Mechanochemical Reactions in the Sn–Zn–S System: Further Studies

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Although ball milling initiates self-sustaining thermal reaction (combustion) in both Sn–S and Zn–S powder blends, the reaction may be gradual when Sn–Zn–S mixtures are processed under the same conditions. Milling experiments were carried out at several Sn–Zn–S compositions, using different milling balls and ball-to-powder ratios. The ignition time was measured and the phase composition was determined at different stages of the process. The activation time before ignition scales with the ball-to-powder ratio in most cases, showing that the "mechanical dose" is suitable to describe the degree of activation. More energetic milling results in earlier ignition, but it also intensifies the formation of reaction products before ignition, thereby promoting gradual kinetics. The initiation and propagation of a combustion front is similar to self-propagating high-temperature synthesis in a powder compact, but heat transfer to the milling tools is a more important factor. © 2000 Academic Press

Key Words: **self-sustaining reactions; ignition time; mechanical activation; Sn–Zn–S system; SHS (self-propagating high-temperature synthesis); ball milling; mechanochemical reactions.**

INTRODUCTION

Probably the most astonishing phenomenon in the field of mechanically induced self-sustaining reactions is the mutual suppression of ignition in some mixed metal–chalcogen systems. This effect was first reported by Rusanov and Chakurov (1) and more detailed investigations on the Sn–Zn–S system were performed in our laboratory (2, 3). The phenomenon is the following: When a mixture of Zn and S powders is processed in a ball mill, self-sustaining thermal reaction (combustion) is initiated after some activation time and the reactants transform to ZnS within seconds. Basically the same happens when a mixture of Sn and S powders is milled, except that the existence of several tin sulfides complicates the situation. Surprisingly, however, some mixtures of the Zn–S and Sn–S blends react gradually under

identical conditions, forming a mixture of Sn and Zn sulfides without combustion.

It is believed that the understanding derived from detailed investigations of the above process will be applicable to other combustive mechanochemical reactions. Ball milling induces self-sustaining processes in a broad variety of highly exothermic systems, including combination reactions in mixtures like Ti–C (4), Mo–Si (5), Ni–Al (6), and Ni–P (7) and displacement reactions between a metal oxide or halide and a more reactive metal (8–11). An important motivation to study combustive mechanochemical reactions is the potential to use ignition as a marker that defines a certain critical state of the powder. The variation of the ignition time with composition and milling conditions can be utilized to study the activation process preceding ignition. The activation stage of combustive and gradual mechanochemical reactions is similar, and the knowledge obtained from the study of ignition has relevance to mechanochemical reactions in general (12, 13). In summary, although the direct focus of this study is the mutual suppression of ignition in the Sn–Zn–S system, we intend to apply our findings to ball milling-induced reactions in general.

In a typical experiment, a mixture of Sn, Zn, and S powders is milled in a ball mill. The temperature of the mill is recorded and its abrupt increase is used as the sign of ignition. The ignition times measured on the (Sn + S)–(Zn + S) system by Rusanov and Chakurov (1) are reproduced as a function of the mole fraction of Zn (x) on Fig. 1. The data points for the binary reactions are incorporated from an earlier paper by the same authors (14). Although several tin sulfides are known, only sulfur concentrations corresponding to the formation of the monosulfide, SnS, were used in this study. The ignition time increases both when Zn + S is added to an Sn + S mixture and when Sn + S is mixed with the binary Zn + S system. In the narrow concentration range of $0.35 < x < 0.4$, combustion does not happen at all; instead a mixture of Sn and Zn sulfides forms gradually. (Similar results were obtained for the Sn–Zn–Se system. The Zn–Cd–Te and Zn–Sn–Te systems exhibit
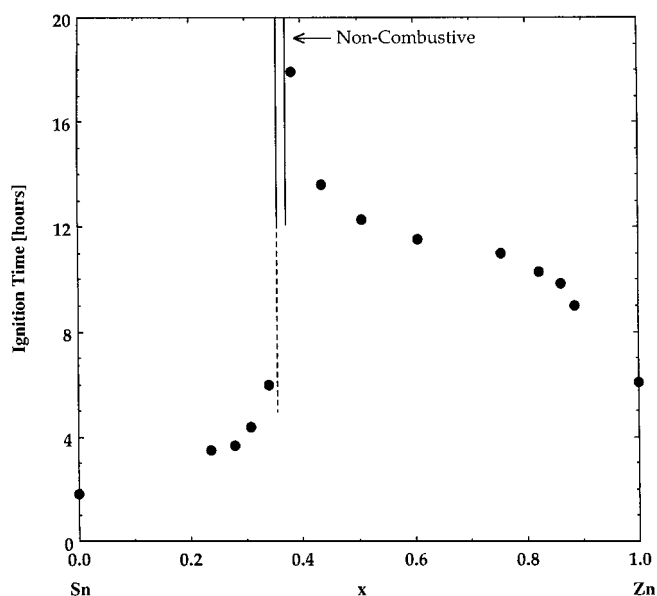
FIG. 1. Ignition time as a function of composition in the $(1-x)(Sn+S)+x(Zn+S)$ system. These data were obtained by Rusanov and Chakurov using a vibratory mill (1).

a broad noncombustive composition range. Only a cusp of the ignition time in the middle of the composition range was observed in the Zn–Cd–S system (1).)

Rusanov and Chakurov explained the above phenomenon as follows (1): Tin reacts with sulfur much more easily than zinc does, as evidenced by the much shorter ignition time of the Sn + S reaction. Consequently, when Zn is added to an Sn–S mixture, it acts as an inert additive, delaying the reaction between Sn and S. Starting with a binary Zn–S mixture, any Sn additive reacts relatively easily with S, but the reaction is not exothermic enough to ignite the reaction between Zn and S. The resulting tin sulfides act as inert additives, delaying the self-sustaining reaction between Zn and S. In this way, the ignition time increases from either end of the concentration scale, leaving a noncombustive region in the middle. X-ray diffraction and Mössbauer spectroscopy data support the early formation of tin sulfides, but not of zinc sulfide, in Sn–Zn–S mixtures.

