermic than the formation of Sn compounds. Based on this property alone, far the shortest ignition times would be expected for the reactions with Zn. The fact that this is not the case suggests that other properties, such as activation energy and the efficiency of ball milling, must also be considered.

An important factor is the formation of product compounds before the ignition of MSR by gradual mechanochemical reaction. XRD results suggest that the formation of Sn compounds happens much more readily than the formation of ZnS or ZnSe\textsuperscript{17,18}. Therefore, Sn compounds are indeed present, thus they can act as inert additives in the quasi-binary systems. The situation is made more complicated by the existence of at least two mixed-valence sulphides, Sn\textsubscript{3}S\textsubscript{3} and Sn\textsubscript{2}S\textsubscript{3} and the analogous selenides. On the microscopic scale, mechanochemical reaction takes place by diffusion between grains, just like any solid-state reaction. Thus independent of the overall composition of a powder mixture, at least four different Sn-S or Sn-Se compounds can form. Little ZnS or ZnSe is produced before ignition and no mixed Sn-Zn-S or Sn-Zn-Se compound was observed.

The ignition of MSRs is investigated partly to gain insight about the mechanism of mechanochemical activation in general. Depending on the energy balance between the reaction heat and the heat loss to the environment, MSR may or may not be ignited, but the activation process is essentially the same. The main advantage of working with

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H) (kJ)</th>
<th>(\Delta H/C) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>205.2</td>
<td>4516</td>
</tr>
<tr>
<td>SnS</td>
<td>107.9</td>
<td>2191</td>
</tr>
<tr>
<td>SnS\textsubscript{2}</td>
<td>153.6</td>
<td>2189</td>
</tr>
<tr>
<td>ZnSe</td>
<td>163.2</td>
<td>3144</td>
</tr>
<tr>
<td>SnSe</td>
<td>94.1</td>
<td>1788</td>
</tr>
<tr>
<td>SnSe\textsubscript{2}</td>
<td>124.7</td>
<td>1743</td>
</tr>
</tbody>
</table>

Table 1 Reaction heat (\(\Delta H = \Delta H_{\text{react}}\)) and “simplified adiabatic temperature” (\(\Delta H/C\), where C is the heat capacity of the products) for the formation of some metal-chalcogen compounds using data from Ref. 22.

Fig. 6 Temperature of the milling vial as a function of time while milling (1-x)(Sn+2Se)+x(Zn+Se) mixtures using a SPEX 8000 mill with 5 g of powder and twenty 6.35-mm balls. From bottom to top, x = 0.5, 0.6, and 0.7.

an MSR is the existence of a reference state, defined by the point of ignition, while in a gradual mechanochemical reaction the phase composition and properties change smoothly. If the composition of the powder charge or the milling conditions is changed slightly, it is reflected by a change of the accurately observable ignition time of an MSR. It is more difficult to detect minor changes of gradual kinetics. Interestingly, even if no MSR is ignited in a milling experiment, the first step is still activation with little chemical change, followed by a period of relatively fast reaction. Fig. 6 shows the temperature-time curves for three (1-x)(Sn+2Se)+x(Zn+Se) mixtures. (The ignition times of the same powder mixtures were presented in Fig. 5.) At x = 0.5, MSR was ignited after 1045 s (17.4 min.) At x = 0.7, on the Zn-rich side of the interval with no MSR, the ignition time was 3530 s (58.8 min.) The characteristic abrupt temperature increase was observed in both cases. No MSR was observed at x = 0.6. Nevertheless, there is a period of relatively fast temperature increase, caused by fast, although not self-sustaining, reaction after 2525 s. That is about the time when ignition would be anticipated by extrapolating the Sn-rich side of the ignition time-concentration curve. Thus the reaction rate increased after 2525 s of activation, even though it did not escalate into an MSR process. Some selenides – mostly of Sn – were produced during this period. They acted as inert additives, thus it took much additional milling, up to about 5160 s of total milling time, before another period of fast reaction started. Some relatively fast temperature increase can be noticed again, although not the sudden jump typical of an MSR. These results support the assumption that the activation process must be quite similar in related systems, even if one reacts according to a gradual kinetics and the other propagates as a self-sustaining reaction. Accordingly, the information obtained from the study of MSR is applicable to similar systems, even if they react gradually.

