

Percolation Phenomena in Explosive Mechanochemical Synthesis of Some Metal Chalcogenides

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Percolation phenomena are observed during the transition from an explosive to nonexplosive mechanochemical synthesis in Met–Met–Halc systems. The transition occurs under the effect of inert additives. In the systems investigated the inert admixtures are unreacted metals and metal chalcogenides synthesized nonexplosively. Two explosive synthesis mechanochemical reactions and two critical volumes x_{c1} and x_{c2} for the transition from an explosive to a nonexplosive mechanochemical reaction, respectively, correspond to the Met–Met–Halc system. Depending on the x_{c1} and x_{c2} values, three possible cases, considered in the percolation theory, are observed. It is shown that the final product synthesized in a nonexplosive mechanochemical way plays the role of an inert impurity. On this basis, a mechanism is proposed which explains the existence of a series of mechanochemical, in principle, nonexplosive reactions. © 1990 Academic Press, Inc.

Introduction

Reference (1) contains data indicating the explosive character of the mechanochemical synthesis of some metal chalcogenides. The transition from an explosive to nonexplosive mechanochemical synthesis after the introduction of inert admixtures is investigated in detail in Refs. (2 and 3). It is established that the time, t_{exp} , till the instant of explosion, increases nonlinearly with the increase of the inert additive amount. The critical volume x_c of the inert admixture needed for a transition from explosive to nonexplosive synthesis is determined (3) for a large number of explosive mechanochemical reactions. A mechanism is suggested (2, 3) which explains this phenomenon on the ba-

sis of the mechanical activation process and the percolation theory (4, 5).

Various materials (metals, inorganic chemical compounds, polymers) can be used as inert additives (3). The purpose of the present paper is to study the explosive mechanochemical synthesis in systems of the type Met–Met–Halc (Met = Zn, Cd, and Sn; Halc = S, Se, and Te) where the initial components, on the one hand, and the synthesized compounds, on the other, can play the role of inert admixtures with respect to one another.

Experimental

The initial substances used for all experiments of mechanochemical synthesis were

Zn, Cd, Sn, and a chalcogen element S, Se, or Te of high chemical purity. The metal and chalcogen element particles in the initial mixtures had sizes smaller than 0.5 mm. The mechanochemical synthesis was carried out in a KM-1 (DDR) vibration one-ball agate mill in air. The proceeding of explosive mechanochemical synthesis was established on the basis of a pulsed increase of temperature in the mill (*J*).

The initial Met–Met–Halc mechanical mixtures used had the following characteristics: (i) The total amount of the initial components was always 2 g; (ii) the stoichiometry corresponded to MetHalc–MetHalc (e.g., ZnS–SnS), and (iii) the $G_{\text{MetHalc}}:G_{\text{MetHalc}}$ weight ratio varied between 7 : 1 and 1 : 5.

The phase composition and the structure of the samples were determined by Mössbauer spectroscopy and X-ray analysis using a method described in Ref (2).

Results and Discussion

Figure 1b shows the time to the explosion during mechanochemical synthesis of the compounds of the Zn–Sn–S and Zn–Sn–Se systems as a function of the $G_{\text{ZnS}}:G_{\text{SnS}}$ and $G_{\text{ZnSe}}:G_{\text{SnSe}}$ weight ratios, respectively. The analogous shapes of the curves allow concentration of the further discussion on the results concerning the Zn–Sn–S system only.

The curve illustrating the experimental results consists of two parts, each of them being characterized by a nonlinear increase of the time to the explosive effect and a transition from an explosive to nonexplosive mechanochemical reaction. The shapes of the curves coincide with those in Ref. (3) concerning the conversion of an explosive mechanochemical reaction to a nonexplosive reaction in the presence of a sufficient amount of inert impurities. The new experimentally established fact is the existence of a critical weight ratio around which the time

to the explosion strongly increases. Irrespective of the explosive synthesis of ZnS and tin sulfides (1, 2), no explosion is observed at the critical weight ratio for the system under consideration. Hence, at the critical weight ratio $t_{\text{exp}} \rightarrow \infty$.

