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Gradual and Combustive Mechanochemical Reactions in the Sn–Zn–S System

L. Takacs[1] and M. A. Susol

Department of Physics, University of Maryland Baltimore County, Catonsville, Maryland 21228-5398

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The mechanochemical formation of ZnS from a mixture of Zn and S powders turns into a self-propagating thermal reaction after 30 min of milling. A similar "explosion" occurs when Sn and S are milled for about the same time to form SnS_2. However, the ignition time is longer or the reaction is gradual in mixtures of the two systems. This phenomenon is investigated as a function of composition. A model is proposed based on the thermodynamic properties and mechanochemical reactions of the binary systems. © 1996 Academic Press, Inc.

INTRODUCTION

In addition to attrition and mixing, high-energy ball milling can also induce mechanochemical reactions. They are utilized in many existing and emerging technologies (1). The process—called mechanical alloying (2) or mechanochemical synthesis (1, 3)— has been used to prepare oxide-dispersion-strengthened alloys (2), amorphous alloys (4), nanocrystalline carbides and silicides (5), complex oxides (6), permanent magnet materials (7), and metal–oxide nanocomposites (8, 9).

Mechanochemical reactions may progress gradually or the mechanical agitation can initiate a self-propagating thermal reaction (combustion, explosion) in sufficiently exothermic reaction mixtures. The formation of metal chalcogenides (3), $MoSi_2$ (10, 11), and TiB_2 (12) from their elemental constituents, displacement reactions between a metal oxide and a more reactive metal (13–16), and the reduction of $TaCl_5$ by Mg (17) were shown to become explosive after a period of mechanical activation. When combining Ni and Al powders (18) or reducing ZnO by Ti (19), combustion is not initiated by continuous milling. However, if milling is interrupted for several hours, combustion occurs almost immediately when milling is resumed. Gradual reactions induced by ball milling can be used to form metastable phases and nanostructured materials, but the high temperature of an unexpected combustion can ruin these products (20).

When a mixture of reactant powders A and B is milled, a mechanochemical reaction can be induced whenever an A–B interface is compressed between two colliding balls or a ball and the wall of the container. The reaction results in local heating around the reaction zone. If, as a consequence, the temperature at a nearby A–B interface exceeds a critical value, T_{crit}, the reaction is initiated there as well. Additional heat is released and the process escalates into self-propagating combustion (19, 21).

Initially, the conditions may not favor combustion. As milling progresses, however, the possibility of combustion emerges: Lattice defects are created which serve as chemically active sites, decreasing T_{crit}. The lattice defects also increase the energy of the system, contributing to the temperature increase when a reaction starts. This excess energy can be as much as 50% of the heat of fusion (22). The reactants get mixed on an increasingly fine scale. Consequently, the reaction heat from an incipient reaction is conducted to a shorter distance before a nearby unreacted A–B interface is reached (21). These changes may make combustion possible after a period of activation. Ignition can happen after a few seconds or several hours, depending on the reaction and the milling conditions. The measurement and explanation of this "ignition time" is the primary objective of this paper.

Inert additives hamper combustion by decreasing the adiabatic temperature, reducing the possible contacts between unreacted surfaces, and reducing heat transfer (3, 21). Small amounts of an inert additive increase the ignition time; larger amounts suppress combustion entirely. Any reaction product, formed noncombustively during the early stages of the milling process, acts as an inert additive. Therefore, once a large amount of product is produced by gradual reaction, the possibility of initiating combustion diminishes.

The mechanism of mechanochemical processes is extremely complex. The dynamics of the mill (23), the thermodynamics of the reaction (19), the development of the microstructure (24), heat conduction (21), diffusion, and lattice defects (25) are important. It is the objective of our

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[1] To whom correspondence should be addressed.

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current investigations to identify and separate the role of these factors by investigating the kinetics of carefully selected groups of reactions.