Searching for similar phenomena in different reactions

The fact that one can take two powder mixtures that are both capable of reacting with an “explosive” self-sustaining kinetics and combine them to end up with a mixture that reacts slowly according to a gradual kinetics is very surprising. The opposite behaviour would be much more plausible: If the reaction begins in one component, it transfers heat to the rest of the powder igniting the other component.
also. The two reactive mixtures support each other rather than act as inert additives for each other. The behaviour of the metal-chalcogen systems is quite unique and follows from the very different properties of the binary mixtures. In order to better understand the details of the phenomenon, it would be beneficial to find other, preferably very different, systems that exhibit similar phenomena.

We investigated two possible combinations, both without success. The first involved the reduction of CuO with Si (AH/C = 6278 K) and Zn (AH/C = 2913 K). Although the reaction with Si is the more exothermic, the hard Si particles do not break up and mix easily, thus the contact area between the different grains is small and does not increase quickly with activation. Thus ignition takes place only after a relatively long activation period. On the other hand, the reaction with Zn is much less exothermic, but the relative softness and pliability of Zn results in larger contact area and easier reaction, resulting in similar, in fact, shorter, ignition times. Based on the asymmetric properties, it was reasonable to expect anomalous concentration dependence similar to the one observed in the metal-chalcogen systems. Here Si could behave as the inert component on the Zn rich side of the concentration scale and Zn could react early to form ZnO that acts as an inert additive in Si-rich samples. Nevertheless, as shown in Fig. 7, the ignition time decreases at both ends of the concentration scale and has a flat minimum in the middle, rather than an increase at the ends and a maximum or an ignition free range. As the behaviour can depend on the milling conditions, three different combinations of powder mass and number of balls were tried. Each curve shows a minimum, although the ignition time of the Si-rich compositions varied more with the milling conditions.

Displacement reactions involving chlorides are less exothermic than the similar reactions with oxides, but the chlorides are softer and consequently they react more easily with a reducing metal. As a result, similar ignition times are observed in spite of the very different properties. We investigated the reduction of ferric chloride-hematite mixtures with Al. The AH/C values for the binary FeCl₃+Al and the Fe₂O₃+2Al reactions are 2633 K and 6586 K, respectively. According to the data in Fig.7, the ignition time of the mixtures has a shallow minimum.

![Fig. 7](image_url) Ignition time as a function of composition in mixtures activated in a SPEX 8000 Mixer Mill with round-ended hardened steel vial. Data for CuO+(1-x)Zn+(x/2)Si (3 g powder with 3 balls, triangles; 1.5 g powder with 3 balls, squares; 3 g powder with 6 balls, diamonds; each with 12.7-mm balls) and (1-x)FeCl₃+(x/2)Fe₂O₃+Al (3 g powder milled with five 9.525-mm balls.)

While these attempts were unsuccessful, it is still possible that some other system may exhibit anomalous concentration dependence. Metal-chalcogen combination reactions with transition metals such as Mn could be of interest. The formation of phosphides may show similar behaviour. More complex reactions, such as the displacement reactions discussed above, would be more interesting. In any case finding systems that show the mutual suppression of ignition in systems that are very different from the metal-chalcogen mixtures could add substantially to our understanding of the ignition of MSR and more broadly of mechanochemical activation in general.

### A simple model for reactions in mixed systems

The unexpected increase of the ignition time and the occasional loss of ignition toward the middle of the concentration scale were explained qualitatively based on the very different physical and chemical properties of the component systems. In the following, a simple probabilistic model is introduced to explain the concentration dependence of the probability of ignition. A cluster of reactive grains is considered. If this cluster is caught between the colliding milling tools, its temperature increases due to the dissipation of mechanical energy. This temperature increase may induce reaction in one of the grains. If that happens, the reaction heat is released, increasing the temperature of the entire cluster that can lead to reaction in another grain. As this will result in further temperature increase, the reaction will be transferred to additional grains and eventually escalate into an MSR. Thus it is reasonable to assume that the probability that the reaction extends to a second grain during a collision determines the probability of ignition. Larger probability results in shorter ignition time, while lower probability leads to longer ignition time and eventually to the loss of ignition.