The investigation of samples with a critical $G_{\text{ZnS}}:G_{\text{SnS}}$ weight ratio of about 1 : 2.5, and different durations of mechanical activation, is of special interest. Figure 2 presents three Mössbauer spectra of samples with a critical weight ratio of the components. According to the spectrum in Fig. 2a, 4-hr mechanical activation has led to nonexplosive synthesis of SnS, but the prevailing phase is unreacted β -Sn. Data from X-ray analysis of the same sample indicate that no ZnS has been synthesized. The spectrum in Fig. 2b corresponds to a sample activated mechanically for 8 hr. This activation proves to be sufficient for practically complete nonexplosive synthesis of tin sulfides. The X-ray analysis shows the formation of a minimum amount of ZnS. The spectrum in Fig. 2c belongs to a sample activated mechanically for 25 hr ($t_{\text{exp}} \rightarrow \infty$). The absence of a line for the initially introduced β -Sn is an indication of complete nonexplosive synthesis of SnS, Sn_3S_4 , Sn_2S_3 , and SnS_2 . The synthesis of tetravalent tin sulfides is possible due to the presence of unreacted sulfur not used for the synthesis of ZnS. According to the X-ray analysis, large amounts of ZnS are formed in a nonexplosive mechanochemical way.

The study of samples with a component ratio to the left of the critical indicates that after 4 to 8 hr of mechanical activation, the Mössbauer spectra obtained are similar to those in Figs. 2a and 2b. Practically complete nonexplosive synthesis of the tin sulfides proceeds till the eighth hour. The explosive effects observed to the left of the critical weight ratio appear after the eighth hour. Therefore, the explosive effect is a result of the explosive mechanochemical synthesis of ZnS. It may be concluded that

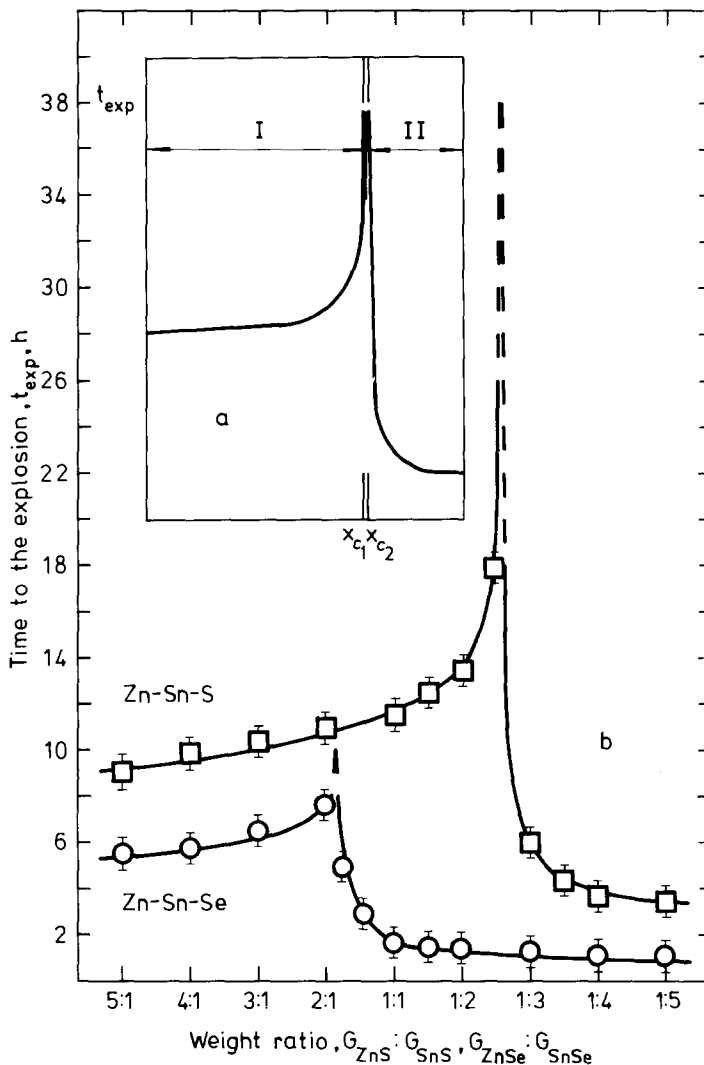


FIG. 1. (a) Dependence of the time to explosion in two explosive mechanochemical reactions on the concentration of the inert impurity. The critical volumes x_{c1} and x_{c2} for the two reactions are close in value or coincide on the concentration axis; (b) Experimental data on the time to explosion for samples from the systems Zn-Sn-S and Zn-Sn-Se versus the $G_{ZnS} : G_{SnS}$ and $G_{ZnSe} : G_{SnSe}$ weight ratios, respectively.