The mechanochemical synthesis of Zn, Cd, and Sn chalcogenides has been investigated by Rusanov and Chakurov (26). All binary reactions showed similar explosive behavior. However, if a mixture of two metals was milled with a chalcogen element, the ignition time increased and some reactions became gradual. The authors explained this surprising observation as a kind of percolation phenomenon, whereby the unreacted metal or the nonexplosively formed product of one reaction acts as an inert additive for the other. The above experiments were carried out using a low-energy vibratory mill, while mechanical alloying is usually carried out in high-energy mills. In order to see if the above phenomena can also be observed during more energetic milling, investigations were carried out on the Sn–Zn–S system using a SPEX 8000 Mixer/Mill, the shaker mill used in most small-scale mechanical alloying experiments.

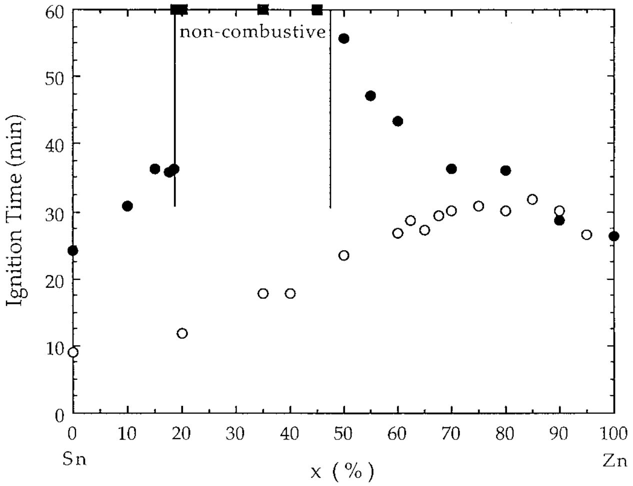

FIG. 1. Ignition times in the simultaneous mechanochemical synthesis of SnS and ZnS (open circles) and SnS_2 and ZnS (closed circles) as a function of the mole fraction of ZnS. Samples in the noncombustive region (■) were milled for 2 hours.

EXPERIMENTAL METHODS

Five-gram batches of powder mixtures were milled using a SPEX 8000 Mixer/Mill (SPEX Industries, Inc.) and round bottom hardened steel vials. The elemental powders and five 1/2-inch diameter steel balls were placed into the vial in an argon-flushed glove box to avoid oxidation. The starting materials were Zn (97%, 7 μm), Sn (99.8%, −325 mesh), and S (precipitated, −60 mesh).

The progress of the reaction was monitored by measuring the temperature with a type K thermocouple attached to the outside of the vial. A sudden increase (occurring within 2 s) indicated the ignition of combustion (14, 15, 18).

The phase composition of the products was determined using a Philips X-ray diffractometer and Cu$K\alpha$ radiation. Phase analysis was performed on the products of combustive reactions and on mixtures milled for preset times with no combustion.

THE IGNITION TIME: RESULTS

The open circles of Fig. 1 illustrate the ignition times for the mechanochemical synthesis of SnS, ZnS, and their mixtures as described by the reaction

$$x\text{Zn} + (1 - x)\text{Sn} + \text{S} \rightarrow x\text{ZnS} + (1 - x)\text{SnS}.$$

Our more energetic milling conditions resulted in combustive reactions over the entire composition range. Instead of the nonexplosive region found by Rusanov and Chakurov around $x = 0.38$ (26), only a shallow maximum is seen at a very different concentration, about $x = 0.8$. The ignition times are more than an order of magnitude shorter.

We also studied the mechanochemical synthesis of mixtures of ZnS and the "saturated" tin sulfide, SnS_2, as described by the reaction

$$x\text{Zn} + (1 - x)\text{Sn} + (2 - x)\text{S} \rightarrow x\text{ZnS} + (1 - x)\text{SnS}_2.$$

This is a more "symmetrical" system in that the ignition times for the Zn + S and Sn + 2S reactions are almost identical. The closed symbols of Fig. 1 indicate that the ignition time increases on both sides of the concentration scale and the reaction is gradual between $x = 0.19$ and 0.45. The way the reaction changes from explosive to gradual is different when approaching from Sn- or Zn-rich compositions. As the concentration of Sn increases on the Zn-rich side, the ignition time increases to over twice the value for the binary Zn + S system before the reaction finally turns gradual. On the Sn-rich side of the diagram, the ignition time increases by only 50% with increasing Zn concentration and the reaction turns gradual abruptly after a linear increase. (Six preparations were performed between $x = 0.18$ and $x = 0.19$; those below $x = 0.185$ exhibited combustive, the others gradual behavior.)

