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Phenomenological Description of Combustive Reactions of Thermite Compositions in Mechanochemical Reactors for the Synthesis of Metal Sulphides as an Example

FARIT KH. URAKAEV[1,3], LASZLO TAKACS[2], VALERII SOIKA[2], VYACHESLAV S. SHEVCHENKO[3],
ALEXEI P. CHUPAKHIN[1] and VLADIMIR V. BOLDYREV[1,4]

[1]*Novosibirsk State University,*
Ul. Pirogova 2, Novosibirsk 630090 (Russia)

[2]*Department of Physics, University of Maryland,*
Baltimore County, Baltimore, Maryland 21250 (USA)

[3]*Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Sciences,*
Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)

E-mail: urakaev@uiggm.nsc.ru

[4]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences,*
Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

Abstract

An investigation of mechanically stimulated self-propagating reactions (MSR) has been carried out for different conditions of mechanical activation in the system Zn–Sn–S using a SPEX 8000 mill. Both the earlier obtained and new results are generalized, with focus on the determination of induction period preceding the ignition of exothermal reaction. The discovered features and some hypotheses concerning the mechanism of MSR are discussed.

INTRODUCTION

Since the first description ofcombustive reactions in ball mills [1, 2], rather long period of time has passed. Hundreds of experimental studies were reported during this time concerning this direction of mechanochemistry and various aspects of its application in inorganic [3–5] and organic synthesis [6–8], in mineralogy and in mineral ore processing [9–11]. In spite of large number of publications, no theoretical description of this phenomenon is available [3, 4]. Modeling of mechanically induced self-propagating reactions (MSR) turns to be hindered by the absence of reliable complex data both on the features of their initiation or gradual running, unlike traditional SHS [12], and concerning the results of systematic investigations of MSR depending on the conditions of mechanical treatment in a definite mechanochemical reactor.

The analysis of literature shows that the most complete and detailed investigations into the features and kinetics of MSR have been carried out for exothermal reactions of metals with elementary sulphur using the ball mill KM-1 [1, 2] and SPEX 8000 Mixer Mill as a mechanical activator for the system Zn–Sn–S [13, 14]. Because of this, the goal of the present paper is generalization of the available and newly published experimental results on the mentioned system, description of the discovered features and some hypotheses concerning the mechanism of MSR in general that could promote the investigation of MSR modeling in mechanochemical reactors [15, 16].

One of the most important and less understood experimental features of MSR in mechanochemical reactors is the existence of the induction period of ignition of the explosive synthesis, which takes many hours in some cases [1–4]. In other words, the ignition of combustive reaction occurs only after mechanical treatment of the powdered reaction mixture for a definite time interval or occurs in glow regime, or gradually [3, 9, 10, 13], which is extremely important for practical purposes and allows obtaining target products and semi-products in high-disperse state (nanocrystal, nanocomposite, *etc.*) [3–5, 11]. Because of this, our investigation focuses on experimental determination of induction periods preceding the explosive combustion of thermite compositions.

EXPERIMENTAL

MSR of $(1 - y)$Zn + ySn + S = $(1 - y)$ZnS + ySnS in a SPEX 8000 mill was studied in ampoules (vials) made of stainless steel with the inner dimensions $l_1 = 3.8$ cm and $l_2 = 6.4$ cm [which is an equivalent of a sphere with the diameter l_1 and a cylinder with the same diameter and the height $l_2 - l_1$, the surface being $P_v = pl_2l_1$ » 76 cm^2 and volume $V_v = p(l_1)^2(3l_2 - l_1)/12$ » 58 cm^3], filled with steel balls of different diameters; the ratio of the weighed portion of reagent mixture m to the mass of ball load M_b was varied, as well as the stoichiometric parameter y, determining the contents of components in the mixture. The initial mean diameter of reagent particles in stoichiometric mixture was [13, 14]: $2R_{10}$(Zn) » 7 10^{-4} cm; $2R_{20}$(Sn) » 45 10^{-4} cm; $2R_{30}$(S) » 250 10^{-4} cm. Relative rate of the collisions of milling bodies was W » 400 cm/s [6, 14].

