The Effect of Inert Additives on the Explosive Mechanochemical Synthesis of Some Metal Chalcogenides

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The effect of different inert additives on the mechanochemical synthesis of SnS was studied. A transition from explosive to nonexplosive mechanochemical reaction was observed. It was shown that this change takes place only when a critical volume x_c is occupied by inert material. The critical volume for a transition from an explosive to nonexplosive mechanochemical synthesis were determined for the chalcogenides of Zn, Cd, and Sn. The x_c values obtained are discussed. On the basis of the new data concerning the critical dimensions r_c of the exploding mechanical aggregates and the percolation phenomena, a mechanism for the transition from an explosive to nonexplosive mechanochemical synthesis is suggested. © 1987 Academic Press, Inc.

Introduction

The data presented in Ref. (*1*) show that the mechanochemical synthesis of some metal chalcogenides is an explosive reaction. This kind of synthesis is characterized by a low degree of interaction between the initial components before the explosion takes place. At a given moment of the mechanical activation an explosion, which is accompanied by mechanical and heating effects, is observed and maximum final product is obtained corresponding to a practically complete synthesis.

The explosive mechanochemical synthesis of the compounds in the system Sn–S was more thoroughly studied in Ref. (*2*). The effect of an inert additive on the nature of the mechanochemical synthesis was also studied. It was established that addition a definite amount of the inert substance con-

verts the explosive synthesis to a smooth, nonexplosive reaction. An explanation of this change was suggested.

It is the purpose of this work to study the effect of different additives on the change in the nature of the mechanochemical synthesis. A great number of explosive mechanochemical syntheses of the chalcogenides of Zn, Cd, and Sn were carried out to determine the mechanism of the transition from an explosive to nonexplosive synthesis.

Experimental

The initial substances for all experiments of mechanochemical synthesis were Zn, Cd, or Sn and a chalcogen element (S, Se, or Te) of high chemical purity. They were taken in amounts corresponding to the stoichiometry of the final compounds. The inert elements used were a polymer, SiO_2,

rhyolite, and Fe. The particle size of the metal component and the chalcogen element added to the initial mixtures was ≤0.5 mm. The average particle size of the inert materials was ~5 μm.

The samples were prepared by joint dispersion of the initial mixtures in a vibration one-ball agate mill KM-1 (DDR) in air. The presence or absence of an impulsive increase of the temperature in the mill indicated whether the mechanochemical synthesis was explosive or nonexplosive (1). The degree of interaction between the initial components to form the final compound was determined by Mössbauer and X-ray analyses using technique and apparatus described in Ref. (2).

In order to determine the effect of the inert additives on the change of the mode of the mechanochemical synthesis of SnS a series of experiments were carried out, the amount of the initial components Sn + S always being 2.5 g. The inert additives used were in weight percentage. When the effect of SiO_2 on the mechanochemical synthesis of the chalcogenides of Zn, Cd, and Sn was studied, the amount of the initial samples was 1.5, 2, and 2.5 g, respectively. This difference is determined by the different time of mechanical activation for these metal chalcogenides until explosive synthesis takes place.

Results and Discussion

The results in Fig. 1 show the effect of different amounts of the inert additives on the time to the explosive effect in the mechanochemical synthesis of SnS, the time increasing nonlinearly as the amount of the inert additive increases. At critical amounts of the inert additives, ~2, 8, 11, and 18 wt% polymer, SiO_2, rhyolite, and Fe, respectively, no explosive effect is exhibited in spite of the continued mechanical activation (≥10 h). Mössbauer analysis shows that complete nonexplosive mecha-
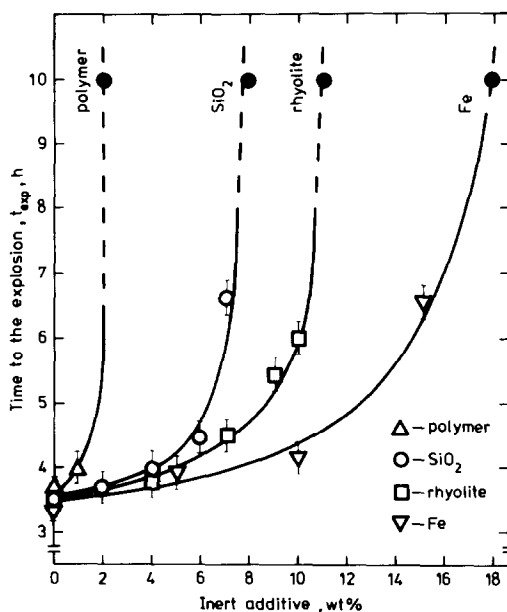