The experiments of Rusanov and Chakurov were performed in a vibrating one-ball agate mill (1), while many experiments on -1mechanochemical reactions use the SPEX 8000 high-energy shaker mill. For this reason, we tried to observe the mutual suppression of combustion using a SPEX 8000 mixer mill (2). Five grams of powder was processed with five half-inch balls in a round-ended steel vial. The main findings of our experiments were the following:

- The typical ignition times decreased from several hours to tens of minutes due to the more intense milling.
- In powder mixtures with composition $(1-x)(Sn+S) + x(Zn + S)$, combustive reaction was observed at any value of x, contrary to the earlier results (1).

- The mutual suppression of combustion did occur when the disulfide of Sn was assumed as the product; i.e., the powder composition was $(1-x)(Sn+2S) + x(Zn + S)$. Gradual kinetics was found for $0.19 \leq x \leq 0.45$.

The different results of the two investigations indicate the sensitivity of combustive mechanochemical reactions to the milling conditions. Further systematic measurements were necessary to clarify the role of the number, size, and mass of the milling balls and the mass of the processed powder. The results of that work are presented in this paper.

Based on earlier findings and explanations (1, 2), the following working model of the initiation of combustion is adopted: Ball milling initiates a self-sustaining process, if (i) the transfer of mechanical energy to the reactant mixture is capable of initiating the chemical reaction in the "miniforging" (15) volume between the colliding tools (balls and the wall of the container) and (ii) the combustion wave is able to propagate through the rest of the reactant powder. The properties of the Sn + S and Zn + S reactions are quite different from this respect. First, the formation of ZnS is much more exothermic than the formation of the tin sulfides (SnS, Sn_2S_3, SnS_2). This is clearly indicated by the ratio of the heat of formation and the room temperature heat capacity of the products, $\Delta H/C$, that is about twice as large for the formation of ZnS than in the case of Sn sulfides (3). In spite of the large difference in $\Delta H/C$, the ignition times are equal for the formation of ZnS and SnS_2 and it is actually shorter for the formation of SnS. Therefore, the difference in exothermicity must be compensated by some other difference that acts the opposite way. Very probably, the reaction between Sn and S is induced more easily between the colliding milling tools. If this hypothesis is valid, approaching ignition is controlled by different features in the case of Zn and Sn. 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 they get extinguished by heat loss to the milling tools. After milling for some time, the degree of activation reaches a critical state, making the propagation of the reaction into other parts of the powder possible. Consistent with this explanation, XRD finds little ZnS but a significant amount of tin sulfides in samples milled until right before ignition.

The objective of this paper is to substantiate and further develop the above model by investigating the mechanochemical behavior of the Sn–Zn–S system as a function of the milling conditions. The concentration of the starting mixtures was selected according to the anticipated reaction products. This is somewhat arbitrary. As we have shown in a study of binary Sn–S and Zn–S mixtures, there is no direct relationship between the stoichiometry of the possible reaction products and the concentration dependence of the ignition time (3). Instead, the mechanical

Type	Notation	Diameter (in.)	Diameter (mm)	Mass (g)
Large steel	L	1/2	12.7	8.40
Medium steel	M	3/8	9.5	3.54
Small steel	S	1/4	6.35	1.05
Aluminum	Al	3/8	9.5	1.22

properties of the powder, the heat transfer properties, and the thermochemical parameters of the reaction are decisive. One could treat the Sn–Zn–S system as truly three-component, rather than investigating quasi-two-component slices only. However, that, combined with several different milling conditions, would result in a very large number of milling experiments. Therefore, this investigation is restricted to compositions providing either SnS and ZnS or SnS_2 and ZnS as the nominal reaction products.

EXPERIMENTAL METHODS

The milling experiments were carried out using a SPEX 8000 mixer mill (SPEX Industries, Inc.) and round-bottom hardened steel vials. The properties of the milling balls are summarized in Table 1. Later in the text, references are made by giving the number and type of the balls; e.g., 7M stands for seven medium (3/8-in.) steel balls.

The starting materials were Zn (97%, 7 μm,) Sn (99.8%, −325 mesh), and S (precipitated, −60 mesh) obtained from Æsar. The powder mass varied from 1 g to 8 g. The elemental powders and the milling balls were placed into the vial in an argon-flushed glove box to avoid the presence of oxygen and moisture.

The progress of the reaction was monitored by measuring the temperature of the milling vial with two type K thermocouples attached to the top and bottom surfaces. In most cases, milling was performed without interruption. In a few cases, the milling process was interrupted, the powder was "aged" for a few hours, and then milling was resumed. The

interruption did not decrease the total milling time; i.e., no "interrupted combustion effect" was observed (6).

The phase composition of some samples was determined using either a Philips X"Pert Θ–Θ diffractometer or a conventional continuous-drive Θ–2Θ goniometer and Cu $K\alpha$ radiation. Phases were identified using the JCPDS data base.

RESULTS AND DISCUSSION

Ball Milling Experiments on the $(1 - x)(Sn + 2S)$ $+ x(Zn + S)$ System

Three typical vial temperature versus milling time curves are shown in Fig. 2. The binary Sn + S mixture (curve a) exhibits combustive reaction after about 1000 s of mechanical activation, as indicated by the sudden increase of the temperature. The temperature change is rather small, due to the small heat of formation of SnS_2 and the relatively small mass of the processed powder. The gradual increase of the base temperature is caused by the dissipation of mechanical energy. The temperature–time curve of the Zn-rich sample shows similar behavior with an ignition time of about 1300 s (curve c). The larger reaction heat results in a larger temperature increase. Curve b is typical of a gradual reaction. Notice the different time scale that explains the seemingly faster increase of the base temperature. Beginning at about the same milling time as the ignition time for the other compositions, the temperature begins to increase a little faster and goes through a broad peak around 1800 s. This peak represents the heat released by a relatively fast, albeit gradual reaction. After the peak, the temperature approaches an equilibrium value that is determined by the balance between the mechanical energy input and the heat transfer to the environment.

