

# Gradual and Self-Sustaining Processes in the Sn–Zn–Se System

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Ball milling induces self-sustaining reaction in binary Sn–Se and Zn–Se powder mixtures. But if such mixtures are blended, the ignition time increases at either end of the concentration scale and the suppression of ignition can take place in an intermediate concentration interval. This phenomenon was investigated in  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  and  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  mixtures, by measuring the ignition time as a function of both composition and milling conditions and investigating activated and reacted mixtures using X-ray diffraction and scanning electron microscopy. At the Sn-rich compositions of the first system, ignition happened as soon as the mill was started, in spite of the rather low adiabatic temperature of the reaction. Simultaneous local melting of Sn and Se is suggested as a possible explanation for immediate ignition. It can also explain the asymmetry of the properties of the binary reactions, namely that Sn+Se is less exothermic but easy to ignite, while Zn–Se is more exothermic but difficult to ignite. Similar asymmetry is considered as the reason for the increase of the ignition time and the loss of ignition in other mixed metal–chalcogen systems.

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## 1. Introduction

Interest in metal chalcogenides is fueled mainly by their potentially useful electronic, thermoelectric, optical, and catalytic properties. Mechanochemistry can be used to prepare metal sulfides, selenides, and tellurides either by direct reactions between their elemental constituents or by exchange reactions to also control the particle size [1]. Combination reactions between a metal (M) and a chalcogen element (Ch) have also been used as model reactions for studying the general features of mechanochemical processes. In particular, many M–Ch reactions are exothermic enough to support mechanically induced self-propagating reaction (MSR). In that case, ball milling mixes and activates the reacting components until a solid-state combustion reaction gets ignited [2]. After ignition, the reaction propagates through the powder charge like a self-propagating high-temperature synthesis (SHS) process [3]. The activation time needed to achieve ignition, called the ignition time and represented by  $t_{\text{ig}}$ , is the most important parameter of an MSR. Investigations of  $t_{\text{ig}}$  as a function of composition and milling conditions have provided useful information on the details of mechanochemical reactions [4].

The MSR behavior of M–Ch systems has been studied extensively since the pioneering work of Chakurov and coworkers started in the late 1970s [5]. Their most puzzling observation was the “percolation phenomenon” in mixed  $M_1$ – $M_2$ –Ch systems, where  $M_1$  and  $M_2 = \text{Zn}$ , Cd or Sn and Ch = S, Se or Te [6]. The binary systems exhibited typical MSR behavior, but when a mixture of

two metals was milled with a chalcogen element,  $t_{\text{ig}}$  varied with composition in a very peculiar way. In some cases, for example in powder mixtures with composition  $(1-x)(\text{Sn}+\text{S})+x(\text{Zn}+\text{S})$  ( $0 \leq x \leq 1$ ),  $t_{\text{ig}}$  increased from either end of the concentration scale and in an interval of intermediate concentrations (in the above case in a narrow interval around  $x = 0.37$ ) no self-sustaining reaction was ignited at all. The non-explosive region was much wider in the Zn–Sn–Te and Zn–Cd–Te systems and only a cusp in the  $t_{\text{ig}}$  versus concentration curve was observed in Zn–Sn–Se. In other mixtures, like in Zn–Cd–S,  $t_{\text{ig}}$  varied monotonically [6].

The original explanation of this mutual suppression of ignition (MSI) phenomenon was based on the difference between the ignition times of the two limiting reactions [6]. In the Sn–Zn–S system, Sn reacted with S more readily than Zn did, as indicated by the threefold difference between the ignition times in the binary systems. Consequently, when a small amount of Zn–S mixture was added to an Sn–S mixture, Zn acted as an inert additive initially, thereby increasing  $t_{\text{ig}}$  [7]. When the main metal component was Zn, a small addition of Sn–S resulted in the gradual formation of SnS (and SnS<sub>2</sub>) early in the ball milling process. But that reaction is not exothermic enough to ignite the combination of Zn with S, thus the formed tin sulfides acted as inert additive, increasing  $t_{\text{ig}}$ . In a narrow interval in the middle of the composition range, neither reaction could turn self-sustaining.

Rusanov and Chakurov carried out their experiments in a low-energy single-ball vibratory mill [6]. Some time ago, we performed similar investigations on the  $(1-x)(\text{Sn}+\text{S})+x(\text{Zn}+\text{S})$  system using a more energetic SPEX 8000 shaker mill and obtained somewhat different results [8, 9]. The ignition times were much shorter as expected, but the threefold difference between its value in the binary Zn–S and Sn–S systems remained unchanged.

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Nevertheless, there was no sign of the MSI phenomenon, and  $t_{\text{ig}}$  showed only a smooth maximum rather than a cusp as a function of  $x$ . We also studied the MSR of  $(1-x)(\text{Sn}+2\text{S})+x(\text{Zn}+\text{S})$  mixtures, where the assumed product is the disulfide,  $\text{SnS}_2$ , rather than the monosulfide,  $\text{SnS}$ , of tin. A broad concentration range was found where the reaction was gradual, in spite of the practically equal ignition times of the binary  $\text{Sn}+2\text{S}$  and  $\text{Zn}+\text{S}$  mixtures (Fig. 1). The width of the concentration range without ignition depends on the milling conditions and not only on the components [9]. Thus further studies were needed to explore the nature of MSI.