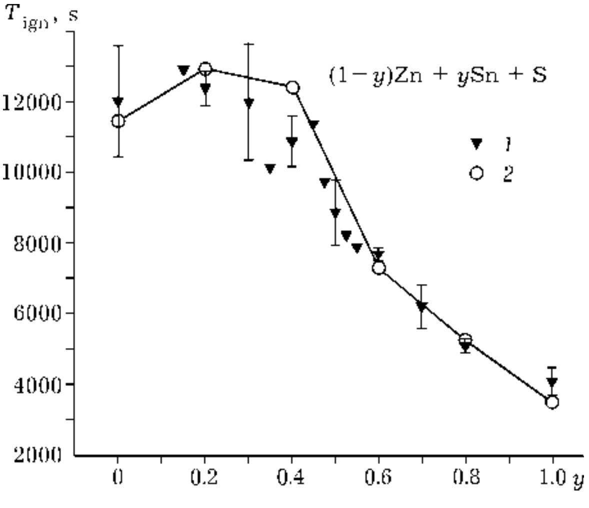

Fig. 1. Reproducibility of experimental data on induction period of the ignition of combustive reaction t* depending on the changes in the conditions of mechanical treatment, plotted as normalized time of ignition for the combustion $T_{ign} = t^*M_b/m$ and the composition (y) of the system Zn–Sn–S (see also [13, 14]): *1*, *2* – data of Table 1 and [14], respectively.

42 series of experiments were carried out with 15 preliminarily prepared initial compositions under variable conditions of mechanical treatment. Table 1 summarizes experimental data and the results on induction period t* of MSR ignition obtained with the samples.

The procedure involving the use of the normalized MSR ignition time $T_{ign} = t^*M_b/m$ was described and verified in [14]; the treatment of experimental induction period t* on the parameter describing the composition (y) was also carried out, taking account of the ratio of ball load mass (M_b) to the weighed portion of mixture (m). Figure 1 shows the results of the treatment of data presented in Table 1 (triangles) at the background of the results obtained earlier (light circles) [14].

One can notice that the results are well reproducible for different conditions of the mechanical treatment for the system Zn–Sn–S. Nevertheless, it should be noted that some worsening of the reproducibility is observed within composition range $0.2 < y < 0.6$.

The next experimental result, which is extremely important for the modeling of mechanochemical processes [17] but very rarely met in experimental studies of MSR is the joint determination of the dependencies of the changes in specific surface S (mean particle

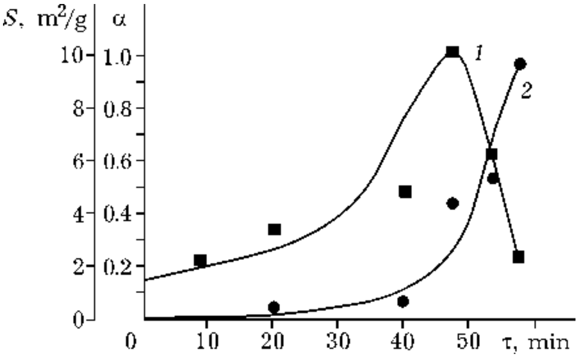

Fig. 2. Consistent changes of the specific surface S (*1*) and the transformation degree (a) of the reaction Zn + S = ZnS (*2*) on the time of mechanical treatment (t) in ball planetary-centrifugal mill KhK871 [2] till the moment of MSR ignition at the 57th minute of activation (see also [1]).

