

# MECHANOCHEMICAL METHOD OF OBTAINING POWDERS OF HIGH-MELTING COMPOUNDS (REVIEW)

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The mechanical method of activating solid-phase reactions has been known for a long time and has found widespread practical application [1]. Compounds such as intermetallides, sulfides, phosphides are synthesized with its aid. Lately this method has been used for chemical reactions by thermal explosion. In this case the role of mechanical activation consists in starting an exothermal reaction which then is sustained by the heat liberation of the chemical reaction. For the first time sulfides [2], carbides, carbonitrides, silicides, and tungstenless hard alloys [3] were synthesized by thermal explosion. Subsequent research [4-9] showed how promising this method is.

The aim of the present work is to generalize the results of investigations in the field of explosive mechanochemical synthesis (EMS), a special form of combustion of oxidant and fuel under conditions of their mechanical activation.

Explosive mechanochemical synthesis of high-melting compounds is carried out in a hermetic mechanical reactor of an energized mill. The initial components can be powders but also any other material suitable for comminution in the form of swarf, cakes, or fragments. The reaction of synthesis is initiated by high-energy mechanical activation of the initial components. In distinction to the self-propagating high-temperature synthesis (SHS), where the reaction is "ignited" by a powerful briefly acting (0.05-6 sec) radiant source (a coil), in EMS the energy is transmitted within a period lasting from a few minutes to tens of minutes. In the process of EMS the excess energy is gradually "pumped" to the reacting components. When this energy attains critical values, the reaction starts and proceeds in explosive kinetics. Like any exothermal reaction, the synthesis of high-melting compounds is marked by considerable heat liberation. The process was therefore studied by an analysis of the thermograms plotted in coordinates wall temperature of the mechanical reaction vessel—time of mechanical activation. It can be seen from Fig. 1, curve 1, that when the reaction proceeds by explosive kinetics, a considerable exothermal effect is found in the thermogram.

Using the thermograms we can obtain the following information:  
determine the power of the mill

$$W = \frac{mc\Delta T}{\tau},$$

where  $m$  is the weight of the mechanical reactor vessel with balls;  $c$  is the mean heat capacity of the material of which the mechanical reactor vessel is made;  $\Delta T$  is the change of temperature of the mechanical reactor vessel during mechanical activation;  $\tau$  is the time of mechanical activation;

calculate the power dose necessary for effecting EMS

$$D = \frac{W\tau_d}{M},$$

where  $W$  is the power of the mill;  $\tau_d$  is the delay time of the reaction;  $M$  is the weight of the charged initial components;

calculate the thermal effect  $\Delta H^\circ_{298}$ .

To enhance the accuracy of the obtained results, the mechanical reactor vessel has to be designed so as to ensure that the demands on a calorimeter are fulfilled and that the initial components are charged per 1 g-mole of substance. In that case the heat liberated in consequence of synthesis corresponds to the required value  $Q \approx \Delta H^\circ_{298}$ .

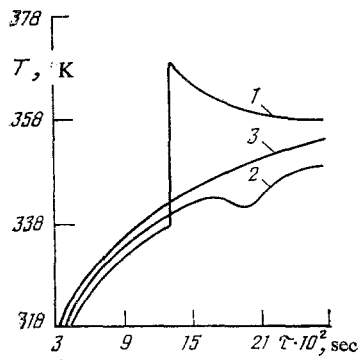


Fig. 1

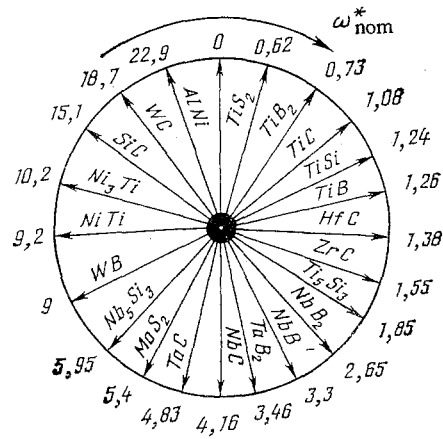


Fig. 2

Fig. 1. Thermograms of the composite PT88N12-C in dependence on the composition of the medium: 1) N<sub>2</sub>, Ar, air; 2) CO<sub>2</sub>; 3) O<sub>2</sub>.

Fig. 2. Diagram of the nominal critical heating rate  $\omega_{\text{nom}}^*$  for various compounds.

$$Q = Mc\Delta T,$$

where  $c$  is the heat capacity of the obtained products;  $\Delta T$  is the temperature jump on the thermogram.

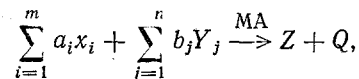
Moreover, when one compound is formed, the maximal temperature of the synthesis (with heat losses not taken into account) can be determined with the aid of a thermogram

$$T_{\text{ad}} = T_0 + \frac{Q_{\text{pr}}}{c},$$

where  $T_0$  is the initial temperature;  $Q_{\text{pr}} = Q + \sum_{i=1}^n \mu_p H_p$  is the heat of formation of the product at  $T_0$  (here,  $n$  is the number of phase transitions;  $\mu_p$  is the fraction of the more high-temperature phase in the product with  $T = T_p$ ;  $T_p$ ,  $H_p$  are, respectively, the temperature and heat of phase transition in the product);  $c$  is the mean heat capacity of the product.