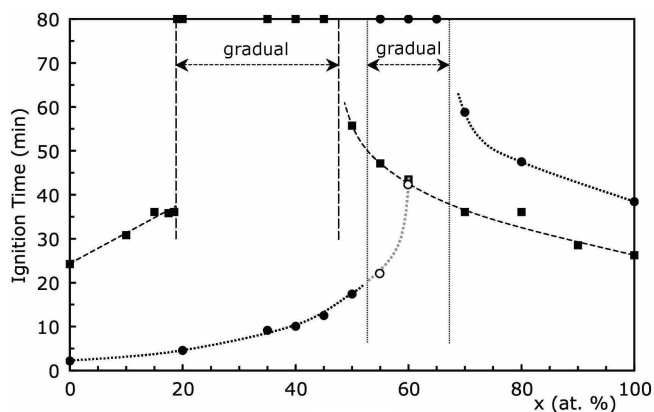


Fig. 1. Ignition time versus composition in  $(1-x)(\text{Sn}+2\text{Ch})+x(\text{Zn}+\text{Ch})$  powder mixtures, with  $\text{Ch} = \text{S}$  (squares, five 12.7 mm balls) and  $\text{Se}$  (circles, twenty 6.35-mm balls). The empty circles correspond to small temperature jumps suggesting limited combustion. The data for sulfide formation are reproduced from Ref. [8]. Points on the top of the frame indicate the compositions of mixtures that did not show MSR.

The above results show that measuring very different  $t_{\text{ig}}$  values in the binary mixtures is not the key to observing MSI. Nevertheless, the asymmetry in the properties of the two metal components and their reactions with the chalcogen must still play a crucial role. In particular, the formation of  $\text{ZnS}$  is much more exothermic than the formation of  $\text{SnS}$  or  $\text{SnS}_2$  as characterized by  $\Delta H/C$ , the ratio of the reaction heat to the room temperature heat capacity of the product. The values of  $\Delta H = -\Delta_f H_{298}$  and  $\Delta H/C$  for the reactions discussed in this paper are listed in Table I, as derived from data in Ref. [10].  $\Delta H/C$  can be understood as a “simplified adiabatic temperature” to characterize the exothermicity of a reaction [4]. As the ignition times for the formation of  $\text{Zn}$  and  $\text{Sn}$  sulfides are not very different, other properties, such as the better efficiency of particle size reduction and mixing, together with lower activation energy, must favor the reaction between  $\text{Sn}$  and  $\text{S}$ . Thus when a mixture of  $\text{Zn}$  and  $\text{Sn}$  is milled with  $\text{S}$ ,  $\text{Sn}$  reacts with  $\text{S}$  first.  $\text{Zn}$  begins to participate in the reaction only after a longer period of activation, but when it does, it results in substantially more self-heating and thereby easier propagation of the reaction.

TABLE I

The enthalpy of formation  $\Delta H$  and the simplified adiabatic temperature  $\Delta H/C$  for the investigated reactions.

Reaction	$\Delta H$ [kJ/mol]	$\Delta H/C$ [K]
$\text{Zn} + \text{S} \rightarrow \text{ZnS}$	205.2	4516
$\text{Zn} + \text{Se} \rightarrow \text{ZnSe}$	163.2	3144
$\text{Sn} + \text{S} \rightarrow \text{SnS}$	107.9	2191
$\text{Sn} + 2\text{S} \rightarrow \text{SnS}_2$	153.6	2189
$\text{Sn} + \text{Se} \rightarrow \text{SnSe}$	94.1	1788
$\text{Sn} + 2\text{Se} \rightarrow \text{SnSe}_2$	124.7	1743

Sulfur melts at a very low temperature (115 °C) thus local melting may affect its reaction with  $\text{Sn}$  and  $\text{Zn}$  during ball milling. The main objective of this work was to investigate, whether replacing sulfur with chemically similar but higher-melting selenium (221 °C) would result in a qualitatively different behaviour. Accordingly, the ignition of MSR was studied as a function of composition in both  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  and  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  mixtures.

## 2. Experimental methods

Milling experiments were carried out using a SPEX 8000 Mixer Mill, round-ended hardened steel vials and steel balls. The number and size of the balls was chosen to obtain convenient ignition times (between a few minutes and about an hour); the actual choices will be given for each series of tests separately. The starting materials were fine powders of 99% purity or better, obtained from Alfa Aesar. Quantities corresponding to the reaction stoichiometry and the chosen total mass were measured and placed into the vial inside an argon-flushed glove box to provide a consistent and inert milling atmosphere. The powders were manually mixed with a spatula before adding the balls and sealing the vial.

The progress of the reaction was monitored by measuring the temperature of the milling vial with a K-type thermocouple taped to its outside surface and covered with a small piece of Styrofoam. A sudden jump signalled the ignition of MSR. Although the magnitude of the temperature change was somewhat arbitrary, the moment of ignition could be determined to better than 5 s uncertainty.

The phase composition of the samples was determined by X-ray powder diffraction using a Philips X’Pert diffractometer operating in the  $\theta-\theta$  mode with a  $\text{Cu}$  tube. Phase analysis was performed by comparing the measured patterns with reference data from the JCPDS database. Scanning electron microscopy was carried out with a JEOL JSM-5600 instrument. In order to obtain SEM samples with representative, uniform, and reproducible morphology, small pellets were cold-pressed from the product powders, broken, and the fracture surfaces were imaged.

