On the Development Mechanism and Kinetics of the Explosive Mechanochemical Synthesis

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Data are summarized for mechanochemical processes leading to aggregate formation in the mechanical activation and the classical theory on thermal explosions. It has been shown that explosion occurs as a result of mechanochemical synthesis through a thermal mechanism. A kinetic equation of explosive synthesis mechanochemical processes has been proposed which accounts for the mechanical activation features and for the suggested thermal mechanism of explosion. On the basis of the specificity of explosive mechanochemical processes it is suggested that explosive mechanochemical processes of synthesis should be regarded as a separate class of chemical reactions. © 1989 Academic Press, Inc.

Introduction

The mechanochemical synthesis of metallic chalcogenides may be either explosive or nonexplosive (*1*). In an explosive mechanochemical synthesis the degree of association α of the reagents is low until the instant of explosion. At a certain instant of mechanical activation in the mechanochemical explosion, α jumps to the maximum value corresponding to completion of the reaction. Of special interest is the mechanochemical explosion first observed by us, which is accompanied by pulsed thermal, optical, and mechanical effects. Later we observed initiation of a high-temperature reaction in the FeS synthesis by the thermal effect during an explosive

mechanochemical reaction in the SnS synthesis (*2*). In (*3*) it has been determined experimentally that any explosive synthetic mechanochemical reaction could be converted into a nonexplosive one by introducing an inert constituent. Dispersion and aggregate-formation processes taking place in the course of the mechanical activation have been investigated (*3–6*). It has been shown that the aggregate-formation process is essential for the subsequent mechanochemical explosion. An explosive mechanochemical synthesis has been observed only after the mechanical aggregates of dispersed product particles have reached critical dimensions (*3*).

Despite considerable experimental work, the mechanism of the mechanochemical ex-

plosion has not been clarified. Neither has a kinetic theory of the explosive mechano-chemical synthesis been developed. Only two efforts (1, 7) have been published on a model for the kinetic description of the above process.

The object of the present work is to clear up the mechanism of the mechanochemical explosion observed in some metallic chalcogenides syntheses and to elaborate on a kinetic theory of explosive mechanochemical reactions.

Experimental Procedures

In order to confront the theoretical and experimental kinetic curves we carried out an explosive mechanochemical synthesis of pure SnS. Analogous results have been published in (1). We carried out an explosive mechanochemical synthesis of SnS in the presence of 6% by weight of an inert admixture of SiO_2. When the synthesis was carried out with 12% by weight of SiO_2 the synthesis was nonexplosive (3). The components Sn + S were admixed in stoichiometric amounts to form SnS. The mechanical activation was carried out in a KM-1 (DDR) vibration one-ball agate mill in air. Several samples were prepared with different time intervals over which the mechanical activation had been carried out, including samples for which an explosion had taken place. A pulsed increase in temperature in the mill served as a signal for the occurrence of an explosive effect (1). For the different samples the degree of association α of the components into the final compound SnS has been determined by monitoring the quadrupolar Mössbauer doublet areas of SnS using a computer. Mössbauer spectra were obtained in a constant acceleration spectrometer with faces whose surface density was 30 mg/cm^2 relative to Sn. A $Ba^{119m}SnO_3$ source with activity of ~4 mCi was used; the isomeric shifts were referred to this source.

Results and Discussion

Development Mechanism of the Explosion during Mechanochemical Synthesis

To obtain kinetic equations for the explosive synthesis mechanochemical processes requires specification of the mechanochemical explosion development mechanism. On the basis of many experimental results (2, 3, 6) we determined that the mechanochemical explosion is connected with the aggregate-formation process, and aggregate formations with the critical size r_c of the constituent units. Hence, in the study of the mechanochemical explosion mechanism we concentrated on the physicochemical processes taking place in the aggregates.