The mutual suppression of ignition has already been observed in this system (2). The goal of the further investigation is to explore how the composition dependence of the ignition time is affected by the number and kind of the milling balls and the amount of the powder. One parameter that certainly plays an important role is the ball-to-powder
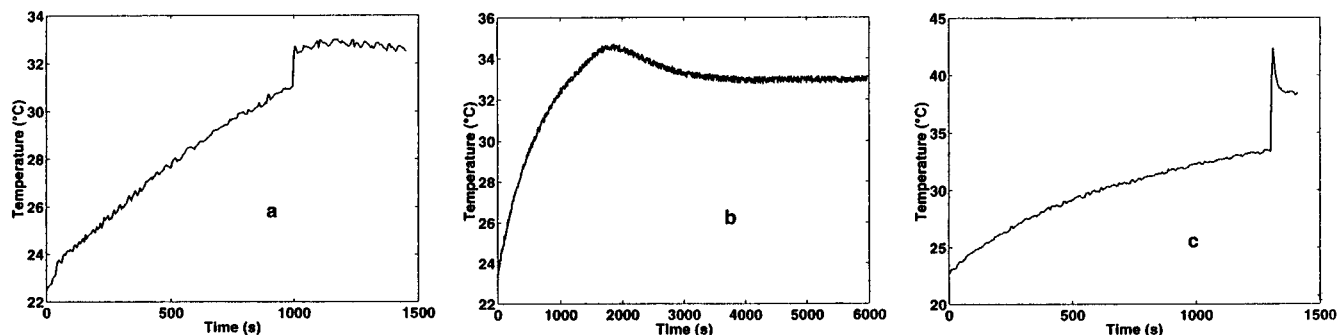

FIG. 2. Vial temperature–milling time curves recorded while milling 2 g of $(1-x)(Sn+2S)+x(Zn+S)$ powder with 7M balls. $x = 0$ (a), $x = 0.25$ (b), and $x = 0.9$ (c).

ratio. As a first approximation, the collision velocity of the impacting balls (about 4 m/s in a SPEX 8000 mill (16)) is determined by the travel length of the balls and the frequency of the motion of the vial. Thus the kinetic energy dissipated during the collisions is proportional to the total mass of the milling balls. The degree of mechanical activation relates to the "mechanical dose," the kinetic energy absorbed by unit mass of powder. Therefore, the milling time is normalized by multiplying it with the ball-to-powder ratio. We present "normalized ignition time" as a function of composition in several figures. Although this approach makes our graphs somewhat model-dependent, it makes recognizing trends beyond the effect of the ball-to-powder ratio easier.

The normalized ignition time of the $(1-x)(Sn+2S) + x(Zn+S)$ system is shown in Fig. 3 for four different milling conditions. Points on the top frame indicate the absence of combustion. In the composition interval where ignition is observed, the normalized ignition times for the different ball–powder combinations agree within experimental error, indicating that the energy absorbed by unit mass of powder is the decisive factor in determining ignition. As the processes during a single collision do depend on the amount of powder caught between the balls (related to the powder mass) and the kinetic energy dissipated in a single collision (related to the size of the balls), the similar normalized ignition times suggest that conditions away from the impact site are responsible for determining whether ignition takes place or not. This may be possible if the critical step of the process is the propagation of the combustion front in loose powder. We will discuss this issue in more detail later.
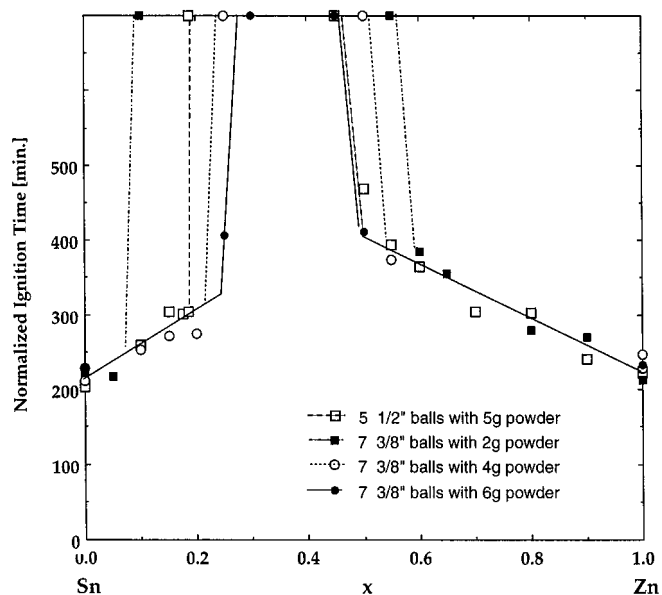
The concentration interval, where ignition does not happen, depends on the milling conditions. A number of experiments were carried out with 7M balls and different powder masses (Fig. 3). The noncombustive interval becomes broader with decreasing mass of powder. This trend is quite counterintuitive, as a smaller amount of powder translates to more intense milling and one would expect easier ignition in the case of more intense milling. Of course, the intuition is correct in the sense that less powder results in shorter ignition time, if ignition does happen. That is already taken into consideration by normalizing with the ball-to-powder ratio. The surprising fact is that the composition range where no ignition is observed is broader when a smaller quantity of powder is used. A possible explanation is the following: If the total powder mass is small, the amount of powder caught between the colliding balls during an individual collision is also small. The energy of the collision is dissipated in this small amount of powder, resulting in a large local temperature increase, intense defect generation, and, consequently, significant production of sulfides in the miniforging volume. At the same time, the powder is not yet capable of propagating the combustion front across the vial. Ignition does not happen, but an increasing amount of product phase is produced. The reaction product acts as inert additive later, hindering the ignition of a self-sustaining process (17). This explanation is supported by the larger sensitivity of the combustive-gradual critical concentration on the Sn-rich side, that relates to the easier formation of Sn sulfides than Zn sulfides before ignition. Results from the earlier investigation with 5L balls and 5 g of powder (2) are also reproduced in Fig. 3. The concentration interval of gradual kinetics is about as wide for that series as it is with 7M balls and 4 g of powder as anticipated.