### 3. Results

#### 3.1. The variation of the ignition time

The ignition time  $t_{\text{ig}}$  of  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  mixtures is shown as a function of concentration in Fig. 1, compared to the behaviour of the sulphur analogues studied earlier [8]. The main qualitative features of the sulfide and selenide systems are similar: the binary reactions are self-sustaining with both S and Se,  $t_{\text{ig}}$  increases on either side of the concentration scale, and the reaction is gradual in an intermediate composition interval,  $0.19 < x < 0.45$  for the S- and about  $0.53 < x < 0.67$  for the Se-containing system. Yet, there are several important differences in the details:

1. The reactions with Se are much faster than with S, thus the total mass of the balls had to be reduced in order to avoid very short ignition times that would have been difficult to measure accurately. As  $t_{\text{ig}}$  is inversely proportional to the ball-to-powder ratio within reasonable limits [11], the required total ball mass can be estimated easily. Twenty steel balls, each 6.35 mm in diameter, were used with Se, compared to 5 balls, 12.7 mm each for the reactions with S. As the powder charge was 5 g, the corresponding ball-to-powder ratios were about 4:1 and 8:1, respectively.
2. While the ignition times of the binary  $\text{Sn}+2\text{S}$  and  $\text{Zn}+\text{S}$  reactions are almost equal, the reaction of Sn with Se is very fast, almost 20-fold faster than the reaction of Zn with Se. The thermodynamic parameters in Table do not explain this behaviour. In fact, the reaction with Se is not very exothermic; it should ignite only after a long activation time.
3. Although no MSR was propagating through the entire powder charge in the selenide system when  $0.53 < x < 0.67$ , the reaction was not strictly gradual either. The temperature of the vial showed small but fast increase at certain times, superimposed on the smooth increase from the dissipation of mechanical energy.

Figure 2 displays the temperature–time recording for the compositions right before, in the middle of, and right after the concentration interval marked “gradual” in Fig. 1. Although the characteristic large temperature “jump” is missing at  $x = 0.6$ , there is a small abrupt temperature increase at 2525 s, suggesting a fast exothermic reaction that involves only a small fraction of the charge. A similar feature was also observed at  $x = 0.55$ . The time of the first limited combustion event on each curve — shown by empty circles in Fig. 1 — fits smoothly on the extension of the ignition time–concentration curve, suggesting that they correspond to a local reaction that does not propagate through the entire charge. The signature of fast, but not abrupt heat release can also be noticed after about 3950 s. This may be the result of

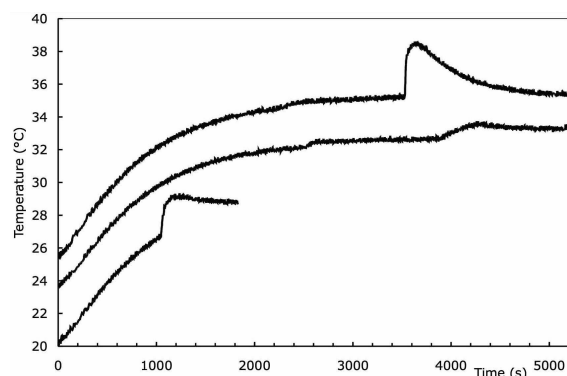


Fig. 2. Temperature of the milling vial as a function of milling time for  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  powder mixtures, with  $x = 0.5$  (lowest curve),  $x = 0.6$  (middle curve, shifted up by  $2^\circ\text{C}$ ), and  $x = 0.7$  (upper curve, shifted up by  $4^\circ\text{C}$ ).

many local combustion events or a period of fast but essentially gradual reaction. Notice that the fast reaction begins later than  $t_{\text{ig}}$  at  $x = 0.5$  and  $0.7$ , suggesting that the selenide formed during the first abrupt reaction and perhaps also by gradual reaction retards this later reaction. These results suggest that although the reaction can be ignited easily by the mechanical action of the colliding balls, the conditions are not favourable for thermal propagation at these compositions.

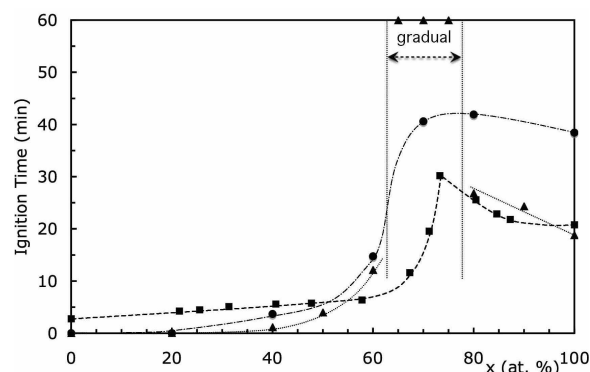


Fig. 3. Ignition time versus composition in  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  powder mixtures. Circles: SPEX mill, twenty 6.35 mm balls. Triangles: SPEX mill, five 12.7 mm balls; the ignition times are multiplied by 2 for easier comparison. Squares: vibratory mill data from Ref. [7], divided by 15.