Studying the binary Sn + yS and Zn + yS systems seemed necessary before developing a model for the Sn–Zn–S reactions. The ignition times are given in Fig. 2 as a function of the S composition, y. The shortest ignition time of a Sn–S mixture is found close to $y = 1$, which corresponds to the stoichiometry of the SnS compound. The reaction turns non-combustive sharply between $y = 0.8$ and 0.9. SnS is the dominant product phase at these concentrations. As y increases, a mixture of SnS, Sn_2S_3, and SnS_2 is formed with varying proportions until the product is dominated by SnS_2 at $y = 2.5$. However, the curve is smooth

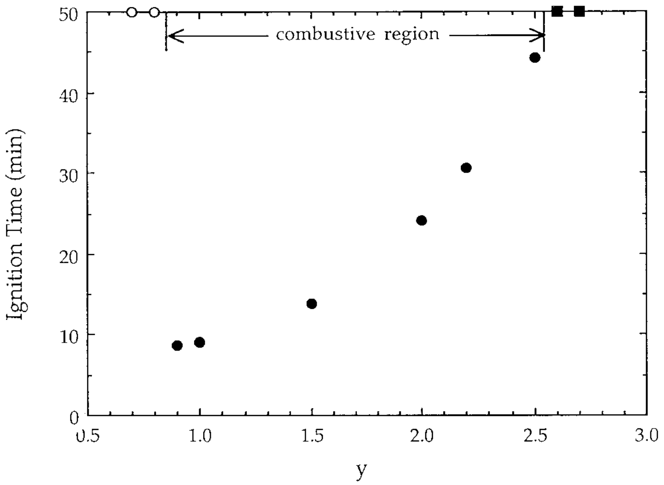

FIG. 2. Ignition times in the mechanochemical synthesis of sulfides in binary Sn + yS (closed symbols) and Zn + yS mixtures (open symbols.)

and monotonic around $y = 1.5$ and $y = 2$, the compositions corresponding to the other sulfides Sn_2S_3 and SnS_2. The ignition time increases fivefold before the reaction becomes gradual for $y \geq 2.6$.

The shape of the ignition time versus concentration curve of the Zn + yS system is very similar. The only stable compound in this system is ZnS, corresponding to $y = 1$, but the shortest ignition time is measured at $y = 0.5$. The increase in the ignition time is sharper for decreasing than for increasing sulfur concentration, similar to the behavior of the Sn–S system. However, the ignition time reaches longer values before the reaction turns gradual.

THE IGNITION TIME: DISCUSSION

Combustion occurs if a reaction produces enough heat to raise the local temperature over a critical value. This thermodynamic condition is usually expressed in terms of the adiabatic temperature, T_{ad}, the final temperature of the products in an isolated reaction mixture (19). We will use a simpler quantity, T', which is defined as the ratio of the reaction heat and the room temperature heat capacity. This quantity would equal the adiabatic temperature increase if no phase transition occurred. True adiabatic temperatures are very high, usually above the boiling point of the products, while the ignition of combustion depends on self-heating below the critical temperature. Therefore, T' may be simpler as well as more relevant when the initiation of combustion is discussed (27).