In order to separate the role of the mass of the milling balls, a few experiments were performed using seven 3/8-in. diameter aluminum balls. The results are compared with those obtained with steel balls of the same number and size (Fig. 4). The mass of the powder load was 2 g in both cases. The milder milling conditions resulted in a narrower noncombustive concentration range again, with a larger difference on the Sn-rich side. This behavior is consistent with the variation as a function of powder mass discussed above. An interesting new feature is that the normalized ignition times agree between the steel and aluminum balls for Sn-rich concentrations, but longer than expected ignition times are obtained when Zn is the dominant component. One can speculate that the activation of the Zn-rich mixture requires a minimum local energy density, rendering a fraction of the collisions ineffective when using the light aluminum balls. It is also possible that the better heat conductivity of aluminum plays some role by removing heat from the collision site more quickly and thereby quenching an incipient reaction more effectively.
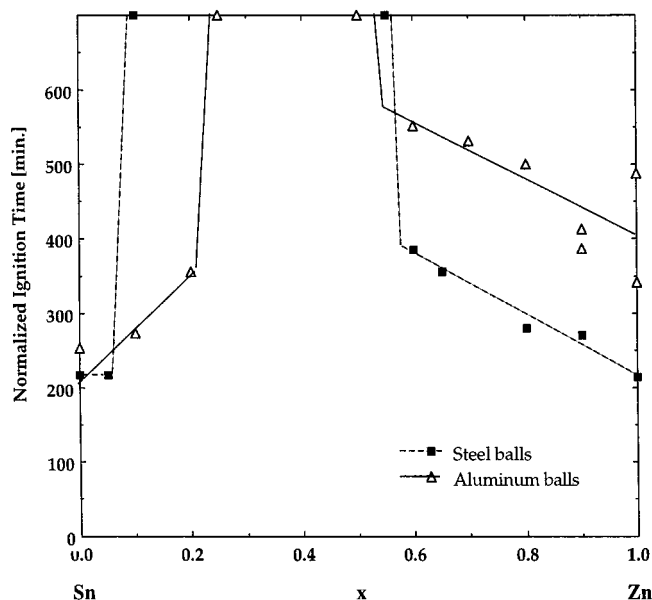

FIG. 3. Normalized ignition times for $(1-x)(Sn+2S)+x(Zn+S)$ mixtures processed with steel balls.

FIG. 4. Normalized ignition times for 2 g of $(1-x)(Sn + 2S) + x(Zn + S)$ mixtures processed with seven 3/8-in. balls.

Ball Milling Experiments on the $(1 - x)(Sn+S) + x(Zn+S)$ System

Chakurov and Rusanov observed the suppression of ignition in this system, in the narrow concentration range of $0.35 < x < 0.4$ (1). Our earlier attempt to demonstrate the phenomenon in a SPEX 8000 mill failed in this system (2). Although the different behavior could be attributed to the very different milling devices employed in the two studies, the question of whether noncombustive kinetics could be achieved in a SPEX 8000 mill by changing the milling conditions remained open.

The earlier milling experiments were carried out on 5 g of powder using 5L balls; the ignition times (multiplied by the ball-to-powder ratio) are reproduced in Fig. 5. Combustion was observed in the entire composition range, but the variation of the ignition time was nonlinear with a shallow maximum at about $x = 0.8$. We speculated that this maximum could increase and probably turn into a region of suppressed combustion, if the milling conditions were modified properly. In particular, the ignition times obtained by Chakurov and Rusanov were much longer than ours. Therefore, using "milder" milling conditions, i.e., decreasing the ball-to-powder ratio, was expected to result in the desired change. Increasing the powder load to 8 g (using 5L balls) did not change the overall shape of the curve. The ignition time increased, although somewhat less than expected on the basis of scaling to the ball-to-powder ratio (Fig. 5). The nonlinearity of the concentration dependence was preserved. Similar results were obtained when milling 10 g of powder with 3L balls (not shown). Milder milling conditions can also be obtained by decreasing the ball size.

However, when 5 g of powder was milled with 10S balls, the ignition times became difficult to reproduce, particularly for Zn-rich mixtures (Fig. 6). Reproducibility was regained when the powder mass was decreased to 2 g, but the ignition time became a closely linear function of the concentration. The concentration dependence obtained for 2 g of powder milled with 7M balls is between the results for 5L and 10S balls (Fig. 5). In summary, our attempts to achieve suppressed combustion by decreasing the milling intensity were not successful. However, it has to be kept in mind that our ignition times are typically shorter than 1 hour, and even the longest one is shorter than 2 hours, while most milling times obtained by Chakurov are significantly longer (Fig. 1). Therefore, our milling intensity is still higher.