TABLE 1

Changes of the induction period of MSR ignition in the system Zn–Sn–Sn depending on the conditions of mechanical treatment in SPEX 8000 mill

Charge		Ball load				Induction period (t^*), s
Composition (y), at. %	m, g	3L	5L	7M	10S	
Zn + S[a]	1			+		420
	1				+	1285
	2		+			510
	4		+			1264
	8		+			2181
	10	+				5008
0.85Zn + 0.15Sn + S	10	+				5108
0.8Zn + 0.2Sn + S	1			+		480
	1				+	1105
	4		+			1241
	8		+			2462
0.7Zn + 0.3Sn + S	1		+			246
	4		+			1148
	8		+			2287
	10	+				5386
0.65Zn + 0.35Sn + S	10	+				4023
0.6Zn + 0.4Sn + S	1				+	967
	4		+			1025
	8		+			2362
	10	+				4007
0.55Zn + 0.45Sn + S	4		+			1081
0.525Zn + 0.475Sn + S	4		+			925
0.5Zn + 0.5Sn + S	3.7		+			862
	4		+			No combustion
	4		+			779
	10	+				3417
0.475Zn + 0.525Sn + S	4		+			782
0.45Zn + 0.55Sn + S	4		+			750
0.4Zn + 0.6Sn + S	1				+	747
	4		+			752
	8		+			1391
0.3Zn + 0.7Sn + S	4		+			650
	10	+				2215
0.2Zn + 0.8Sn + S	1				+	504
	4		+			454
	8		+			1001
Sn + S[b]	1				+	No combustion
	2		+			»
	3		+			»
	4		+			424
	5		+			510
	8		+			665

Note. L – ball, diameter: 12.7 mm, mass: 8.4 g; M – diameter: 9.525 mm, mass: 3.54 g; S - diameter: 6.35 mm, mass: 1.05 g.

[a] In general, with increasing mass of weighed portion, the time of ignition increases; it decreases with increasing diameter and number of balls.

[b] At small weighed portions, react gradually; with increased weighed portions, start burning, time of "igniton" increases.

size) and the extent of gradual reaction a on the time of mechanical treatment t. At least one this result [2] has been obtained by one of the pioneers of MSR for the reaction Zn + S = ZnS in a ball planetary-centrifugal mill of the type KhK871 [16, 17] (see Fig. 2, which demonstrates the existing interconnection between $S(t)$ and $a(t)$).

One can see that till 47 min treatment, the curves S and a (or, more exactly, two straight lines with substantially different slopes, see also [1]) go in-phase, while within the period (47–57 min), preceding the explosive synthesis of zinc sulphide, they go out-of-phase.

RESULTS AND DISCUSSION

Three stages of mechanical activation are likely to be observed, preceding or leading to explosive combustion of thermite compositions. At the first stage, at the background of weak increase of the specific surface, mechanical activation of one of the components of the mixture occurs, leading to substantial changes of its physicochemical properties. For example, the case of sulphur being one of the components of the mixture has been described in [15]; it involves mechanochemical polymerization and amorphization of sulphur at the first stage of mechanical treatment. Even a small increase in S can hardly be explained by grinding of relatively plastic metal particles (works on mechanical alloying of metals [5] very rarely describe data concerning S, because of its insignificant changes) or sulphur [14, 15]. So, it is reasonable to assume that the increase of S is due to the gradual formation of metal sulphides as nano-sized species [13] that get separated from metal particles as a result of the shearing contact strain [17] and thus may make the major contribution into gradual increase of S at the first stage of mechanical activation of the system Zn–S (see Fig. 2, 0–40 min).

At the second stage, the changed properties of one of the components (sulphur) cause the acceleration of the gradual reaction and, as a consequence, the increase of the growth rate of S (see Fig. 2, 40–47 min.) and the temperature of reaction mixture.

At the third stage (see Fig. 2, 47–57 min) the agglomeration of particles starts due to the heat of the accelerating exothermal reaction, as a result of gradual increase of temperature in the lined layer of particles (the heating of the wall of the vial of SPEX 8000 cannot be now neglected, because more sensitive measurements [18] can help detecting this fact not only at the moment when the ignition of combustion occurs [1, 4–11]). Agglomeration or the increase of the reaction contact surface S^* between reagents (the decrease of S is conditioned by an increase of S^*) finally leads at the 57th minute to the explosive reaction.