The Binary Sn–S and Zn–S Systems

Thermodynamics alone is not capable of explaining the variation of the ignition time. In the binary Sn–S system, the value of T' is almost the same for the formation of SnS (2500°C) and SnS_2 (2490°C) (26). Therefore, the increase in the ignition time between $y = 1$ and $y = 2$ (Fig. 2) must be the result of some "kinetic difference," e.g. a change in the ductility of the powder mixture and the resulting change in the mixing and milling processes. As y increases beyond $y = 2$, T' starts increasing also, as the unreacted sulfur contributes to the heat capacity without increasing the reaction heat. The combination of thermodynamic and kinetic factors results in a gradual change from combustive to gradual behavior. Decreasing T' alone can explain the abrupt cessation of combustion at $y = 0.8$.

The competing thermodynamic and kinetic factors may also explain the behavior of the Zn–S system. The adiabatic temperature increase is the largest at $y = 1$, where the only product is ZnS. Any deviation results in unreacted Zn or S, decreasing T'. There must be some kinetic reason for having the shortest ignition time at a different composition, $y = 0.5$. If we assume changes similar to the ones in the Sn–S system, kinetic effects will tend to increase the ignition time at large y and decrease the ignition time at low y. The parallel effects of decreasing T' and slower kinetics result in gradually increasing ignition times and finally the cessation of combustion at large y. The two effects compete at low y, resulting in the shift of the minimum from $y = 1$ to $y = 0.5$ and the rather abrupt change from combustive to gradual behavior at about $y = 0.3$.

The cessation of combustion as a function of composition can also occur gradually or abruptly in other systems. Dilution of the reaction mixture with an inert additive decreases T'. It also decreases the contact between unreacted surfaces and increases the range of heat transport between possible reaction zones. The parallel actions of thermodynamic and kinetic effects result in gradually increasing ignition time followed by the cessation of combustion both in metal–chalcogenide combination reactions (3) and metal–oxide displacement reactions (21). A sudden change is observed when magnetite is reduced with magnesium in a mixture of Fe_3O_4 + yMg. When $y = 4$, all magnetite is reduced to metallic Fe with no excess Mg, the ignition time is about 30 min. As y decreases to 1.7, the ignition time decreases monotonically to below 20 min. Reversing this trend over a narrow concentration range, the reaction becomes gradual for $y < 1.6$ (28). Competing thermodynamic and kinetic factors can explain this behavior. As y decreases, the powder mixture becomes dominated by the brittle oxide particles. The tendency to cold weld into larger particles decreases and the milling efficiency increases. As a consequence, the ignition time decreases although T' decreases simultaneously. At some point T' decreases below a critical value where reaction thermodynamics no longer allows for self-propagating combustion.

The Sn–Zn–S System

Now we return to explaining the behavior of the Sn–Zn–S system (Fig. 1, closed symbols). First we discuss the simultaneous production of SnS_2 and ZnS.

The reaction between Zn and S is highly exothermic; $T' = 4760°C$, almost twice the value for the reactions between Sn and S. The fact that the ignition time for the stoichiometric Zn + S reaction is not significantly shorter than that for the Sn + 2S reaction indicates that it is difficult to initiate the reaction between Zn and S, probably due to a higher critical temperature. Heating curve measurements support this assessment. In Sn-rich Sn–Zn–S systems, Zn behaves much like an inert additive. When Sn sulfides start forming, the temperature increase is too small to initiate the sulfidation of Zn. As the Zn content, x, increases, the ignition time increases and the reaction becomes gradual at $x = 0.185$. Atypical of an "inert" additive, the transition is very sharp, suggesting that it is dominated by the decrease of T' below a critical value.

Starting from the Zn-rich side, Sn does not act as an inert additive. When the temperature increase is sufficient to initiate the formation of ZnS, Sn participates in the reaction as well. Tin sulfides or mixed Sn–Zn sulfides form. As the sulfidation of Sn is less exothermic than the sulfidation of Zn, the reaction heat decreases with increasing Sn concentration, lowering T'. However, this decrease is less than it would be for an inert additive, resulting in a slower increase of the ignition time. When x decreases to below 50%, the heat produced by an incipient reaction is no longer enough to initiate the sulfidation of Zn; the heat produced by the sulfidation of Sn alone is not enough to sustain combustion, and reaction becomes gradual. Tin sulfides formed noncombustively prior to ignition could act as inert additives (26). However, X-ray diffraction indicates that very little if any tin sulfide forms before ignition.