The results obtained on the $(1-x)(Sn+2S) + x(Zn+S)$ system showed that more energetic milling conditions, in particular smaller powder mass, could result in broader intervals of noncombustive kinetics. That result suggested that noncombustive kinetics could probably be obtained in the $(1-x)(Sn+S) + x(Zn+S)$ system by decreasing the amount of powder. Moderate reduction of the powder mass made the variation of the ignition time more linear. This was observed with 4 g of powder milled with 5L balls (not shown), 2 g of powder and 7M balls (Fig. 5), and 2 g of powder with 10S balls (Fig. 6). When the powder mass was decreased to 1 g, ignition was no longer obtained for the Sn-rich compositions (Fig. 7). The noncombustive interval is broader for the larger ball mass, just as in the $(1-x)(Sn+2S) + x(Zn+S)$ system. An important difference is, however, that gradual kinetics is observed in the binary Sn+S system and for Sn-rich compositions, not in the
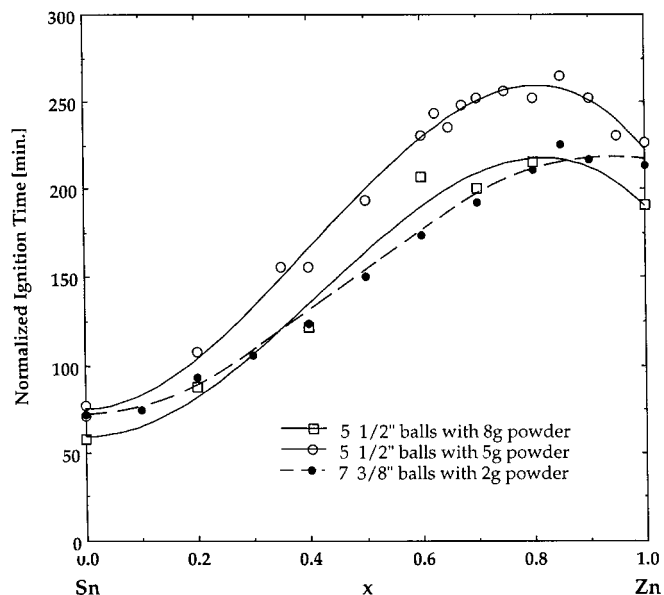

FIG. 5. Normalized ignition times for $(1-x)(Sn + S) + x(Zn + S)$ mixtures processed with steel balls.

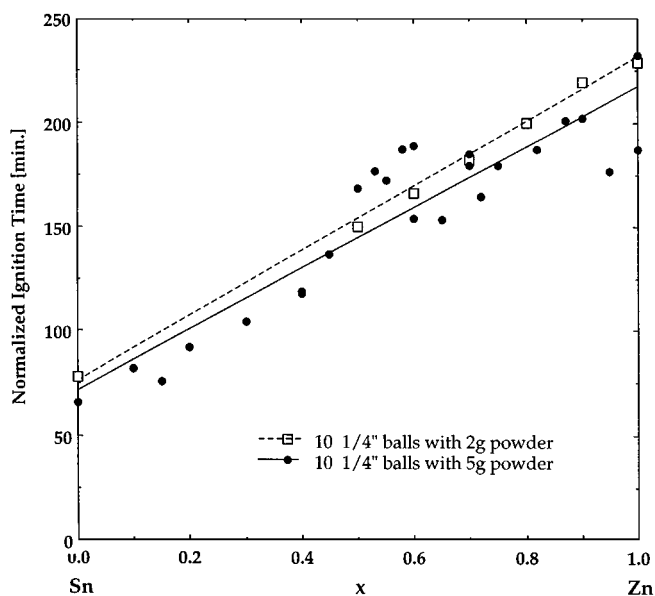**FIG. 6.** Normalized ignition times for $(1-x)(Sn+S)+x(Zn+S)$ mixtures processed with 1/4-in. (S) steel balls.

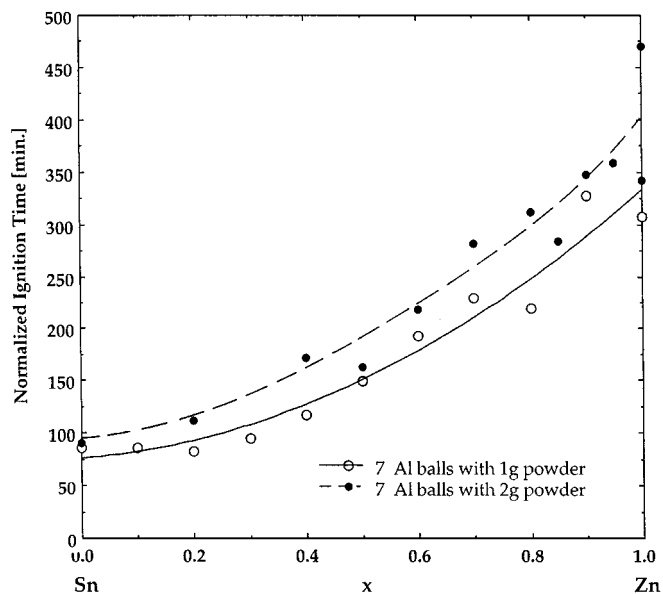**FIG. 8.** Normalized ignition times for $(1-x)(Sn+S)+x(Zn+S)$ mixtures processed with aluminum balls.

middle of the concentration scale. For the compositions where combustion does happen, the normalized ignition time is independent of the ball size. Surprisingly, it decreases linearly with increasing Sn concentration, until the reaction turns gradual abruptly. This behavior may be a consequence of the easier reaction of S with Sn. As the Sn concentration increases (x decreases) initiating the reaction becomes easier and the ignition time decreases. At the same

time, the high reactivity between Sn and S makes early reactions in the miniforging volume easy, but these reactions are extinguished easily due to the low reaction heat. By the time the powder becomes activated enough to propagate combustion, ignition is suppressed by the inert additive effect.

A series of milling experiments was also carried out using Al balls; the results are shown in Fig. 8. Notice that combustion was achieved even with 1 g of powder, due to the less energetic impacts and consequently lower product formation before ignition became possible. Another remarkable feature is the nonlinear variation of the ignition time. On the Sn-rich end of the composition scale, the normalized ignition times are similar to the values measured with steel balls. However, the ignition times are about 50% longer with Al than with steel balls for Zn-rich compositions. As mentioned in connection with the data in Fig. 4 earlier, the less energetic impact of the Al balls is probably the primary reason for the difference. The better heat conductivity of Al may also play some role, although that alone would have a larger effect on experiments with smaller sample mass, in contrast to the results in Fig. 8.