The strong influence of the milling conditions is demonstrated by the results on the  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  system (Fig. 3). The ignition times obtained with vibratory mill (squares) are finite in the entire concentration range and show a “cusp”, but no region without MSR [5]. When twenty 6.35 mm steel balls are used to mill 5 g of powder (circles), the cusp is replaced with a broad asymmetric. The concentration dependence of  $t_{\text{ig}}$  is very asymmetric. For  $x \leq 0.2$ , the self-sustaining reaction ignites immediately upon starting the mill; no activation is needed. Figure 4 shows the vial temperature as

a function of milling time for the immediate reaction at  $x = 0$  and at a composition ( $x = 0.6$ ) showing the typical “jump” at ignition after activation. The fast temperature increase right after starting the mill signals the immediate ignition of MSR in the case of the binary Sn+Se reaction. As the Zn content is increased,  $t_{\text{ig}}$  increases, especially quickly between  $x = 0.6$  and  $0.7$ . The ignition time of the binary Zn+Se reaction is quite long, about 38 min. Nevertheless, the substitution of some Sn for Zn still increases  $t_{\text{ig}}$  slightly.

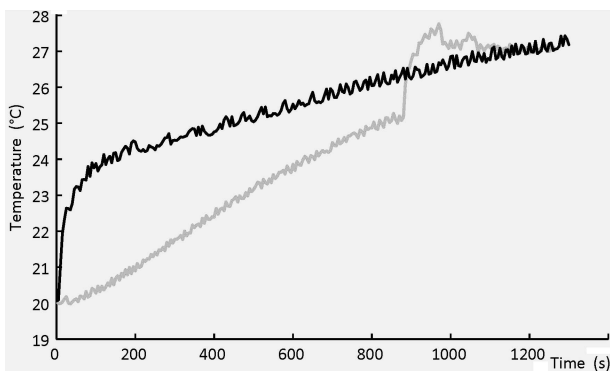


Fig. 4. Vial temperature versus milling time for  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  powder mixtures milled with twenty 6.35 mm balls. Immediate ignition is observed for  $x = 0$  (black line) while  $t_{\text{ig}} = 885$  s at  $x = 0.6$  (gray curve).

At somewhat higher milling intensity, in this case when using five 12.7 mm balls, typical MSI phenomenon was observed between about  $x = 0.63$  and  $0.77$  (Fig. 3, triangles). The concentration dependence of  $t_{\text{ig}}$  remained very asymmetric, with essentially instantaneous ignition on the Sn-rich side and  $t_{\text{ig}}$  of about 9.4 min on the Zn-rich side. The temperature of the milling vial increased smoothly when mixtures with gradual kinetics were milled; periods of fast increase, similar to those observed for  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  mixtures, did not occur. It is of interest to note that a similar change from gradual reaction to MSI behaviour could not be attained in the analogous reactions with S [9]. Although, as usual, the reaction became gradual when the amount of the milled powder was decreased, it happened first at the Sn rich end of the concentration scale and not at intermediate compositions.

The change of milling intensity from using twenty 6.35 mm balls to five 12.7 mm balls not only introduces an interval with no ignition, but also changes the shape of the entire ignition time versus concentration curve. Usually  $t_{\text{ig}}$  is inversely proportional to the ball-to-powder mass ratio, if all the other conditions — in particular the composition of the starting mixture and the impact velocity of the balls — are kept constant [12]. The reason for this proportionality is that the degree of mechanical activation depends on the total mechanical dose (energy/mass) absorbed by the powder and reaching the level of activation required for ignition takes

less time if the dose rate is larger due to using more or heavier balls or absorbing the energy in a smaller amount of powder. This proportionality is not valid in the  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  system (Fig. 3), not even at the binary Zn+Se end. The ball-to-powder mass ratio doubles when going from twenty 6.35 mm balls to five 12.7 mm balls without changing the powder mass (circles to triangles) but  $t_{\text{ig}}$  does not simply reduce to one half at every composition. (As the ignition times were doubled for the data with five 12.7 mm balls to aid comparison, the two curves should coincide in Fig. 3.) This behaviour suggests that factors other than mechanical activation in the solid state — particle size reduction and defect accumulation — must be at work.

### 3.2. X-ray diffraction phase analysis

X-ray diffraction phase analysis has been carried out on every sample. This was particularly important when no temperature jump indicating ignition was observed, thus knowledge of the phase composition was needed to establish whether milling was interrupted before the start of the reaction or the reaction has happened already, but gradually, without any clear signature in the temperature-time recording. Some XRD patterns of  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  mixtures are shown in Fig. 5. Similar results were obtained for the other investigated systems.

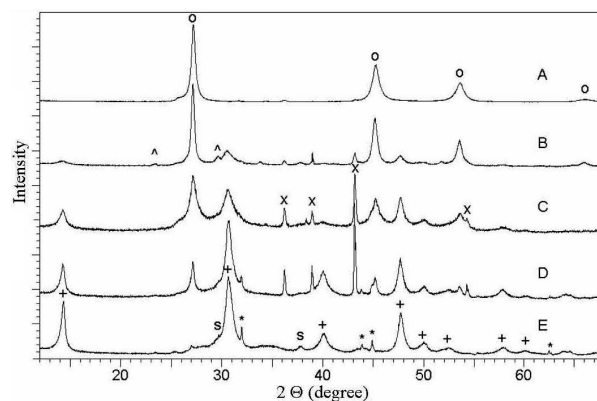


Fig. 5. XRD patterns of selected  $(1-x)(\text{Sn}+2\text{Se})+x(\text{Zn}+\text{Se})$  powder mixtures after milling 5 g batches of powder with twenty 6.35 mm balls. Patterns A, B, D, and E for  $x = 1, 0.7, 0.5,$  and  $0$  were taken after MSR; pattern C for  $x = 0.6$  was taken after 90 min of milling. Symbols o, +, s, x, \*, and ^ correspond to the phases ZnSe, SnSe<sub>2</sub>, SnSe, Zn, Sn, and Se, respectively.