for $G_{ZnS} : G_{SnS}$ weight ratios ranging from 5:1 to 1:2.5, the increase of the time to the explosive effect is associated with an increase in amount of nonexplosively synthesized tin sulfides which play the role of inert admixtures. With a component weight ratio of about 1:2.5, the inert impurity has a critical volume x_c . The explosive mecha-

nochemical synthesis of ZnS changes to nonexplosive.

Investigation of samples with component weight ratio to the right of the critical shows that after 3-hr mechanical activation the Mössbauer spectra are similar to those in Fig. 2a. The explosive effects observed to the right of the critical weight ratio arise

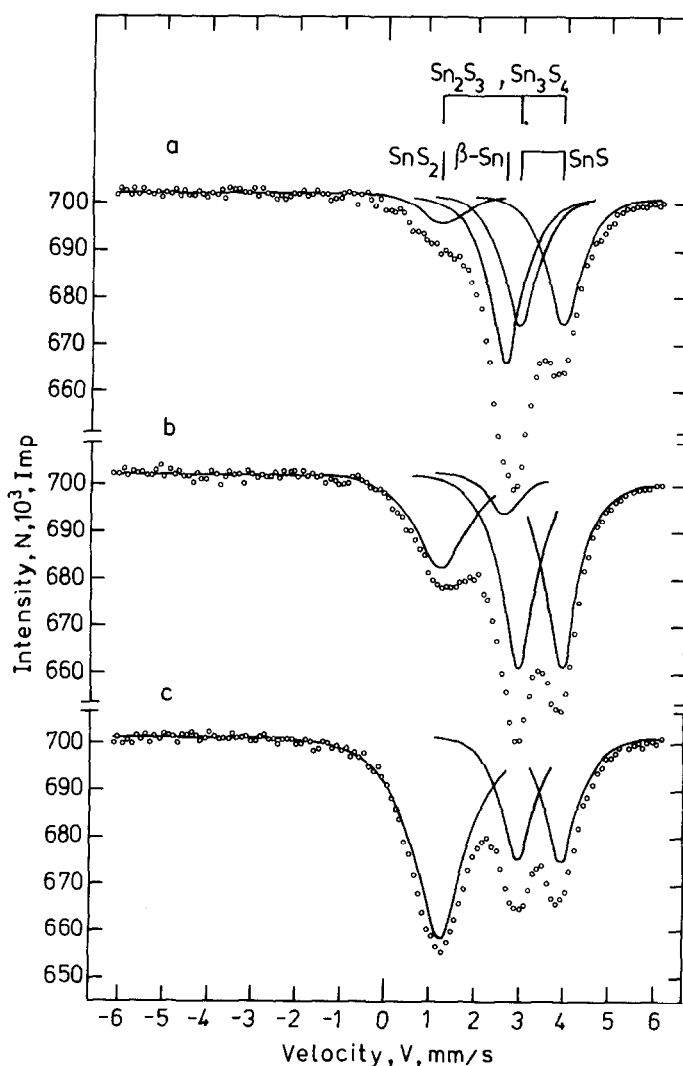


FIG. 2. Mössbauer spectra of samples from the system Zn-Sn-S. The samples have a critical $G_{\text{ZnS}} : G_{\text{SnS}}$ weight ratio of about 1 : 2.5. The mechanical activation has a duration of (a) 4, (b) 8, and (c) 25 hr.

after the third hour and are due to the explosive mechanochemical synthesis of tin sulfides. Owing to the short duration of the mechanical activation, the unreacted Zn plays the role of an inert impurity. It may be concluded that at $G_{\text{ZnS}} : G_{\text{SnS}} = 1 : 2.5$, the increase in the time to the explosive effect is associated with the increasing amount of the inert impurity. With a weight ratio of about 1 : 2.5, the inert admixture

has a critical volume x_{c_2} . This leads to a transition from an explosive to nonexplosive mechanochemical synthesis of SnS.