In Fig. 1 two aggregates with critical size are shown schematically. The aggregate in Fig. 1a comprises only two parts while that of Fig. 1b comprises many fine dispersed particles of the starting material. The contact surface of the aggregate of Fig. 1a is simply πr_c^2. The contact surface of the aggregate of Fig. 1b is hundreds or thousands of times greater than that of Fig. 1a depending on the degree of dispersion. This fact is important because chemical interactions occur at the contact surface under the mechanical effects of grinding. As a consequence of the surface mechanochemical reaction heat Q_+ is released within the aggregate volume. We shall not discuss here the elementary mechanism of mechanochemical reaction initiation. Every one of the well-known mechanisms—the local-heating mechanism, the magma-plasma mechanism, the dislocation mechanism, or the short living centers mechanism—could determine the precise conditions favorable to the chemical interaction (8). Part of the heat, Q_-, is passed on to the environment. The thermal balance of the two aggregates in Fig. 1 is completely different. An explosive mechanochemical synthesis can occur only for the case in Fig. 1b (3). In this situa-
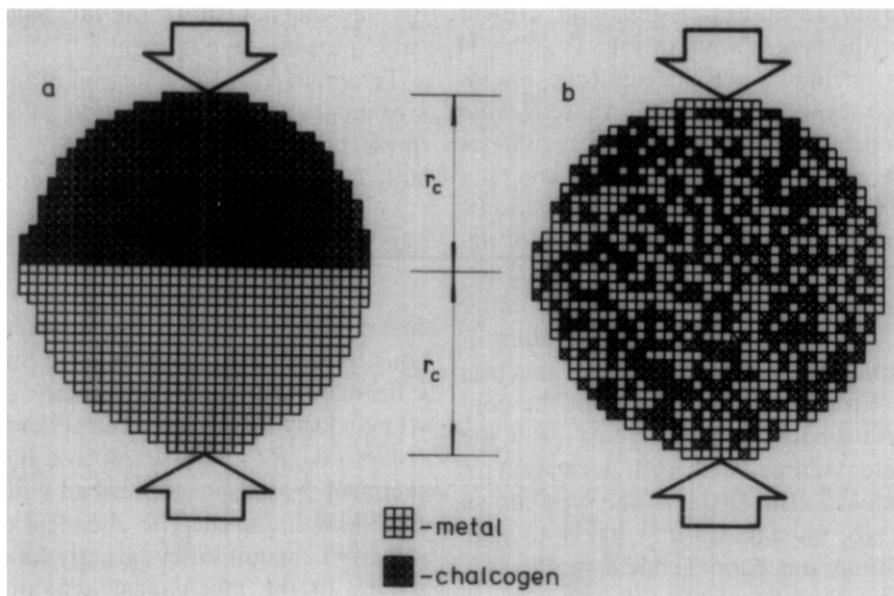
FIG. 1. Formation of mechanical aggregates with critical size r_c from metal and a chalcogen element: (a) aggregates typical for the initial state of dispersion (first stage of dispersion); (b) aggregates typical for the instant just before the mechanochemical explosion (second stage of dispersion).

tion a disruption in thermal balance and implementation of the inequality $Q_+ > Q_-$ (self-heating process) is possible. Under self-heating conditions the exothermic mechanochemical reaction is self-accelerating and inherent generating thermal explosions. Following the classical work (9–11) the condition for an explosion to occur is given by $\delta > \delta_c$, where

$$\delta_c = \frac{QE_A}{\lambda RT^2}\, r_c^2 n\nu \, \exp\left(-\frac{E_A}{RT}\right),$$

$$\delta = \frac{QE_A}{\lambda RT^2}\, r^2 n\nu \, \exp\left(-\frac{E_A}{RT}\right). \quad (1)$$

Here δ_c is a number determined by the body geometry, e.g., for spherical aggregates $\delta_c = 3.32$; δ is a dimensionless parameter depending on: Q, chemical reaction thermal effect; E_A, activation energy; λ, heat conductivity factor; r, aggregate radius; n, particle concentration; ν, frequency factor; R, universal gas constant; and T, absolute temperature. For a given chemical reaction

the parameters Q, E_A, λ, ν, n, R, and T are fixed; thus implementation of the condition $\delta > \delta_c$ depends only on the formation of mechanochemical aggregates with dimensions $r \geq r_c$. Application of this condition shows once more the importance of the aggregate-formation process for the mechanochemical explosion development.