X-RAY DIFFRACTION STUDIES

Phase analysis by X-ray diffraction (XRD) adds an important dimension to understanding the mechanochemical reactions explored in this work. The product of combustive reactions and the kinetics of gradual reactions were studied. Special attention was paid to the state immediately preceding ignition.
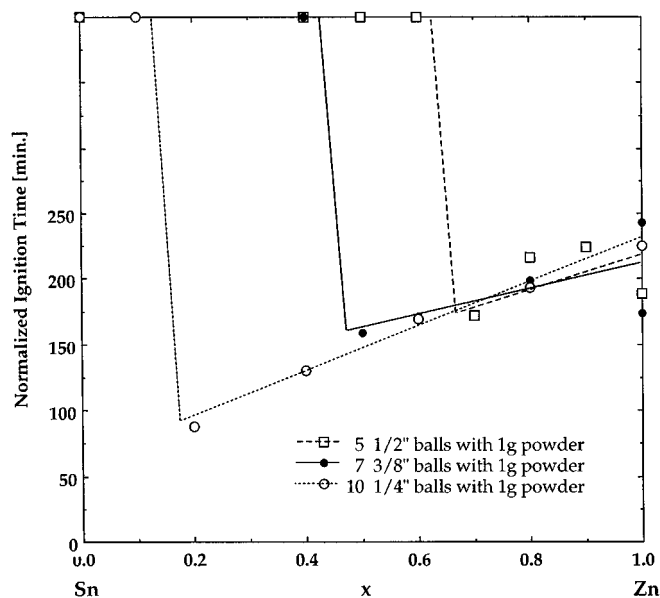

FIG. 7. Normalized ignition times for 1 g of $(1-x)(Sn+S)+x(Zn+S)$ mixture processed with steel balls.

FIG. 9. X-ray diffractograms of $(1-x)(Sn+2S)+x(Zn+S)$ mixtures milled 5 minutes past ignition. Only a few prominent peaks are marked: $\square$, Sn; $\triangle$, Zn; $+$, SnS; $*$, SnS$_2$; $\dagger$, Sn$_2$S$_3$; $\bigcirc$, ZnS.

Typical results on the products of combustive reactions in the $(1-x)(Sn+2S)+x(Zn+S)$ system are shown in Fig. 9. Each sample was prepared by milling 5 g of elemental powder mixture with 5L balls. In order to get results that are reproducible and comparable, the mill was always kept running for 5 min after ignition. (If the mill is stopped immediately after ignition, a mixture of phases with rather unpredictable proportions is observed.) The expected products are mixtures of SnS$_2$ and ZnS. The reaction between Zn and S is more exothermic than the reaction between Sn and S. As a consequence, the formation of ZnS is almost complete, while a mixture of Sn–S phases is produced. The dominant form of ZnS is wurtzite (hexagonal) but the presence of the high-temperature phase sphalerite (cubic) cannot be ruled out due to line broadening and the overlap of the most intense lines with the lines of wurtzite. Ball milling was found to promote the formation of sphalerite (18). However, the product here is formed by a high-temperature reaction. Therefore, the dominance of wurtzite is expected. As far as the tin sulfides are concerned, SnS$_2$ (berndtite) is clearly present, but a large fraction of the sample is Sn$_2$S$_3$ (orthorombic) and a small quantity of SnS (herzenbergite) is also found. Traces of Sn and—to a lesser extent—Zn survive the high-temperature reaction and continued milling. Stoichiometry requires the presence of unreacted S as well, but it is not observed by XRD due to the low scattering amplitude and probably amorphization. It is surprising that the reactions are quite far from complete in spite of the high temperature.

Results on the gradual reaction in a $(1-x)(Sn+2S)+x(Zn+S)$ mixture with $x=0.45$ are presented in Fig. 10. The first XRD pattern was taken after 50 min of milling. The diffraction lines are somewhat broadened, but they correspond to the reactants; only traces of the products are

possible. This state is close to the end of the "activation period". A sample containing 5% more Zn is driven close to ignition by the same amount of milling. Yet, its XRD pattern is practically the same, showing the existence of a similar activation period for both gradual and combustive reactions. Further discussion on the state immediately before ignition will follow later.

Even though a self-sustaining process is not initiated, the rate of the reaction increases significantly after the activation period. In 100 minutes, practically all Sn reacts with S to form very finely dispersed SnS$_2$. Part of the product may be noncrystalline. Interestingly, much of the Zn is still unreacted at this point, showing again that S reacts with Sn much more easily than with Zn. After 360 min of milling, the sample consists of finely divided SnS$_2$ and ZnS particles.

XRD patterns for the $(1-x)(Sn+S)+x(Zn+S)$ compositions are shown in Fig. 11. These samples show self-sustaining kinetics for any x. All samples were milled until 5 min after combustion. The product phases SnS (herzenbergite) and ZnS (wurtzite) dominate the diffraction patterns as anticipated, but a significant amount of unreacted Sn is also present. Very little, if any, Zn remains unreacted after the treatment.

Although there are no mixed Sn–Zn sulfides listed in the JCPDS data base, the existence of such phases is possible. Analogous mixed oxides, such as ZnSnO$_3$ and ZnSn$_2$O$_4$, do exist. In no case did we find any evidence of a mixed sulfide phase. No diffraction lines remain unexplained by the known Zn–S and Sn–S phases; no shift of diffraction lines was observed that could signify substitution of Sn for Zn or Zn for Sn in a known phase. Consequently, reactions in the ternary Sn–Zn–S system require the separation of Sn and Zn, probably contributing to the lack of combustion in systems close to the middle of the composition range.