FIG. 1. Mechanochemical synthesis of SnS in the presence of different inert additives. The time prior the observed explosion is shown as a function of the amount of the inert material added. With samples activated mechanically for 10 h no explosive effect is observed. The synthesis of Sns is practically complete and nonexplosive.

nochemical synthesis of SnS takes place. The effect of all inert additives on the nature of the SnS synthesis is analogus, which is in agreement with the results in Ref. (2).

The calculation of the critical relative volume of the inert additive by

$$x_c = \frac{V_{in.ad.}}{\sum_i V_i},$$

where $V_{in.ad.}$ is the volume of the inert material and $\sum_i V_i$ is the total volume of the initial components metal + chalcogen + inert additive, shows that in the four cases in Fig. 1 the critical volumes within experimental error are $x_c = 0.13 \pm 0.03$. In calculating x_c we have not taken into account the partial volume of SnS synthesized nonexplosively before the explosion. A conclu-

sion may be drawn that there is a critical amount of the inert additive which brings about the transition from an explosive to nonexplosive mechanochemical synthesis. In spite of the great differences in the physicomechanical properties (hardness, density, heat conductivity, brittleness, adhesion, etc.) of the four inert additives, this transition occurs only when a critical part of the volume of the sample x_c is occupied by the inert material no matter what it is.

The critical volume of the inert additive needed for the transition from explosive to nonexplosive mechanochemical synthesis was studied for the chalcogenides of Zn, Cd, and Sn. Only SiO_2 was used as an inert material. Figure 2 shows the values obtained for the critical volume as a function of the enthalpy of formation, ΔH°_{298}, for the different compounds. It should be noted that the process of oxidation during the synthesis of the metal tellurides is rather strong and the metal oxides obtained should be considered inert additives. In the calculation of x_c, however, this factor was

not taken into account since the quantitative determination of oxides is difficult.

The analysis of the results in Fig. 2 makes it possible to draw some conclusions: (1) For every explosive mechanochemical reaction there is a characteristic critical volume of the inert additive bringing about the transition from explosive to nonexplosive synthesis. (2) The dependence of the critical volume on the enthalpy of formation of the various metal chalcogenides may be presented by separate curves (curves 1, 2, and 3). This fact may be accounted for by the different reactivities of the chalcogen elements (S, Se, Te). (3) In the case of the metal sulfides, selenides, and tellurides (curves 1, 2, and 3, respectively), the increase of the enthalpy of formation leads to an increase of the critical volume of the inert additive needed for the transition from explosive to nonexplosive synthesis. (4) There is a value of the critical volume $x_c \sim 0.5$ at which all explosive mechanochemical reactions in the synthesis of the metal chalcogenides become
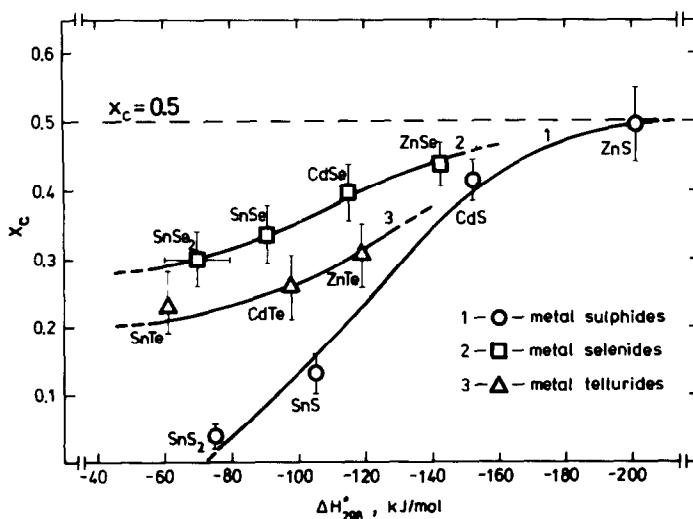