The above discussion leads to the following conclusions:

(1) The process of mechanochemical activation of components occurs in two parallel paths through two sequential stages: synthesis surface reaction and self-accelerating explosive synthesis. Two stages in the output component dispersion are necessary for the explosive mechanochemical reaction to occur. Throughout the first stage (stage of dispersion and defect formation) the specific surface of the products increases continuously whereas the contact surface between the reagents remains in contact. It is

difficult to form aggregates with critical sizes of the type shown in Fig. 1b. This is the reason that a self-accelerating (explosive) synthesis is unlikely. An explosive mechanochemical process of synthesis throughout the first dispersion stage is only possible for certain types of aggregations. Throughout the second stage (stage of aggregation) finely dispersed mechanical aggregates are formed with conditions under which self-heating and self-acceleration of the exothermal mechanochemical reaction occur. With the sharp increase of the contact surface between the reagents inside the aggregate volume, and with formation of aggregates of critical size of the type shown in Fig. 1b, an explosion is likely to take place during mechanochemical synthesis.

(2) The condition for self-heating, $Q_+ > Q_-$, is fulfilled only for aggregates with size $r \geq r_c$. The heat Q_+ is a consequence of the synthesis surface reaction. As an additional heat source favoring the self-heating process is the recrystallization process of the strongly defective metallic component (12). Under self-accelerating conditions the synthesis surface reaction switches over to an aggregate bulk volume reaction. A mechanochemical explosion then arises.

(3) The mechanochemical explosion develops into a thermal explosion. Its initiation is a consequence of the mechanical impact of the milling body over the aggregate with critical size r_c.

Kinetics of the Explosive
Mechanochemical Synthesis

The kinetics of solid-state reactions of the type $A_{solid} + B_{solid} \rightarrow AB_{solid}$ has been detailed for example in (13). With regard to this Alexandrov's work (14) is of relevance. The explosive mechanochemical reactions investigated by us are of the same type, but to obtain the kinetic equations for them one must account for the various features of the mechanical activation process and for the thermal mechanism of the mechanochemical explosion development.

To obtain a kinetic equation of the explosive mechanochemical process of SnS synthesis by the reaction $Sn + S \rightarrow SnS$ we start from the differential equation

$$\frac{dN^{Sn}}{dt} = -kN^{Sn} \qquad (2)$$

describing the kinetics of first-order reactions. Here N^{Sn} is the number of Sn atoms, k the chemical reaction velocity constant set generally by the Arrhenius equation $k = \nu \exp(-E_A/RT)$. The explosive mechanochemical synthesis is described with a two-stage kinetic curve. The chemical reaction velocity constant differs greatly for the two stages. In the mechanical activation process the mechanochemical reaction runs in two parallel paths. For this reason we represent k as

$$k = k_1' + k_2'. \qquad (3)$$

The constant k_1' determines the velocity of the synthetic surface reaction. The constant k_2' determines the chemical reaction velocity in the course of its self-acceleration (the mechanochemical explosion). The synthesis surface reaction velocity is proportional to the contact surface (8). It is assumed that through the first stage of dispersion the contact area between both reagents increases linearly as $S = k_1''t$. Here k_1'' is the velocity of area increasing in the course of dispersion. Then k_1' becomes

$$k_1' = \frac{k_1''t}{S_0} \nu \exp\left(-\frac{E_A}{RT}\right), \qquad (4)$$

where S_0 is the tin output surface.