In Ref. (3) it is shown that a definite critical volume x_c of the inert admixture needed for a percolation transition from an explosive to nonexplosive synthesis corresponds to each explosive mechanochemical synthesis reaction. This fact is attributed to the different enthalpies of formation, ΔH_{298} of

the different compounds. The transitions from explosive to nonexplosive mechanochemical syntheses in the Zn–Sn–S system can be considered as typical percolation processes and should be interpreted in accordance with the results in Ref. (3). The two synthesis mechanochemical reactions of ZnS and SnS have critical volumes x_{c_1} and x_{c_2} for a percolation transition to nonexplosive synthesis. In this more complicated case the critical volumes x_{c_1} and x_{c_2} practically coincide in site on the axis of the weight ratios. For that reason, two regions I and II (Fig. 1a), are formed, each of them characterized by an explosive reaction.

Two more cases are possible on the basis of the different critical volumes (3) and the percolation theory (4). If the enthalpies of formation of the metal chalcogenides in the Met–Met–Halc system are large, critical volumes x_{c_1} and x_{c_2} also have high values. That is why three regions are distinguished (Fig. 3a). Regions I and II are characterized by an explosive mechanochemical synthesis reaction each. In region III including parts of regions I and II, both mechanochemical reactions are explosive. The time to the mechanochemical explosion in this case is determined by the reaction with a shorter time to the explosive effect.

In the second case the enthalpy of formation of the metal chalcogenides in the systems and the critical volumes x_{c_1} and x_{c_2} have low values. This leads to the formation of an independent region III in which both reactions of mechanochemical synthesis are nonexplosive (Fig. 4a). Regions I and II have one explosive synthesis mechanochemical reaction each. Figures 3b and 4b present experimental results confirming the above conclusions. The critical volumes for the cases in Figs. 1b and 4b can be calculated. The values obtained are in agreement with those given in Ref. (3). X-ray studies of the samples have evidenced a complex structure. For that reason, exact calculation of the critical volumes is difficult. For in-

stance, the X-ray studies of the samples of the system Zn–Sn–S indicated the structures of SnS, Sn₃S₄, and Sn₂S₃ to be the same as those described in Ref. (2). The compound SnS₂ exhibits structures which correspond to ASTM 23-677 and ASTM 31-1399. The synthesized zinc sulfides have both sphalerite and wurtzite structures. In the case of compounds synthesized nonexplosively, the broadened diffraction lines evidence defect structures. Even after an explosive mechanochemical synthesis, the X-ray analysis confirmed the presence of noticeable amounts of unreacted initial components (Zn, Sn, and S). Mössbauer and X-ray studies of all samples revealed the formation of zinc and tin sulfides alone. The synthesis of mixed compounds of the type ZnSnS₃ (6) or mixed oxides is also possible, but their amounts are probably below the sensitivity of the methods applied. In agreement with Ref. (2), during explosive synthesis of SnS there was also incomplete high-temperature synthesis of ZnS as a consequence of the heating effect of the explosive mechanochemical reaction.

Figure 5 shows the results from the investigation of the Zn–Cd–Sn–S system. The initial mechanical mixtures of Zn, Cd, Sn, and S have a total weight of 2 g. The time to the explosion area is plotted over the concentration triangle of the system.