FIG. 2. Mechanochemical synthesis of the chalcogenides of Zn, Cd, and Sn. The critical volume x_c of the inert material SiO_2 needed for a transition from explosive to nonexplosive synthesis is shown as a function of the enthalpy of formation ΔH°_{298} of the corresponding compounds.

nonexplosive. (5) If curve 1 is extrapolated to a zero critical volume of the inert additive it will be seen that a limiting enthalpy of formation exists, $\Delta H^\circ_{298} \sim 70$ kJ/mol, below which the synthesis of some metal sulfides may be only nonexplosive. Data supporting this conclusion are adduced in Ref. (1).

In the syntheses under study the mechanical activation is in fact a process of dispersion and defect formation in the initial mixtures of metal + chalcogen element (3, 4). The dispersion process of the initial components proceeds in three stages (5). In the first stage the particle size progressively decreases. The second stage is characterized by the formation of aggregates from the finely dispersed particles of the initial components. In the third stage the aggregates reach a definite size which does not change with the time. These three stages are greatly influenced by both the type and the operation of the disperser and the mechanophysical characteristics of the materials (6). That is why the time before the observed explosion correlates with the mechanical and physical properties of the dispersed samples. Our studies (7) showed that the formation of aggregates during the second stage of the dispersion process is essential to the occurrence of the explosive mechanochemical reaction. The explosion takes place only when the mechanical aggregates, made up of finely dispersed, defected, and highly compact particles of the initial components and the already synthesized compound reach a definite size. This fact indicates that there is a critical radius of the mechanical aggregates r_c at which the mechanochemical reaction taking place on the surface changes into one proceeding throughout the aggregate under the impact of the grinding body and resulting in a mechanochemical explosion (2).

Figure 3a is a schematic presentation of an aggregate for which $r_1 \geq r_c$. No inert material is added, $x = 0$, and, therefore, the

synthesis is explosive. It is also explosive if $x \ll x_c$ (Fig. 3b). These two cases correspond to the explosive mechanochemical synthesis or pure metal chalcogenides and of metal chalcogenides in the presence of small amounts of inert additive. They are illustrated by the initial sections of all curves in Fig. 1.

The fact that the explosive mechanochemical reaction proceeds only when the aggregates reach a critical size shows that the observed transition from explosive to nonexplosive synthesis should be related to the hindering of the aggregate formation. On the other hand, the transition from explosive to nonexplosive mechanochemical synthesis is analogous to the percolation phenomena studied by Last and Thouless (8) and Watson and Leath (9). Thus, the results shown in Figs. 1 and 2 may be interpreted by the percolation theory known from the classical calculus of probability (10). The percolation phenomena studied in Refs. (8) and (9) are related to the conductivity of accidental networks of resistances while in our case these phenomena are due to heat transfer between the separate parts of the mechanical aggregates. In Ref. (2) we suggested a mechanism of the transition from explosive to nonexplosive synthesis in the presence of a sufficient amount of inert material. The aim of this work is to widen the interpretation of this mechanism by including the aggregate formation process and the percolation phenomena.

The total heating effect of the exothermic reaction in the aggregates with critical size r_c is the observed explosion itself. The addition of a sufficient quantity of the inert material is the reason for the aggregates to break down into pieces thermodynamically. The radius of each piece is less than r_c and, therefore, only nonexplosive mechanochemical synthesis is possible in them. If the size of the separate pieces of the aggregate is greater than r_c the condition for