Let’s consider a cubic cluster of 3x3x3 grains, equal in size, each either an equimolar powder mixture of metal M and chalcogen Ch, capable of the reaction M₁ + Ch → M₂Ch or metal M₂ and the same chalcogen Ch, capable of the reaction M₂ + Ch → M₃Ch. The mean composition of the sample is xM₁ + (1-x)M₂ + Ch. If this cluster is compressed between two colliding surfaces during ball milling, its temperature is increased to T₁. The probability that the central grain is M₁ + Ch mixture is x, and that it reacts due to the temperature increase is proportional to

\[ P₁ = x \alpha \exp(-E₁/T₁), \]

where k₀E₁ is the activation energy and α is the frequency factor of the reaction. If all the heat is used to increase the temperature of the cluster, the temperature increases to

\[ T_{2₁} = T₁ + Q₁/27C, \]

where Q₁ is the reaction heat and C is the heat capacity of a single grain, assumed to be the same for every grain for sake of simplicity. Similarly, the probability that the central grain contains M₂ and Ch and it reacts to form M₃Ch due to the initial temperature increase is proportional to

\[ P₂ = (1-x) \beta \exp(-E₂/T₁), \]

and it raises the temperature of the cluster to

\[ T_{2₂} = T₁ + Q₂/27C. \]

Let’s assume that the probabilities are small, so that the probability of initiating reaction in more than one grain at a time is negligible.

The temperature increase to T₂₁ or T₂₂ increases the probability of further reaction in a neighbouring grain. For example, if the initial reaction took place in an M₁ + Ch mixture than the probability of a...
second, thermally ignited reaction in a grain that happens to consist of \(M_2 + Ch\) is
\[
P_{12} = (1-x) \beta \exp(-E_2/T_{23}).
\] (5)
Similar probabilities can be assigned to the other possible cases.

Combining the above expressions, the probability of “ignition,” defined as an initial reaction in the centre of a cluster followed by further reaction in one of the neighbouring grains due to the initial heat release is proportional to
\[
P(x) = P_1 (P_{11} + P_{12}) + P_2 (P_{21} + P_{22}).
\] (6)
For most reasonable combinations of the parameters, the function \(P(x)\) is close to a straight line or has a maximum at an intermediate concentration. But if the properties of the two reactions are very different, it is possible that the variation has a minimum. The curve shown in Fig. 8 was obtained using parameters resembling the properties of the Zn-Sn-S system: \(Q_1 = 205.2\) kJ/mol for the formation of ZnS, \(Q_2 = 107.9\) kJ/mol for the formation of SnS; the average of the heat capacities of ZnS and SnS is \(C = 47.35\) J/mol K (the individual values differ only by 10%). It is more difficult to initiate the formation of ZnS, thus its activation energy was chosen to be \(E_1 = 25000\) K while for the formation of SnS \(E_2 = 12500\) K. The pre-exponential factors \(\alpha = 10^{16}\) and \(\beta = 2 \times 10^{10}\) were chosen to make the probabilities of the binary reactions in Zn+S and Sn+S about equal.

Although this model is far too simple to address most issues related to the ignition of self-sustaining reactions, it shows that asymmetry of the physico-chemical properties of the two reacting mixtures can lead to decreasing probability and consequently to increased ignition time or loss of ignition, when the mixtures are combined.

**Conclusions**

The mutual suppression of ignition, this far only observed in a few mixed metal-chalcogen systems, is a unique and complex phenomenon that can serve as a vehicle to gain more insight about the mechanism of the ignition of self-sustaining reactions and of mechanical activation in general. Although the main features, namely the increase of the ignition time when one reactive mixture is blended with another and the possible loss of MSR in an intermediate concentration range, are the same in every case, the details are sensitive to the composition and the milling conditions.

This interesting phenomenon calls for further investigations. Finding new systems that exhibit similar behaviour would be of interest, especially if reactions other than the combination of metals with a chalcogen element would be involved. Using a broader variety of mills and milling conditions could provide new insight also. Only ignition time data were presented in this paper. However, detailed investigations of the activated states using XRD to obtain phase composition, grain size and strain, microscopy to study changes of the microstructure, calorimetry to test reactivity, etc. are also essential for learning about the actual processes during activation and ignition. Some results are available in the literature, but more investigations are needed to understand this phenomenon and to utilize it to better understand mechanochemical processes in general.

**Notes and references**

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