FIG. 10. X-ray diffractograms of the $(1-x)(Sn+2S)+x(Zn+S)$ mixture at $x=0.45$ as a function of milling time. Only a few prominent peaks are marked: $\square$, Sn, S; $\triangle$, Zn; $*$, SnS$_2$; $\bigcirc$, ZnS.
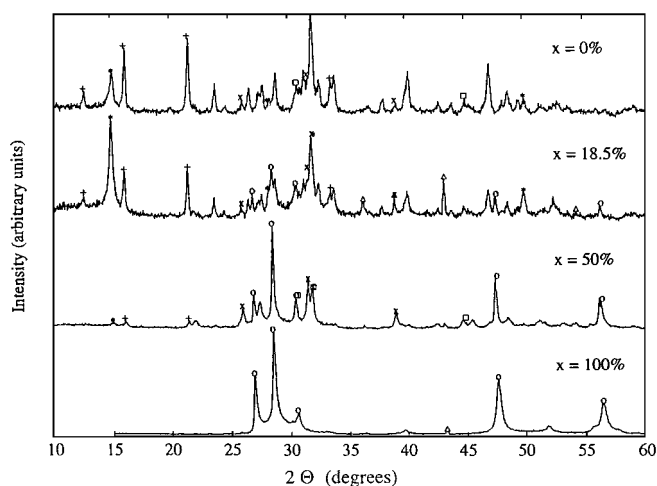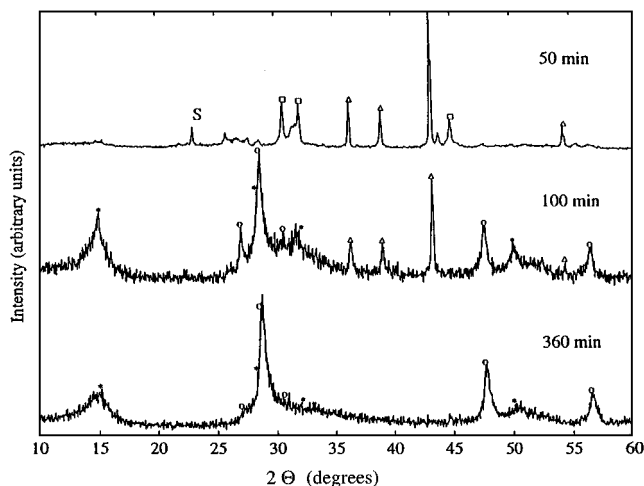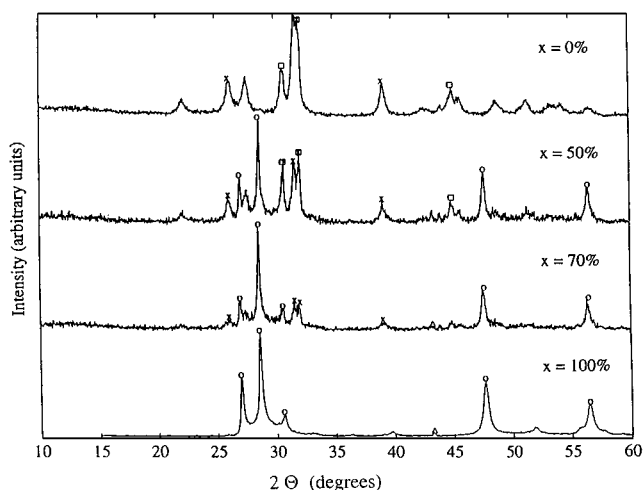
FIG. 11. X-ray diffractograms of $(1-x)(\text{Sn}+2\text{S})+x(\text{Zn}+\text{S})$ mixtures milled 5 minutes past ignition. Only a few prominent peaks are marked: □, Sn; △, Zn; ×, SnS; ○, ZnS.

Several attempts were made at investigating the state of the activated powder immediately before ignition. Typically, a mixture with known ignition time was milled to about 90% of the ignition time and the resulting powder was analyzed by XRD. Measurements were performed on binary Sn–S and Zn–S mixtures as well as ternary ones with different compositions. As the ignition time is uncertain to about 5%, it is impossible to tell exactly how far a particular sample is from the critical state. Nevertheless, all diffraction patterns taken before ignition are dominated by the reactants; very little reaction takes place even if the sample is milled very close to ignition. This statement is more strictly valid for the formation of ZnS in both binary and ternary mixtures; even the existence of small traces is questionable. Tin sulfides, particularly SnS_2, were positively identified in some samples, although the relative intensity of its diffraction peaks never exceeded a few percent. Two points have to be borne in mind though: First, it is possible that the amount of product increases substantially during the last few minutes before ignition. A small increase of the vial temperature, that starts minutes before ignition, has been observed in some other systems indicating the beginning of the reaction before ignition (19). Second, even a few small product particles may influence the reaction kinetics significantly, if they act as nucleation sites.

GENERAL REMARKS

In order to use ignition to mark a certain state of activation, the particulars of ignition itself need to be understood. Although many details of the process remain ambiguous, the results given in the previous section offer some insight.

Ignition occurs at a hot spot, and the combustive reaction propagates from there into other parts of the milling vial. This process is similar to SHS (self-propagating high-temperature synthesis) reactions in powder compacts (20). It is controlled by the energy balance: Heat is released by the chemical process and increases the local powder temperature. Part of the heat is conducted toward the neighboring volume elements, increasing the temperature and initiating further reaction there. Heat is also lost to the environment, limiting the temperature and cooling the powder after the passing of the reaction front. There are two important differences between SHS in a powder compact and in a ball mill: First, in a mill, the geometry is very complicated and it is changing continually. Also, the mixing effect of the mill contributes to the heat transfer and carries combustion from one part of the vial to another. The powder is not uniformly compacted. Second, the heat loss to the milling tools (balls and the milling container) is very intense, as a large portion of the powder is in the relatively thin layer covering the tools. Heat loss to the atmosphere is intense in the loose powder due to mixing by the moving balls.