Pattern A of Fig. 5 was obtained from a binary Zn+Se sample after MSR. In this case, ignition occurred after 2305 s of milling and the mill was kept running for an additional 1835 s. The transformation is practically complete, as expected for a highly exothermic reaction that propagates easily ( $\Delta H/C = 3144$  K.) The main product is cubic ZnSe (JCPDF 37-1463); the small shoulder at about 26° may indicate the presence of some hexagonal ZnSe (JCPDF 15-0105.) The pattern of the binary

Sn+2Se sample (curve E) is more complicated. This mixture ignited very fast, after only 130 s, and milling was continued for an additional 1070 s to obtain a uniform sample. Although SnSe<sub>2</sub> (JCPDF 23-0602) is the dominant phase, the presence of some unreacted Sn is clear and a trace of Se may also be present. A small amount of SnSe (JCPDF 48-1224) is also observed. The reaction is incomplete, because it is not very exothermic,  $\Delta H/C = 1743$  K, thus it did not propagate into every segment of the powder charge.

Spectra B, C, and D represent intermediate  $(1-x)$  (Sn+2Se)+ $x$ (Zn+Se) compositions with  $x = 0.7, 0.6,$  and  $0.5$ . The phase composition varies gradually, in spite of the fact that MSR took place at  $x = 0.7$  and  $0.5$ , but not at  $x = 0.6$ . This result suggests that the seemingly gradual reaction at  $x = 0.6$  may in fact be a series of local combustion events, none of them producing enough heat to propagate beyond the powder trapped between the colliding tools. Nevertheless, its mechanism is not substantially different from the MSR reaction observed at lower or higher Zn concentration. ZnSe and SnSe<sub>2</sub> are the main product phases. Interestingly, the amount of unreacted Zn increases with the increasing Sn fraction, suggesting that a less exothermic reaction can leave more Zn behind and supporting the idea that Zn acts as an inert component in Sn-rich powders. On the other hand, Sn reacts very easily upon direct mechanical action, thus the amount of unreacted Sn is much less. The width of the XRD peaks relate to the duration of milling after MSR, as relatively large crystals with few defects form during the high temperature reaction, but further milling reduces the size of the coherently scattering grains and introduces lattice strain. The typical grain size estimated using Scherrer's equation is between 15 and 30 nm. Pattern D has the narrowest lines, as the sample was milled only for 780 s after MSR. The lines of pattern B are broader, as the milling time after ignition was 1665 s. Pattern C represents a sample that was milled for 5400 s without a global high temperature reaction, thus it has broader lines, indicating smaller grains and larger random strain.

A series of 3 g samples, milled for several pre-set durations with five 12.7 mm steel balls were prepared at the composition  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  where the reaction is gradual. The samples represent a time series from a mixture of the starting components to the final products. The XRD spectra at some representative states of the reaction are shown in Fig. 6. The first 60 s of milling results in broadening of the peaks, especially of Se, indicating grain size reduction and the accumulation of defects (pattern A). No product is observed at this stage. The sample milled for 480 s (pattern B) represents an early stage of the reaction. Beside the expected final products, namely SeSe and ZnSe, a considerable amount of SnSe<sub>2</sub> is detected. This is not surprising, as the reaction takes place at interfaces between the reactant particles, where diffusion rates rather than the overall composition determine the initial products and their relative amounts. Sn

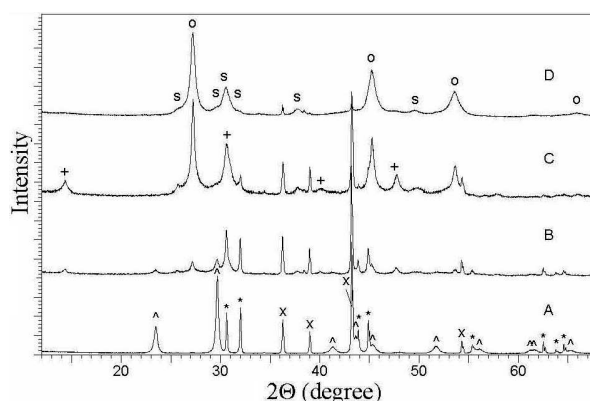


Fig. 6. XRD pattern of  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  powder mixtures after milling 5 g batches of powder with five 12.7 mm balls. Patterns A, B, C, and D were taken after 1, 8, 18, and 80 min of milling, respectively. The symbols used to identify phases are the same as in Fig. 5.

reacts with Se faster than Zn, as can be seen qualitatively by comparing the intensities of the  $(1\ 0\ 1)$  line of Sn at about  $32.0^\circ$  and the  $(0\ 0\ 2)$  line of Zn at about  $36.3^\circ$  in patterns A and B. Very little unreacted Sn is left after 1080 s of milling (pattern C), but the amount of Zn metal is still considerable. The relative amount of SnSe<sub>2</sub> and SnSe is difficult to judge due to the overlap of the lines, but the presence of both is obvious. After very long time, SnSe<sub>2</sub> combines with Sn to form SnSe and the final phases are SnSe and ZnSe, corresponding to the overall composition (4800 s, pattern D). A trace of Zn metal is still present.