$r_1 \geq r_c$
$x = 0$

$r_2 \geq r_c$
$x \ll x_c$

$r_3 > r_c$
$x > x_c$

-positions occupied by the inert additive

-formation of continuous chains of the inert additive
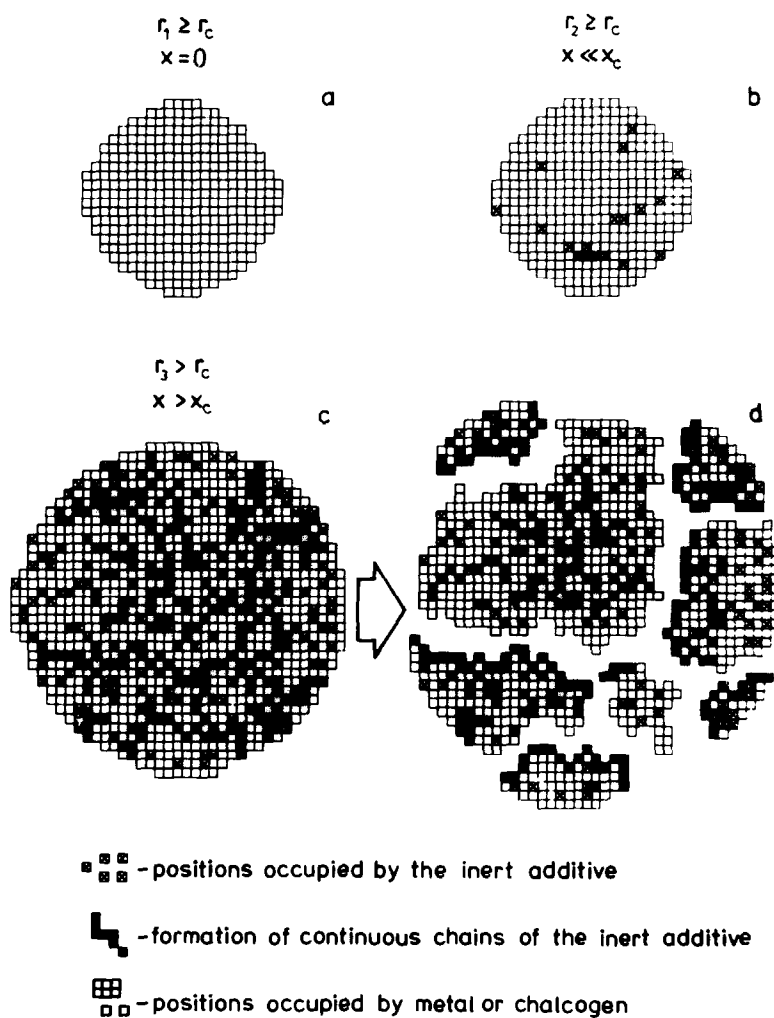
-positions occupied by metal or chalcogen

FIG. 3. A schematic presentation of explosive mechanical aggregates $r_{1,2} \geq r_c$ made up of finely dispersed initial components metal + chalcogen: (a) without an inert additive ($x = 0$) and (b) in the presence of small amounts of the inert additive ($x \ll x_c$). Five percent of the sites in the aggregate were occupied by the inert additive and were assigned by a computer. A schematic presentation of the thermodynamic (c) and mechanical (d) disintegration of a large mechanical aggregate made up of metal + chalcogen + inert additive ($x > x_c$). The computer assigned 40% of the sites in the aggregate to the inert material.

the explosive synthesis is fulfilled but it will have only a local heating effect and the exothermic reaction throughout the whole sample, i.e., the mechanochemical explosion, will not take place.

Figure 3c is a computer-modeled schematic presentation of a mechanical aggre-

gate. Forty percent of the sites in the aggregate are assigned to the inert material by the computer. Smaller volumes outlined by the inert additive, which has a heat-insulating effect, are formed. At the same time the accumulation of the inert material along given directions or on given surfaces makes

it possible for the aggregate to break down into pieces, each having a radius less than r_c. This process is illustrated in Fig. 3d. The cases in Figs. 3c and 3d show two ways of hampering the aggregate formation process when a sufficient quantity of the inert materials is added to the sample. A physical result of the process of inhibiting the aggregate formation is the observed transition from explosive to nonexplosive mechanochemical synthesis.

Figure 4a is an electron micrograph showing the formation of explosive mechanical aggregates $r \sim r_c$ of Sn + S + 6 wt% SiO_2. In spite of the 6 wt% SiO_2 used, the reaction is explosive since $x < x_c$. So aggregate formation is obligatory. Figure 4b is an electron micrograph showing the mechanical breakdown of aggregates of Sn + S + 12 wt% SiO_2. The amount of the inert additives is greater than the critical amount, $x > x_c$, and the mechanochemical synthesis is nonexplosive. The aggregate formation in the second stage of the mechanical activation is greatly hindered in this case. The electron micrographs in Figs. 4a and 4b show how the mechanical aggregates are formed and then broken down. These two processes are illustrated in Figs. 3b and 3d.