This is the most complicated system in which we have observed percolation phenomena. In this case, three explosive synthesis mechanochemical reactions may proceed. Each of the explosive reactions of the synthesis of ZnS, CdS, and SnS has its own critical volume of percolation transition to nonexplosive synthesis. Two of the sides of the concentration triangle represent the Zn–Sn–S and Zn–Cd–S systems, for which data are presented in Figs. 1 and 3. The third side is the Cd–Sn–S system. No percolation transition is observed in this case. All syntheses are explosive, and the time to the explosion changes

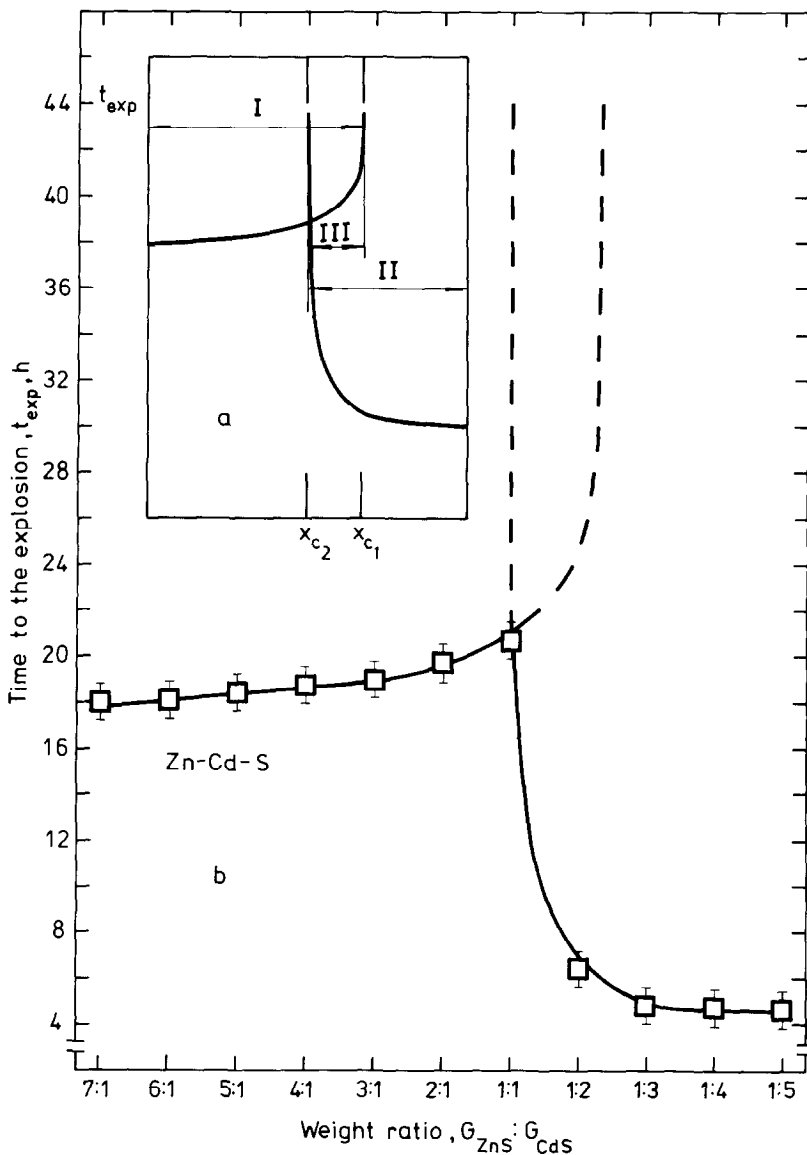


FIG. 3. (a) Dependence of the time to the explosion for two explosive mechanochemical reactions on the concentration of the inert admixtures. The critical volumes x_{c1} and x_{c2} for the two reactions have high values. (b) Experimental data on the time to the explosion for samples from the Zn-Cd-S system versus the $G_{\text{ZnS}} : G_{\text{CdS}}$ weight ratio.

smoothly from that for synthesis of pure CdS (≈ 4 hr) to that for the synthesis of pure SnS (≈ 3 hr). The absence of a percolation transition is explained by the close

values of the times to the explosion synthesis of the two compounds. Only when the times to the explosion strongly differ in value, nonexplosive synthesis of one com-