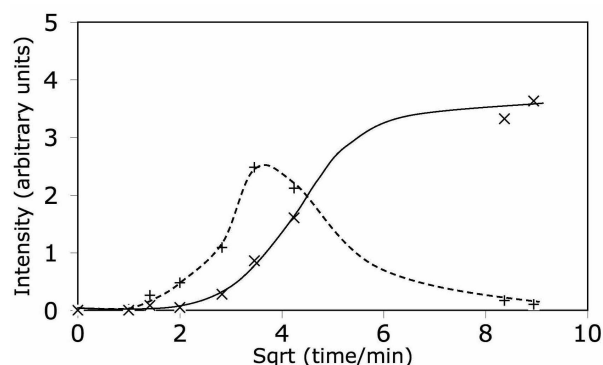


Fig. 7. Semi-quantitative kinetics of the formation of SnSe<sub>2</sub> (+) and ZnSe (x) in a  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  powder mixture, estimated from XRD line intensities.

The intensity of appropriate diffractions lines was used to investigate the reaction kinetics (Fig. 7). As the main lines of SnSe are broad and overlap with intense lines from other phases, the amount of SnSe is difficult to determine. But the relative amounts of SnSe<sub>2</sub> and ZnSe were obtained successfully as a function of milling time by comparing the intensities of appropriate well-resolved lines. The important point is that the formation of Sn selenides (in particular the intermediate SnSe<sub>2</sub> phase) clearly precedes the formation of ZnSe.

### 3.3. Scanning electron microscopy

Ball milling causes mixing and morphological changes such as comminution and agglomeration, in addition to the observed chemical changes. Typical secondary electron SEM images of a  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  sample milled with five 12.7 mm balls for several different periods are shown in Fig. 8. Image 8a shows an early stage of the process after only 1 min of milling. Some large ( $\approx 5\mu\text{m}$ ) rounded Zn particles are visible, mixed with more randomly shaped Sn and Se powder particles. Signs of deformation, mixing, and agglomeration are visible on the scale of a few  $\mu\text{m}$ . Practically every particle shows signs of flattening or breaking after 4 min (image 8b); this is the time when the reaction between Sn and Se starts. Mixing is more thorough at this point, as can better be seen by comparing a pair of SEM images obtained from the same area, one using secondary electrons for mainly morphological contrast (Fig. 9a) and the other back-scattered electrons that provide stronger elemental contrast (Fig. 9b). On the back-scattered electron image Zn is darker and Sn is lighter than expected from morphology alone. Very soft Sn is smeared into layers or fragmented into micron or submicron particles at this stage, forming ample interface between Sn and Se that makes the formation of Sn selenides easy. On the other hand, much of Zn is still in larger particles, thus the interface area between Zn and Se is not sufficient for substantial reaction. It is still possible to identify regions of pure reactants, such as the light Sn particle near the top of the right edge of the image, or the lower part of the particle in the upper left corner. The large dark particle on the lower part of the right side is mostly Zn. Returning to Fig. 8c, it is clear that milling for 12 min results in more uniform powder morphology, although the reaction of Sn and Se is incomplete and only about 25% of Zn reacted at this point. Fines smaller than 100 nm can be resolved at higher magnification. The final product consists of micron-size particles with fine inner structure and it is quite uniform (Fig. 8d).

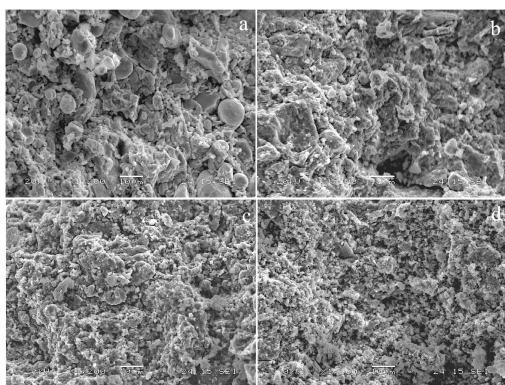


Fig. 8. Secondary electron SEM images of  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  powder mixtures milled with five 12.7 mm balls for 1, 4, 12, and 70 min (parts (a), (b), (c), and (d)).

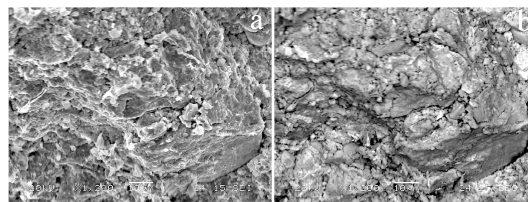


Fig. 9. Comparison of the secondary electron (a) and backscattered electron (b) image of a  $0.3(\text{Sn}+\text{Se})+0.7(\text{Zn}+\text{Se})$  sample after milling for 4 min.

## 4. Discussion

Let us consider two metal–chalcogen powder mixtures,  $\text{M}_1\text{–Ch}$  and  $\text{M}_2\text{–Ch}$  that separately react with a self-sustaining reaction during ball milling. ( $\text{M}_1$  and  $\text{M}_2$  are simple metals, Sn and Zn in this paper, and Ch is a chalcogen element.) If the two mixtures are blended in various proportions, it may be possible to obtain a mixture that does not ignite, but only forms the chalcogenide products gradually. This MSI phenomenon is rather surprising. One would rather expect the opposite behavior, namely that whichever component ignites first, it should also ignite the other. The reactions should promote rather than hinder each other. In fact, such behavior was observed in mixed systems such as  $(1-x)(\text{CuO}+\text{Zn})+x(\text{CuO}+\frac{1}{2}\text{Si})$  and  $(1-x)(\text{FeCl}_3+\text{Al})+x(\frac{1}{2}\text{Fe}_2\text{O}_3+\text{Al})$  [13]. Thus finding detailed explanation of the MSI behaviour may contribute to our understanding of mechanical activation and ignition in general.