Let us note other MSR features important for modeling. Traditional SHS processes [12] occur rapidly (seconds) and, as a rule, are accompanied by complete or partial fusion of the initial components and reaction products, which hinders subsequent investigation or application of reaction products. Replacement of SHS with MSR excludes this disadvantage in general, but other unexplained effects accompanying MSR (besides the major one, *i. e.* the occurrence of induction period of ignition) hinder direct usage of this advantage. Below we list these features characteristic of MSR only: [3]:

1) the absence of ignition in some reaction mixtures surely able to burn, or explosion-free decomposition of an explosive substance [16];

2) the effect of the stopped mechanical treatment and its further resuming: non-additive synergism of interrupted combustion [9];

3) mutual suppression of combustion in complicated mixtures such as Zn–Sn–S [13, 14];

4) multiple combustion with the consumption of small fraction of reagents (ignition and extinction with a series of local MSR [18]);

5) the effect of off-stoichiometry of mixture on the induction period of MSR ignition [9, 19];

6) substantial effect of the size of initial particles in thermite mixture on the mechanism and induction period of MSR igniton [20].

The occurrence of these effects provides not only the achievement of some specific results but also serves for theoretical investigation.

CONCLUSION

Experimental data and the observed features of MSR in the system Zn–Sn–S are described, as well as the hypothesis concerning stage-by-stage mechanism of MSR in general that may help the development of further investigations into modeling of MSR processes in mechanochemical reactors.

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REFERENCES

1 Chr. G. Tschakarov, G. G. Gospodinov, Z. Bontschev, *J. Solid State Chem.,* 41 (1982) 244.

2 Chr. G. Tschakarov, Ph. D. Thesis, Burgas, 1983 (in Bulgarian).

3 L. Takacs, *Mater. Sci. Forum,* 269–272 (1998) 513.

4 P. Yu. Butyagin, in M. E. Vol'pin (Ed.), Chemistry Reviews, vol. 23, part 2, Harwood Acad. Publ., Amsterdam, 1998, p. 89.

5 T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, *Uspekhi khimii,* 70 (2001) 52.

6 G. Mulas, L. Schiffini, G. Cocco, *Mater. Sci. Forum,* 235–238 (1997) 15.

7 G. Mulas, S. Loiselle, L. Schiffini, *J. Solid State Chem.,* 129 (1997) 263.

8 G. Cao, S. Doppiu, M. Monagheddu *et al., Ind. Eng. Chem. Res.*, 38 (1999) 3218.

9 L. Takacs, *Mater. Lett.*, 13 (1992) 119.

10 N. J. Welham, *J. Mater. Res.,* 14 (1999) 619.

11 F. Kh. Urakaev, V. S. Shevchenko, A. P. Chupakhin, *Fiz.-tekhn. probl. razrab. polez. iskopayemykh*, 6 (2001) 78.

12 A. G. Merzhanov, Protsessy goreniya i sintez materialov, ISMAN, Chernogolovka, 1998.

13 L. Takacs, M. A. Susol, *J. Solid State Chem.,* 121 (1996) 394.

14 A. Bakhshai, V. Soika, M. A. Susol, L. Takacs, *Ibid.,* 153, 2 (2000) 371.

15 F. Kh. Urakaev, L. Takacs, V. Soika *et al.*, *Zhurn. fiz. khim.,* 75 (2001) 2174.

16 F. Kh. Urakaev, V. S. Shevchenko, V. V. Boldyrev, *Dokl. RAN,* 377 (2001) 59.

17 F. Kh. Urakaev, V. V. Boldyrev, *Powder Technology,* 107 (2000) 93.

18 L. Takacs, *Appl. Phys. Lett.,* 69 (1996) 436.

19 L. Takacs , M. A. Susol, *Mater. Sci. Forum,* 225–227 (1996) 559.

20 F. Kh. Urakaev, L. Takacs, V. S. Shevchenko, *Zhurn. fiz. khim.,* 76 (2002) 1052.