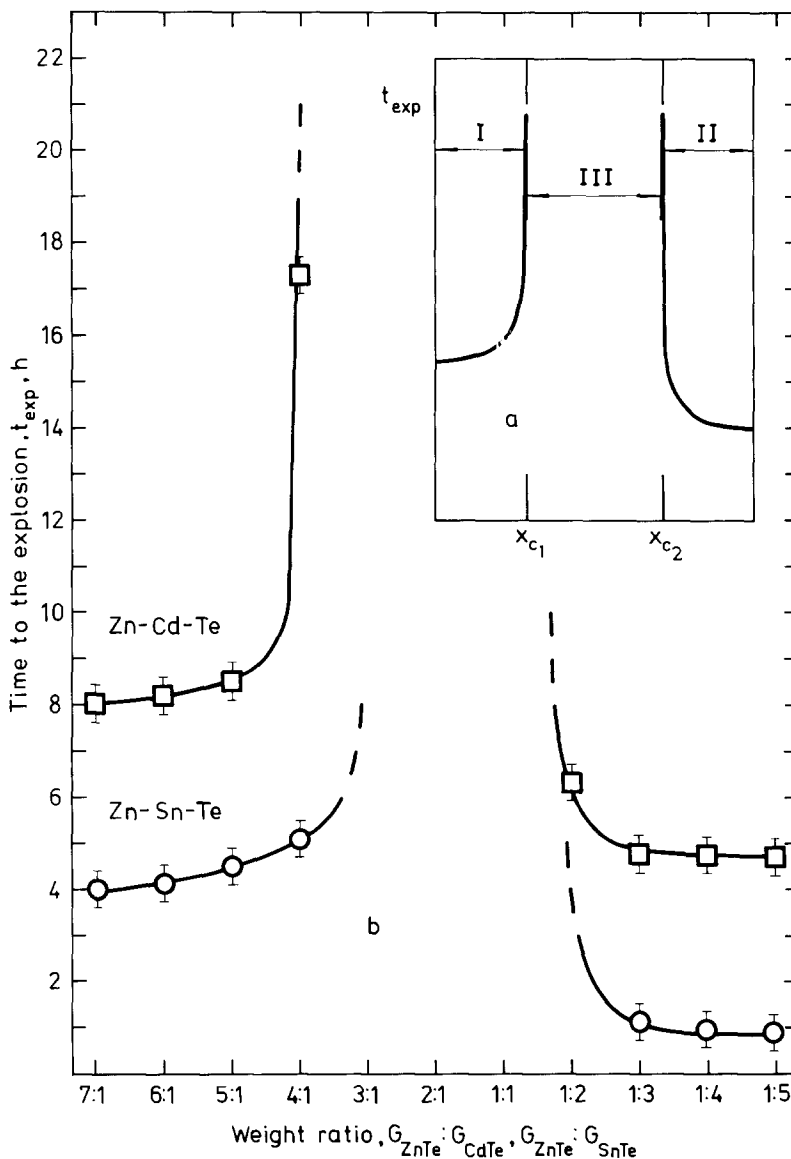


FIG. 4. Dependence of the time to the explosion for two mechanochemical reactions on the concentration of the inert impurity. The critical volumes x_{c1} and x_{c2} for the two reactions have low values. (b) Experimental data on the time to the explosion for samples from the systems Zn-Cd-Te and Zn-Sn-Te versus the $G_{ZnTe} : G_{CdTe}$ and $G_{ZnTe} : G_{SnTe}$ weight ratios, respectively.

pound is possible, the latter playing the role of an inert admixture with respect to the other compound synthesis. Four regions are established on the concentration triangle of the Zn-Cd-Sn-S system. In

regions I, II, and III, the explosive reaction is that of the synthesis of ZnS, CdS, and SnS, respectively. In region I the role of an inert impurity belongs to CdS and SnS synthesized in a nonexplosive mechano-