The reason the simultaneous formation of SnS and ZnS (open circles in Fig. 1) behaves differently relates to the behavior of the binary Sn + yS system. When some Zn + S is added to an Sn + S mixture, only Zn acts as an inert additive. The S intended for the sulfidation of Zn reacts with Sn forming higher sulfides. The ignition time increases slowly, similarly to how the binary Sn + yS system behaves close to $y = 1$ (Fig. 2.) Combustion remains possible, but the ignition time increases slightly. When Zn + S is added to the Sn + 2S mixture, both Zn and S act as inert additives. The sulfidation of Sn is more sensitive to the presence of extra S, similar to the behavior of the binary Sn + yS system above $y = 2$. This increased sensitivity makes the suppression of combustion possible.

The exclusion of Zn from the reaction at the Sn-rich side can also explain why the longest ignition times in the monosulfide system are observed around $x = 0.8$ under high-energy conditions while the nonexplosive concentration is $x = 0.38$ in low-energy milling (26). The temperature increase at the start of combustion originates from self-heating described by T' and also from the mechanical energy of the collision. On the Zn-rich side, reaching the critical temperature becomes easier at higher milling intensity, the ignition time gets shorter, but no change in the course of the reaction occurs; both Sn and Zn sulfides form as before. On the Sn-rich side, however, Zn may begin to participate in the reaction at a lower Zn concentration, decreasing the ignition time more decisively and shifting the maximum toward larger Zn concentrations.

The mechanochemical preparation of SnSe and ZnSe is very similar to the preparation of the sulfides, but the heats of formation are larger. The larger chemical energy results in shorter ignition times and a shift of the nonexplosive concentration toward larger Zn content (26) similar to the effect of the larger mechanical energy in the sulfide system.

ABOUT THE REACTION KINETICS

Although the ignition time is an informative, easily measurable, and reproducible parameter, its measurement has to be supplemented by studies of the material at different stages of the process. As an example, X-ray diffractograms on some SnS_2 + ZnS preparations are shown in Fig. 3. Curve a is taken from a mixture at $x = 50\%$ after 50 min of milling. This is only a few minutes before combustion is expected. The diffractogram is dominated by the lines of the reactants; only very weak lines are present from noncombustively synthesized Sn sulfides and some ZnS is also present. This observation contradicts the assumption of Rusanov and Chakurov (26), who assumed that a significant amount of SnS is synthesized before combustion could occur, and this SnS acts as an inert additive. The diffractogram of a sample at $x = 45\%$ after the same milling time is almost identical, although this is a noncombustive composition. Whether combustion happens or not is clearly a threshold effect; there is no obvious difference pointing toward one or the other kinetics. The microstructure of these samples is also very similar, as revealed by SEM. After combustion, the sample consists of the product phases as expected (Fig. 3). Interestingly, the gradual transformation at $x = 45\%$ also accelerates during the next 50 min, but the products are clearly very different. Much of Zn and virtually all Sn form nanocrystalline ZnS and SnS_2, and a noncrystalline sulfide phase.

It is interesting that the reaction rate increases after the first 50 min of activation even when the reaction remains gradual. Similar fast but not combustive reactions were observed in the mechanochemical synthesis of nickel sulfides (29). These results show that "activation," thorough mixing, and the formation of lattice defects are necessary for the mechanochemical reactions to progress at a substantial rate. Whether the reaction turns combustive or it