To describe the sharp acceleration in chemical reaction at the mechanochemical explosion we define k_2' as

$$k_2' = \frac{1}{(\delta_c - \delta)} \nu \exp\left(-\frac{E_A}{RT}\right). \qquad (5)$$

Using in Eq. (1) the fact that the aggregate radius increases linearly with time, $r = k_2''t$, where k_2'' is the velocity of aggregate radius increase, Eq. (5) becomes

$$k_2' = 1 \Big/ (r_c^2 - k_2''^2 t^2) \frac{QE_A n}{\lambda RT^2}. \qquad (6)$$

With reference to Eqs. (3), (4), and (6), the solution of differential Eq. (2) is

$$N^{Sn} = N_0^{Sn} \exp\Big[- k_1'' \nu \exp\Big(- \frac{E_A}{RT}\Big) t^2 \Big/ 2S_0$$

$$- \lambda RT^2 \ln \Big|\frac{r_c + k_2''t}{r_c - k_2''t}\Big| \Big/ 2r_c k_2'' QE_A n \Big], \quad (7)$$

where N_0^{Sn} is the output number of tin atoms. Introducing the constants

$$k_1 = k_1'' \nu \exp\Big(- \frac{E_A}{RT}\Big) \Big/ 2S_0,$$

$$k_2 = \lambda RT^2 / 2r_c k_2'' QE_A n$$

we obtain

$$N^{Sn} = N_0^{Sn} \exp\Big(-k_1 t^2 - k_2 \ln \Big|\frac{r_c + k_2''t}{r_c - k_2''t}\Big|\Big). \qquad (8)$$

If during synthesis side reactions of the type $Sn + 2S \rightarrow SnS_2$ are suppressed then $N^{SnS} = N_0^{Sn} - N^{Sn}$ and $N^{SnS}/N_0^{Sn} = \alpha$. Here N^{SnS} is the number of synthesized SnS molecules. For the kinetic equation of the SnS explosive synthesis mechanochemical reaction we finally obtain

$$\alpha = 1 - \exp\Big(-k_1 t^2 - k_2 \ln \Big|\frac{r_c + k_2''t}{r_c - k_2''t}\Big|\Big). \qquad (9)$$

The first term in the exponent describes the kinetics of SnS synthesis surface reaction. The second term of the exponent describes the kinetics of the self-accelerating (explosive) mechanochemical reaction. The value of the logarithmic function $\ln|(r_c + k_2''t)/(r_c - k_2''t)|$ increases toward infinity as the increasing aggregate radius $k_2''t$ tends to r_c. The physical cause of this increase is re-

lated to the velocity (self-accelerating) increase of the mechanochemical reaction and to the mechanochemical explosion at $k_2''t = r_c$. We also note that the aggregate-formation process is unlikely to occur during the first stage of dispersion. Then for the first dispersion stage, as well as for the mechanochemical processes carried out without aggregate-formation, the kinetic equation (9) reduces to the well-known (13, 14) Avrami-Erofeev equation