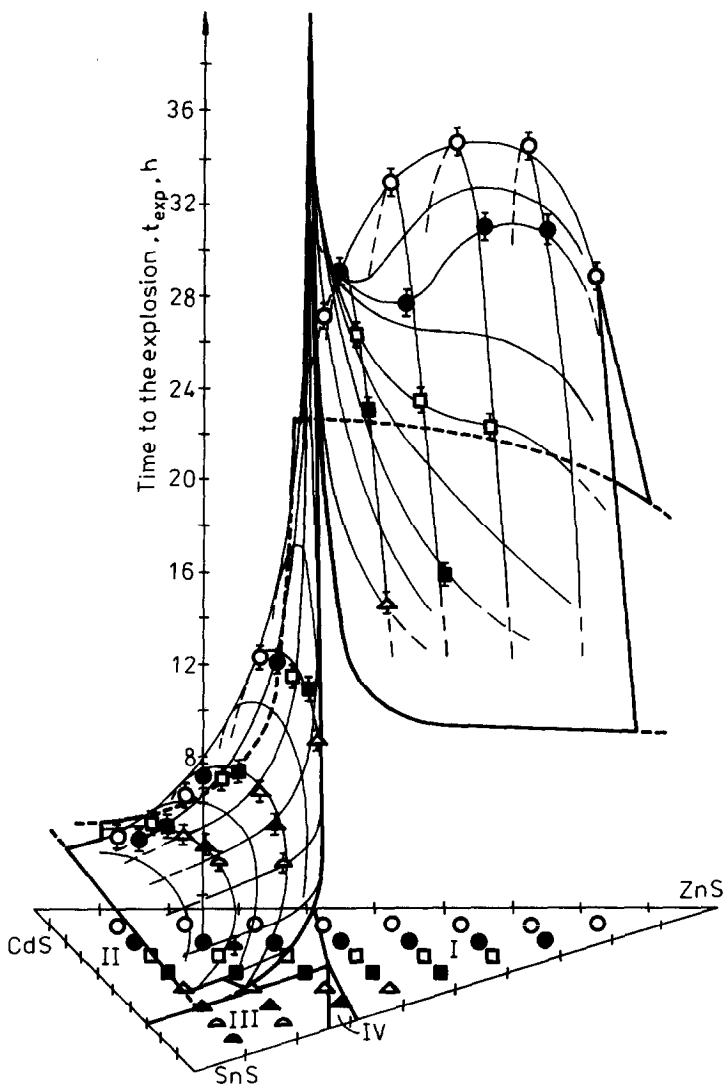


FIG. 5. Dependence of the time to the explosion on the concentration for three explosive mechanochemical reactions. The time to the explosion area is plotted over the concentration triangle of the Zn-Cd-Sn-S system.

chemical way. The role of an inert additive in regions II and III is played by unreacted Zn. The small region IV comprises samples with high values of the time to the explosive effect. With two of the samples, there was no explosion regardless of the prolonged activation ($t_{\text{exp}} \rightarrow \infty$).

Conclusion

In Ref. (2), the transition from an explosive to nonexplosive mechanochemical synthesis under the effect of an inert impurity (SiO_2) was investigated and assumed to be a perco-

lation phenomenon. In the present paper, the mechanochemical synthesis in more complex systems of the type Met–Met–Halc was investigated, and analogous transitions were observed. Inert admixtures of the type of SiO_2 were not introduced, but on the basis of experimental data (Figs. 1, 3, and 4) it may be concluded that the transitions from an explosive to nonexplosive synthesis are effected by nonexplosively synthesized compounds (metal chalcogenides) and the unreacted metal component which behave as inert impurities.

Percolation transition from an explosive to nonexplosive synthesis of metal chalcogenides occur only when the volume occupied by an inert admixture has a critical value. For the systems investigated there are two critical volumes, x_{c1} and x_{c2} , which correspond to the two explosive synthesis reactions. For that reason, three possible cases of percolation transitions are observed, which is in agreement with the data for the different x_c values (3) and the percolation theory (4). This result directly proves that the observed transition from an explosive to nonexplosive mechanochemical synthesis is a typical percolation transition. This is also confirmed by the study of the more complicated system Zn–Cd–Sn–S.

Nonexplosive synthesis reactions of the type Met–Halc are known (1). They are characterized by a high rate. Already at the beginning of mechanical activation of the initial components, large amounts of the final product are synthesized. In the present paper we have shown that the final product of nonexplosive mechanochemical synthesis plays the role of an inert admixture. If its volume is larger than the critical one, the reaction would proceed to completion nonexplosively. This is a possible mechanism explaining the existence of mechanochemical reactions which are in principle nonexplosive.

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