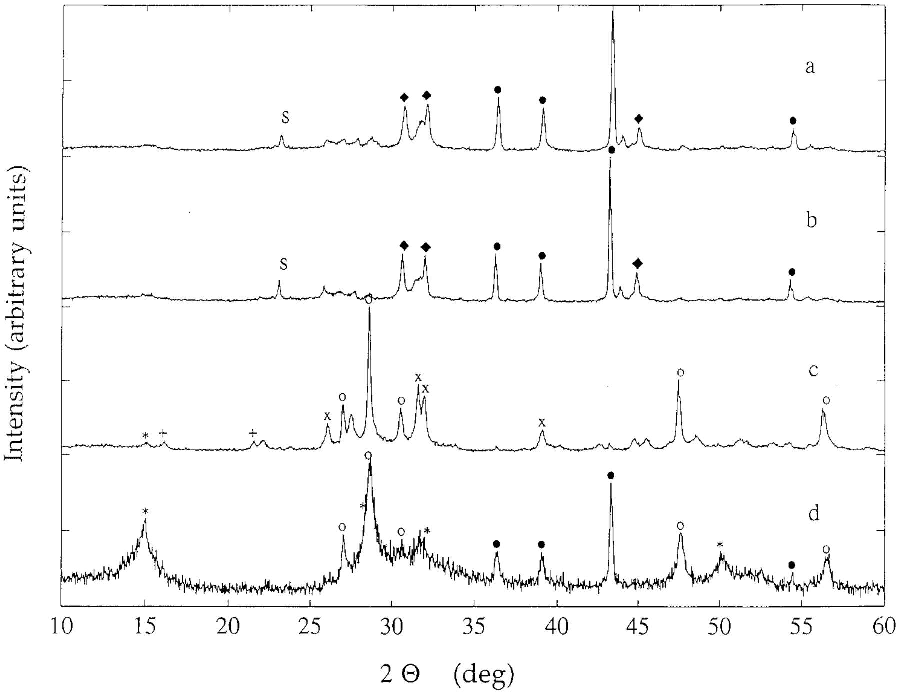

FIG. 3. X-ray diffractograms of $x(\mathrm{Zn} + \mathrm{S}) + (1 - x)\ (\mathrm{Sn} + 2\mathrm{S})$ mixtures ball milled for times t. (a) $x = 50\%$, $t = 50$ min; (b) $x = 45\%$, $t = 50$ min; (c) $x = 50\%$, $t = 55$ min; (d) $x = 45\%$, $t = 100$ min. Only some diffraction peaks are marked: (●) Zn, (◆) Sn, (○) ZnS, (*) SnS_2, (+) Sn_2S_3, (×) SnS.

becomes faster but still gradual after this period depends on the details of the energy balance. It is also possible that combustion starts at some point, although it does not escalate into the entire volume of the milling vial (18). A small abrupt temperature increase corresponding to such limited combustion was observed on the gradual-combustive borderline in the reduction of magnetite by magnesium (28). A more detailed discussion of the phase transformations in both combustive and noncombustive sulfide systems will be presented separately (30).

CONCLUSIONS

Mechanochemical reactions are extremely complex phenomena occurring in a far-from-equilibrium state. In order to understand these reactions, investigations of systems with well-defined "markers"—the ignition of combustion and its suppression—are beneficial. The following phenomena were observed in the formation of Sn and Zn sulfides:

(1) The mechanochemical reactions producing mixtures of SnS and ZnS are combustive at any Sn-to-Zn ratio, contrary to what was observed by Chakurov and Rusanov (26). This is the consequence of the higher impact energy of the mill used in this study.

(2) Noncombustive compositions do exist when the simultaneous preparation of SnS_2 and ZnS is attempted even at the higher milling energies. The behavior can be explained assuming that Zn acts similarly to an inert additive in the Sn-rich systems and Sn decreases the reaction heat in the Zn-rich systems.

(3) The concentration dependence of the ignition time in binary systems does not reflect the stoichiometry of the possible product phases.

(4) The change from combustive to gradual reaction as a function of composition can occur abruptly or it can be preceded by an increase in the ignition time. The actual behavior depends on the interplay of thermodynamic and kinetic factors.

(5) The mechanochemical reactions in the Sn–Zn–S system occur in two steps: activation, during which mixing and defect formation take place, but very little product forms, and fast reaction, which may escalate into combustion.

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