$$\alpha = 1 - \exp(-kt^n), \quad n = 2.$$

In Fig. 2 we summarized the experimental and theoretical results for $\alpha - t$ kinetic curves of the SnS mechanochemical synthesis. Use of Eq. (9) shows that the mechanical aggregate dimension through the second stage of dispersion follows the logarithmic-normal distribution. Accounting for the aggregate size distribution is essential to obtain correct kinetic curves. Through the second stage of dispersion the aggregate mean size may be less than the critical dimension r_c, but because of the logarithmic-normal distribution of the aggregates the condition $r > r_c$ is fulfilled for some of them. These aggregates satisfy the conditions for an explosive mechanochemical synthesis. In the time interval just prior to the explosion an explosive mechanochemical synthesis may take place in addition to the surface synthesis reaction, but it has a local character and affects only particular aggregates. This causes an increase of the chemical reaction velocity just before the explosion. Such features are observed in kinetic curves 1 and 2 (Fig. 2) for the SnS explosive mechanochemical synthesis in the absence of an inert admixture (kinetic curve 1) and in the presence of an inert admixture of 6% by weight of SiO_2 (kinetic curve 2). At a certain instant of the mechanical activation the aggregate mean size equals the critical size r_c; i.e., the conditions for an explosive synthesis are then fulfilled for practically all sample aggre-
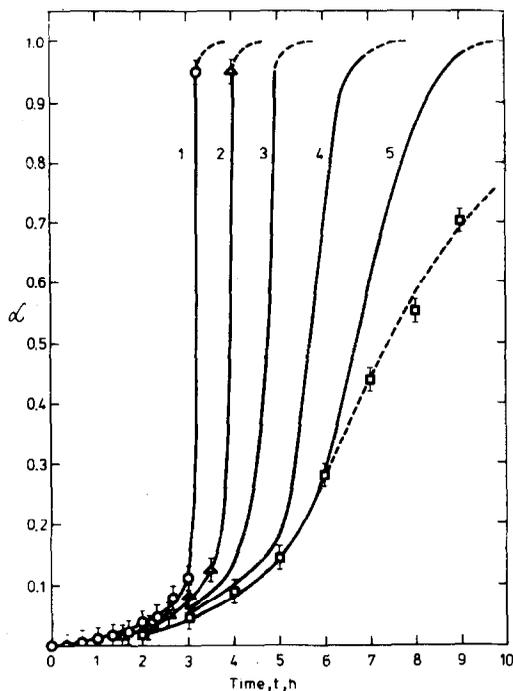
FIG. 2. Experimental and theoretical results of the SnS mechanochemical synthesis kinetics. Kinetic curves: curve 1, explosive mechanochemical synthesis of pure SnS; curve 2, explosive mechanochemical synthesis of SnS in the presence of 6% by weight of an inert admixture of SiO_2; curve 5, explosiveless mechanochemical synthesis of SnS in the presence of 12% by weight of an inert admixture of SiO_2. Kinetic curves 3 and 4 are obtained under conditions intermediate between those for kinetic curves 2 and 5. Kinetic curve 3 is typical for an explosive mechanochemical synthesis, while kinetic curve 4 is typical for a smooth explosiveless mechanochemical synthesis.

gates. At that point the mechanochemical explosion takes place and on curves 1, 2, and 3 (Fig. 2) a jump in α ($\Delta\alpha = 0.2 \div 0.6$) is observed. The difference in timing of the explosive effect in the kinetic curves 1, 2, and 3 arises from the presence of an inert admixture which diminishes the intensity of the mechanical impact on the output components Sn + S. The velocities of dispersion k_1'' and aggregate formation k_2'' thus decrease; as a consequence the mechanochemical explosion appears later. Mössbauer and X-ray structure investiga-

tions of the samples of kinetic curves 1 and 2 confirmed the assumption that no side reactions have taken place in an SnS explosive mechanochemical synthesis. This is the reason that the correspondence between the experimental and theoretical results in the $\alpha - t$ kinetic curves is very good.

In Fig. 2 are shown experimental results of the SnS mechanochemical synthesis in the presence of an inert admixture of 12% by weight of SiO_2. Since the inert material is present in amounts greater than the critical one, the SnS mechanochemical synthesis is explosionless (3). In examining the theoretical kinetic curve 5 of this process one notes that the velocity of aggregation increasing k_2'' through the second stage of dispersion has been very strongly diminished, due to the suppression of the aggregate-formation process (3). Forming aggregates with critical size has been suppressed; therefore, the mechanochemical synthesis is explosiveless. Under such conditions the synthesis mechanochemical reaction proceeds via a typical surface reaction. We do not fully exclude the possibility of an explosive mechanochemical synthesis in certain aggregates. Therefore this synthesis could have a local character. However, an explosive mechanochemical synthesis over the whole sample volume (mechanochemical explosion) cannot be realized. The kinetic curve of an explosiveless mechanochemical synthesis is a smooth one.