If we make use of the terminology of the percolation theory the explosive mechanochemical reaction should be related to the formation of an endless cluster of finely dispersed initial components (metal + chalcogen). The exothermic reaction proceeding in this cluster determines the explosive nature of the synthesis. When a critical amount of the inert material is added a percolation transition takes place and the conditions for the formation of an endless cluster are not fulfilled. The mechanochemical reaction may be explosive only in some separate regions. The critical volumes x_c obtained for the different mechanochemical reactions should be considered percolation thresholds. They determine the

nature of the mechanochemical reaction. If the amount of the inert additives is such that $x < x_c$, then the mechanochemical reaction will be explosive, while if $x \geq x_c$ the reaction proceeds nonexplosively.

Therefore, the percolation concept in the cases concerned comes too (1) the inert additive decreases the probability of contact and chemical interaction between the reagents, and (2) when the inert additive quantities are critical the rising of a self-accelerating explosive mechanochemical reaction is suppressed since the formation of aggregates with critical sizes is impossible.

Study (11) of fast reactions in explosive substances shows that crystals of them with sizes greater then critical are always explosive. If the size is smaller than the critical size the crystals disintegrate slowly. These results are in conformity with the thermal explosion theory and the critical sizes. On the basis of the results described in this paper we consider that the mechanochemical explosion development mechanism should be related to the thermal explosion development mechanism. It is possible then to develop a transition pattern from explosive to nonexplosive character of the mechanochemical synthesis based merely on the thermal explosion theory.

With respect to the mechanism of the transition from an explosive to nonexplosive mechanochemical reaction it is difficult to make a definite interpretation of the various values for x_c. It may be assumed that the difference in the x_c values is due to the following reasons: (1) Different mechanical properties (brittleness, adhesion), solid-state properties (hardness, density, heat conductivity), and physicochemical properties (enthalpy of formation, activation energy) of the dispersed materials (metal + chalcogen + synthesized compound). (2) Peculiarities in the process of aggregate formation for each individual mechanochemical reaction. (3) Different
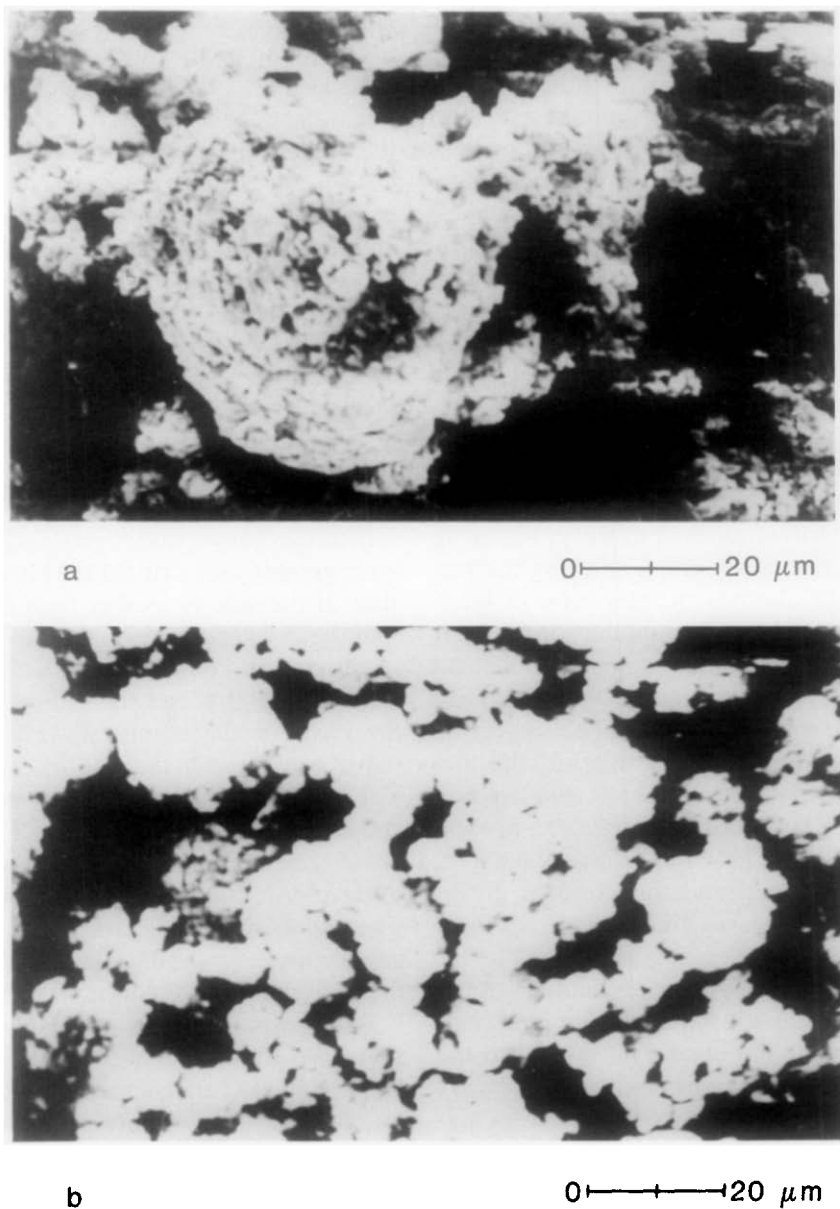
FIG. 4. (a) Electron micrograph showing the formation of explosive mechanical aggregates $r \sim r_c$ made up of Sn + S + 6 wt% SiO_2. The amount of the inert additive is less than the critical amount ($x <$ x_c). The samples are mechanically activated for 4 h. After further mechanical activation for 0.5 h an explosive effect of the synthesis of SnS is observed. (b) Electron micrograph showing the mechanical disintegration of the aggregates made up of Sn + S + 12 wt% SiO_2. The amount of the inert additive is greater than the critical amount $x > x_c$. The samples are activated for 4 h. Further mechanical activation for 12 h does not result in an explosive affect. The mechanochemical synthesis of SnS is a smooth, nonexplosive reaction.