It is natural to assume that the initial hot spot is in the powder volume compressed between the colliding milling tools (13). In that case, the kinetic energy of the balls is the source of extra energy, both in the form of local heating and due to the creation of activated sites. If the kinetic energy of the collisions is small and the impacts are cushioned by a thick layer of powder, the ignition time is rather uncertain. This is indeed observed when 5 g of powder is milled with 10S balls (Fig. 6). For larger ball-to-powder ratios, hot spots are created easily and ignition depends on the development of a reaction front. As a result, the reproducibility of the ignition time is much better, about 5%.

Heat loss to the milling tools may quench the reaction before it could propagate into other parts of the container. This effect is increasingly important, if smaller amounts of powder are processed. Indeed, as a decreasing amount of powder is milled with the same balls, the concentration interval where gradual reaction is observed gets broader (Fig. 3). This does not mean that no reaction takes place between the colliding surfaces. The case is just the contrary. As the energy of the collision is concentrated into a decreasing amount of powder, more incipient reaction takes place, but the reaction is quickly quenched by heat loss. This factor, combined with the fact that S reacts more easily with Sn than with Zn, may explain why no combustion is observed in the $(1-x)(\text{Sn}+\text{S})+x(\text{Zn}+\text{S})$ system close to the Sn-rich end of the concentration scale and why the concentration range with gradual kinetics gets wider when larger balls are used (Fig. 7). This interpretation is valid only if it is a collision that starts combustion. On the other hand, most milling times scale with the ball-to-powder ratio quite closely, indicating the importance of the absorbed mechanical dose. Whether a self-sustaining process extends to the entire

volume of the milling vial depends on reaching a certain level of activation; the way the initial "hot spot" is created is secondary.

If the amount of powder is large, the local temperature increase due to collisions is small, but the heat loss to the milling tools is also less important. In this case, a model based on the self-ignition of powder particles may be appropriate. Rusanov and Chakurov (1) based their explanation on combining such a model (21) with the changing degree of agglomeration of the powder particles. Unfortunately, it is difficult to compare the details of their results with ours: They did not investigate trends as a function of powder mass and their milling conditions were very different from ours. In any case, the much longer ignition times found in their experiments show that their milling conditions were milder. Consequently, a model based on random self-ignition of a reactive agglomerate may be more appropriate in their case.

The difference between the properties of the Sn–S and Zn–S systems is fundamental to the current explanation of the suppressed combustion in ternary systems. In particular, the ease with which Sn and S react with each other compared to the lower reactivity between Zn and S plays an important role. The necessity of some sort of asymmetry in the properties was also stipulated by Rusanov and Chakurov (1). However, they assumed that the ignition times of the binary systems had to be very different in order to observe suppressed combustion in their mixture. Our results contradict this assumption: the ignition times for the binary $Sn + 2S$ and $Zn + S$ reactions are practically the same, yet mixing them results in noncombustive processes. On the other hand, the ignition time for $Sn + S$ is about one-third of that for $Zn + S$, but the reactions in the $(1 - x)(Sn + S) + x(Zn + S)$ system are combustive under most conditions.

Melting may also play a role, particularly in the propagation of the combustion wave. Melting may limit the reaction temperature and increases atomic mobility. Cyclo-octasulfur (β-S) melts at 119.25°C to a thin liquid. Polymerization takes place in a narrow temperature range starting at 159°C, as shown by a large increase of viscosity (22). The viscosity begins to decrease after a maximum at about 175°C, but it is still rather large when Sn melts at 232°C. Therefore, molten S and Sn can react easily. At the melting temperature of Zn (419°C) sulfur evaporates quickly. (The boiling point of S is 445°C at atmospheric pressure.) Therefore, much S can be lost from the reaction zone before it could react with Zn. The different thermochemical properties of the $Sn + S$ and $Zn + S$ reactions have been confirmed by DTA investigations combined with XRD. While melting is important once a high-temperature reaction has started, it may not be the decisive step as far as the initiation of the reaction is concerned. Selenium melts at 221°C (close to Sn) and the melting point of Te is 449°C, 30°C above the melting point

of Zn. Their viscosity decreases monotonously with increasing temperature. Yet, the features of the reactions involving Se and Te are very similar to those involving S, suggesting that the properties of the solid powder mixture determine if and when ignition happens.

CONCLUSIONS

A large number of experimental data were collected on the ignition time in the Sn–Zn–S system. Several interesting trends were observed that contribute to identifying the important basic steps of the process. In particular, they already show that any theoretical model must pay equal attention to the mechanochemical activation before ignition and to the initiation process itself.

The activation time before ignition scales with the ball-to-powder ratio in most cases. Consequently, the "mechanical dose" is an appropriate parameter to describe the degree of activation. It also follows that the ignition time depends primarily on the state of the powder and not the local processes creating the initial hot spot.

Larger powder quantities favor self-sustaining reactions due to the relative unimportance of heat loss to the milling tools. When a small amount of powder is milled, the reaction may start between the colliding surfaces, but the combustion front gets quenched by the heat loss.

The suppression of combustion in the $(1 - x)(Sn + 2S) + x(Zn + S)$ system was observed in a SPEX 8000 mill earlier (2), although only with one combination of balls and powder mass. In this paper, suppressed combustion was also demonstrated in the $(1 - x)(Sn + S) + x(Zn + S)$ system by milling relatively small amounts of powder. However, the concentration interval where gradual kinetics was observed includes the binary $Sn + S$ mixture. This is different from suppressed combustion in the $(1 - x)(Sn + 2S) + x(Zn + S)$ system, where gradual kinetics was observed only in the middle of the composition range. Consequently, the two phenomena are similar, but not identical. Different conditions may apply in the two cases.

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