Let us consider the situation in some more detail. First, it is of interest to note that only two-component reactions, namely the combination of either Sn or Zn with Se, were observed. There was no detectable alloying of Sn and Zn before the formation of the selenides. This is not surprising, as the Sn–Zn phase diagram shows very limited mutual solubility and no intermetallic compound. Nevertheless, the size difference between Zn and Sn atoms is less than 6% and ball milling produces metastable phases and supersaturated solid solutions in other systems [14], thus the lack of Sn–Zn alloys is not self-evident. Only binary ZnSe, SnSe, and SnSe<sub>2</sub> form, without any sign of a metastable ternary compound in the XRD patterns. There is no lattice parameter shift that would suggest Sn–Zn substitution in the known phases. The main reason may be that the reactions between the metals and the chalcogenide take place before thorough mixing and alloying of the metals would be possible. This interpretation is supported by the fact that the MSI phenomenon was observed in Zn–Cd–Te where alloying and substitution between the metals is more likely, yet no mixed Zn–Cd chalcogenide products were reported [6]. This question deserves further investigation. But for the forthcoming discussion, we assume that the Sn+Se and Zn+Se reactions share the chalcogen reactant and heat transfer couples the two processes, but otherwise they take place independently.

The ignition and propagation of a self-sustaining reaction requires substantial self heating, represented by a high value of  $\Delta H/C$ . If the conditions are otherwise equal, more exothermic reactions tend to ignite more easily, i.e. after a shorter activation time. Comparison of the  $\Delta H/C$  data from Table I with the ignition times ( $t_{\text{ig}}$ ) of the binary reactions shows rather unexpected behavior. The formation of ZnSe is much more exothermic than the formation of the tin selenides, yet  $t_{\text{ig}}$  is much longer in a binary Zn–Se mixture than in Sn–Se mixtures. Actually,  $t_{\text{ig}}$  of the Zn+Se reaction is quite ordinary, 38.4 min with twenty 6.35 mm balls (Fig. 1). In comparison,  $t_{\text{ig}}$  of the Zn+S is 27 min using five 12.7 mm balls. Using the inverse proportionality between the ball-to-powder ratio and  $t_{\text{ig}}$  [14], about 54 min would be expected for Zn+S with twenty 6.35 mm balls. As  $\Delta H/C$  is larger for Zn+S than for Zn+Se, it predicts the opposite order between the ignition times, but the difference is small and other circumstances, such as hardness differences, may explain it. The real surprise is the anomalously short ignition time of the Sn–Se reactions. In the Sn+2Se stoichiometry, it is about 2.2 min, almost 20 times shorter than for the Zn+Se reaction, while the Sn+Se mixture ignites as soon as the mill is started. The ignition time is zero, i.e. the reaction is started by the first energetic impact without any prior activation. (Chakurov's ignition time was 42 min for Sn+Se, 21 min for Sn+2Se, and 312 min for Zn+Se using a low-intensity mill [5]. The more energetic Zn+Se reaction is the slower one also in that case, but ignition in the Sn–Se mixtures is far from instantaneous.)

Although it takes a long activation time to ignite the formation of ZnSe, the reaction is highly exothermic. Thus when the MSR propagates through a Zn+Se powder mixture, it consumes the entire charge within seconds. Little or no reactant is left behind. In contrast, the reaction between Sn and Se is much less exothermic. Although it ignites very quickly, the reaction does not propagate well thermally. As a result, it remains incomplete and much Sn and Se remain unreacted after the MSR. The combination of the virtually zero ignition time and the presence of a substantial amount of starting material after combustion makes it possible to miss the MSR entirely [15, 16].

The key question following from the above behavior is this: What is unique about the Sn+Se system that results in practically immediate ignition under energetic milling conditions, in spite of the low reaction heat and adiabatic temperature? How can easy ignition be reconciled with the sluggish propagation and incompleteness of the reaction? Comparison of the properties of the elements involved suggests that the reason may be the relatively low and nearly identical melting temperatures of Sn (232 °C) and Se (221 °C). When a small amount of powder mixture is caught between two colliding balls or a ball and the wall of the container, the particles rub against each other and activation and possibly some reaction take place locally. But most of the energy of the collision transforms to heat, possibly resulting in local

melting. According to the critical analysis of Koch, the temperature increase of the powder compressed between the colliding milling tools in a SPEX 8000 mill is typically 100–300 °C [17]. Thus in an Sn–Se mixture, both components can melt and they melt almost simultaneously, allowing the reaction to proceed quickly in the liquid phase. The result is immediate ignition. The process is not very exothermic, thus the thermal propagation of the reaction is sluggish and heat loss to the milling vial and balls can easily quench it. Also, as ignition happens early when the powder is not thoroughly mixed yet, some reactants can be left behind while the reaction consumes most of the charge. The very short but finite  $t_{\text{ig}}$  in Sn+2Se mixtures can be rationalized on similar grounds.