amounts of the synthesized metal oxides which should be regarded as inert materials. (4) Different amounts of the compounds which are synthesized nonexplosively and which, in a way, may also be considered inert materials.

It is comparatively easy to explain the increase of the critical volume x_c with the increasing enthalpy of formation ΔH°_{298} (Fig. 2, curves 1, 2, and 3). According to the mechanism discussed above, the inert additives act as heat insulators within the mechanical aggregates. Obviously, the reactions having a high ΔH°_{298} will need greater amounts of the inert additive and, hence, greater critical volume in order to break the thermodynamic contact between the subvolumes within the whole aggregate.

Conclusion

The effect of different additives (a polymer, SiO_2, rhyolite, and Fe) on the nature of the mechanochemical synthesis of SnS was studied. No matter what inert additive was used a transition from an explosive to nonexplosive reaction was observed. Results with Fe were discussed in Ref. (2). This transition takes place only when the inert material, no matter what it is, occupies a critical part of the volume x_c of the sample. That fact supports the suggestion that the transition from explosive to nonexplosive mechanochemical synthesis is a typical percolation process. A great number of physical phenomena have been explained by percolation theory (12) and the present work shows that the percolation phenomena may also be associated with the mechanochemical process.

The effect of the inert material SiO_2 on the mode of the mechanochemical synthesis of the chalcogenides of Zn, Cd, and Sn was studied. It was shown that any explosive mechanochemical reaction of synthesis of metal chalcogenides may be rendered nonexplosive by addition of a critical amount of inert material. The critical volume of the additive x_c needed for this transition was determined for every explosive reaction. The influence of the mechanical, solid-state, and physicochemical parameters on the x_c values was discussed.

On the basis of the critical dimensions r_c of the exploding mechanical aggregates and the percolation phenomena, a deeper insight into the mechanism of the transition from an explosive to nonexplosive mechanochemical synthesis was suggested.

These results contribute both to clarifying the nature of the mechanochemical synthesis and to the development of its kinetic theory.

Acknowledgment

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