For the explosionless mechanochemical synthesis (kinetic curve 5) the experimental and theoretical values of α differ greatly for mechanical activation time intervals greater than 6 hr. These differences are related to the presence of side reactions which are not accounted for in the kinetic description. The Mössbauer spectra in Fig. 3 show this feature. After 6 hr of activation large quantities of SnS are already synthesized in an explosionless mechanochemical manner
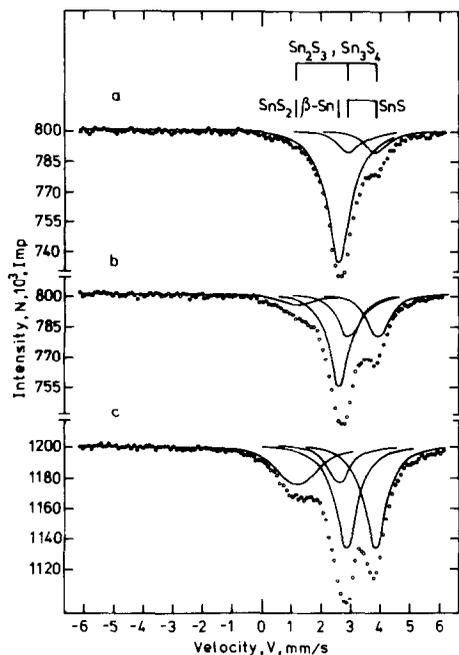
FIG. 3. Mössbauer spectra of samples from the explosiveless SnS mechanochemical synthesis in the presence of 12% by weight of an inert admixture of SiO_2 (kinetic curve 5, Fig. 2): (a) 4-hr mechanical activation; (b) 6-hr mechanical activation; (c) 9-hr mechanical activation.

(Figs. 3a and 3b). Conditions prevail for synthetic side reactions producing SnS_2, Sn_2S_3, and Sn_3S_4 via reactions of the type $SnS + S \rightarrow SnS_2$, etc., leading to a decrease in SnS. This can be well seen from the spectrum in Fig. 3c where the Mössbauer line with isomer shift $\delta = +1.15 \pm 0.05$ mm/sec of SnS_2 and the four-valent tin in the compounds Sn_2S_3 and Sn_3S_4 is encountered with substantial intensity. This is the reason for the discrepancy between theoretical and experimental values of α.

Conclusion

The main results of the present work may be summarized as follows:

(1) A summary of data drawn from the investigation of the explosive mechano-

chemical processes, of the aggregate-formation process in mechanical activation, and a comparison with the classical thermal explosion theory leads to the conclusion that the mechanochemical explosion originates and develops by a thermal mechanism. Specification of the mechanism of the mechanochemical explosion development is essential to the formulation of a kinetic equation for the synthesis mechanochemical explosive process.

(2) In the present work we propose a kinetic equation which accounts for the specifics of the mechanical activation process and we suggest a thermal mechanism of the mechanochemical explosion. The theoretical and experimental results for the explosive mechanochemical synthesis of SnS are in very good accord. The proposed kinetic description applies to all explosive synthesis mechanochemical reactions, since all of them are of the type $A_{solid} + B_{solid} \rightarrow AB_{solid}$.

(3) Finally, we consider the position of the explosive synthesis mechanochemical processes in the context of two-stage processes. As can be seen from Fig. 2 all five kinetic curves obviously relate to two-stage processes. But three of them (kinetic curves 1, 2, and 3) are explosive and two (kinetic curves 4 and 5) are explosiveless. The conclusion is drawn that the explosive synthesis mechanochemical process occurs in two stages, but not every two-staged synthesis process is an explosive one. This fact makes it necessary to relegate the explosive synthesis mechanochemical processes to a separate class with three major features: (1) A strong jump of α occurs in the explosive mechanochemical synthesis kinetic curve at the moment of a mechanochemical explosion; this change in α varies from 0.2 to 0.6. (2) Pulsed thermal, light, and mechanical effects accompany the explosive mechanochemical synthesis, in common with typical explosive processes. (3) In an explosiveless mechanochemical synthesis the synthesis of the final com-

pound is simply the result of mechanical activation. In an explosive mechanochemical synthesis the synthesis of the final compound results not only from the mechanical activation but also leads to a mechanochemical explosion.

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