On the other hand, only Se can melt during an impact on Zn–Se powder, as the melting point of Zn is much higher (420 °C) and it is probably not reached during collisions in the mill. But melting of Se alone does not accelerate the local reaction much, while the molten Se acts as a lubricant and decreases the efficiency of mechanical activation by protecting the Zn particles from deformation and breakage. The consequence is longer ignition time. But the reaction between Zn and Se is highly exothermic. Thus once it ignites, it propagates well thermally and consumes the entire charge.

The above ideas can also be used to explain the variation of  $t_{\text{ig}}$  at intermediate compositions. When a small amount of Zn is added to an Sn–Se mixture, it only contributes to the reaction after much activation, during the final full-blown MSR. Initially Zn behaves as an inert component. Sn and Se can melt and react locally, without involving Zn in the reaction, just like some Sn remains unreacted after MSR in the binary Sn–Se systems. XRD patterns recorded at compositions with no ignition showed that the Sn selenides form before ZnSe does, also suggesting that Sn and Se react early during activation, while Zn acts initially as an inert component (Fig. 6). Eventually, milling results in particle size reduction and mixing, leading to the formation of both Sn and Zn selenides. When Zn is the main metal component and only a little Sn is present, some selenide (SnSe or SnSe<sub>2</sub>) can form early, possibly aided by local melting. But the released reaction heat is far too little to initiate the reaction of Se with Zn. The formed tin selenides get mixed into the charge where they act as inert additives and delay ignition. Both mechanisms operate in the concentration interval with no MSR.

Although the role of melting in ignition requires further investigation, it can also explain the lack of inverse proportionality between the ignition time and the ball-to-powder mass ratio for the  $(1-x)(\text{Sn+Se})+x(\text{Zn+Se})$  system. When different milling ball combinations were used, the ignition time varied with concentration in a rather different way, even for the concentrations far from the concentrations with no ignition. The lack of proportionality suggests that processes other than activation in the solid state must be involved. Melting can be an obvious explanation.

In summary, simultaneous melting of Sn and Se in the powder trapped between the colliding tool surfaces, combined with the relative inertness of Zn, may explain the asymmetry of the Sn+Se and Zn+Se reactions and consequently rationalize the concentration dependence of the ignition time in a tin monoselenide-based  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  series, including the occurrence of MSI in an intermediate concentration interval. But notice that while simultaneous melting could account for the immediate reaction between Sn and Se and it also provides a possible way to explain the asymmetry of the reactions, melting is not essential for explaining MSI. The only necessary conditions are that Sn and Se react with each other easily, forming inert  $\text{SnSe}_2$  and  $\text{SnSe}$  while Zn acts as a relatively inert component until after substantial activation.

Whether local melting plays a role or not requires further investigation. When a low energy mill was used, any melting was unlikely, yet an asymmetry existed and the MSI phenomenon (a cusp in the composition dependence) was observed [6]. No immediate ignition was observed in the Sn+2Se-based series in this work (Fig. 3) thus the effect of melting is not clear there either. The sulfur analogues show similar but not identical behavior. As sulfur melts at a much lower temperature ( $115^\circ\text{C}$ ), it probably acts as a lubricant for both Zn and Sn. On the other hand, the melting point of tellurium is  $450^\circ\text{C}$ , thus the role of melting must be very limited in the equivalent reactions with Te. Thus although the possibility of simultaneous melting of Sn and Se can explain the asymmetry between the Sn+Se and Zn+Se reactions as the root cause of MSI, other explanations may also be possible.

Understanding the origin of MSI requires further testing. More empirical data on  $t_{\text{ig}}$  as a function of various parameters, including composition and milling parameters, as well as detailed characterization of powders at various stages of activation are necessary. Studies of the Te analogues are needed to test the role of melting. The mechanical properties, such as hardness, can influence the efficiency of milling [18]. In fact, the similar hardnesses of Sn and Se can also contribute to the very fast reaction. Also, mechanochemical reactions tend to happen more easily when heavier atoms are involved. Thus the atomic weight increase from Zn to Sn and from S to Se can also be a factor. If so, ignition in Sn–Zn–Te mixture should be very fast. The role of agglomeration and local heat transfer must be explored as well.

## 5. Conclusions

As it was proposed earlier, the loss of MSR in mixed metal–chalcogen systems is the consequence of the very different properties of the binary systems, so that either one of the initial components (in the present case Zn) or a product formed gradually without ignition (here  $\text{SnSe}$  or  $\text{SnSe}_2$ ) can act as an inert component relative to the rest of the system and retard ignition. Strong support for this

general explanation was derived from the behavior of the  $(1-x)(\text{Sn}+\text{Se})+x(\text{Zn}+\text{Se})$  system, milled with a high-energy SPEX 8000 mill. In that case, ignition in the Sn-rich compositions happens immediately after starting the mill, suggesting simultaneous local melting of Sn and Se as a possible explanation. The coincident melting of Sn and Se can also provide a mechanism for the asymmetric behavior of the Sn+Se and Zn+Se reactions and explain MSI in this system. Further studies are needed to clarify the role of melting. In other systems or at lower milling energies, melting may not play any role and hardness, atomic mass, and other properties may determine the behavior upon mechanical activation. In any case, the connection between the MSI and the asymmetry between the properties of the limiting reactions remains valid.

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