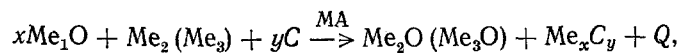
To study the kinetics of formation of the final product, we carried out x-ray phase analysis of the components subjected for a certain time to mechanical activation. According to the results, in EMS the final product does not form before the exothermal effect manifests itself in the thermogram [10]. Thus the combination of thermograms with the data of x-ray phase analysis is a fairly efficient and simple method of investigating the process of mechanochemical synthesis of various high-melting compounds.

Mechanochemical synthesis of high-melting compounds can be effected by various methods. The simplest of them is direct synthesis, where the reaction occurs between two or several elements:



where  $x$  is Hf, Ta, Zr, Ti, Nb, and other elements;  $Y$  is C, B, Si, S; MA is mechanical activation;  $Z$  is a chemical compound;  $Q$  is the thermal effect of the reaction.

A more complex synthesis is the combination of reactions of reduction and synthesis:



where  $\text{Me}_1\text{O}$  are oxides of any metals or nonmetals with lesser chemical affinity to oxygen than  $\text{Me}_2(\text{Me}_3)$  has;  $\text{Me}_x\text{C}_y$  are carbides or other high-melting compounds (in dependence on the type of oxidant). This method is of particular interest because, firstly, cheap initial raw materials (oxides) can be used, and secondly it yields compounds (e.g., WC) which cannot be produced by direct synthesis [11].

TABLE 1. Mechanochemical Dose, Heat of Reaction, and Energy of Formation of the Initial Oxide per 1 Mole Oxygen

Parameter	Oxide										
	CuO	Cu <sub>2</sub> O	CrO <sub>3</sub>	MoO <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	WO <sub>3</sub>	VO	TiO <sub>2</sub>	TiO	B <sub>2</sub> O <sub>3</sub>
<i>D</i> , kJ/g	0,30	0,30	0,40	0,50	0,55	0,60	0,70	0,72	1,10	1,25	9,0
<i>Q</i> , kJ	440	430	405	350	340	330	320	170	130	80	180
$-\Delta H$ , kJ	160	175	195	250	265	275	280	430	470	525	420

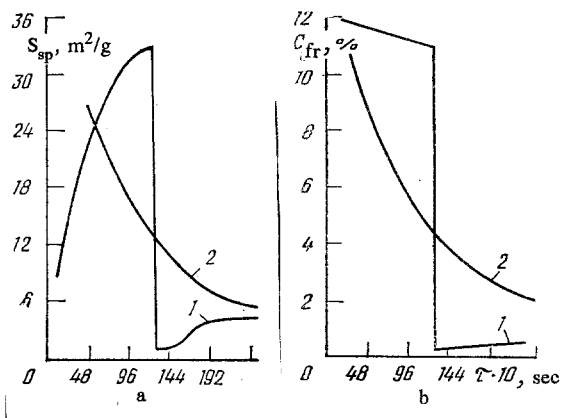


Fig. 3. The influence of explosive (1) and S-shaped (2) kinetics of the formation of titanium carbide on the specific surface of the powder (a) and on the content of free carbon of the final product (b).

To change EMS into some other kinetic regime, mechanical activation has to be temporarily interrupted and a comparatively low-melting initial component has to be used, or else mechanical activation has to be effected in a certain gaseous atmosphere [9]. When the kinetics of formation of a high-melting compound changes, the thermogram of the process also changes. For instance, the thermogram with endothermal effect (Fig. 1, curve 2) corresponds to quasi-explosive, and the thermogram without thermal effects (curve 3) to the S-shaped kinetics of formation of titanium carbide [9].

A number of publications [2, 4-10] dealt with the investigation of the regularities of EMS of high-melting compounds. It was established that the delay time necessary for initiating EMS is correlated with the chemical affinity of the elements to the oxidant [11]. As a rule, elements with greater affinity to the oxidant are also more suitable for explosive synthesis. Analogous properties also manifest themselves in more complex reactions, in particular in reactions of reduction [12]:

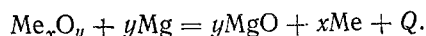


Table 1 shows that the mechanochemical energy dose necessary for initiating the reaction of reduction by explosive kinetics increases with decreasing thermal effect of the reaction (an exception is boric anhydride).

Proceeding from the theory of dynamic regimes of thermal explosion, Popovich [13] analyzed the influence of the heating rate of the mechanical reactor vessel on the process of EMS. He suggested the introduction of the so-called nominal critical heating rate  $\omega_{\text{nom}}^*$ , which is a qualitative indicator of the relation of some system to thermal explosion. Figure 2 presents the theoretical diagram of the nominal critical heating rate that is indispensable for the synthesis of a number of compounds by explosive kinetics. Such a diagram makes it possible to assess the suitability of a certain system for thermal explosion. For instance, titanium sulfide tends more to thermal explosion than titanium borides, carbides, and silicides. To convert qualitative indicators into quantitative ones, it was suggested to assume that there exists a linear correlation between

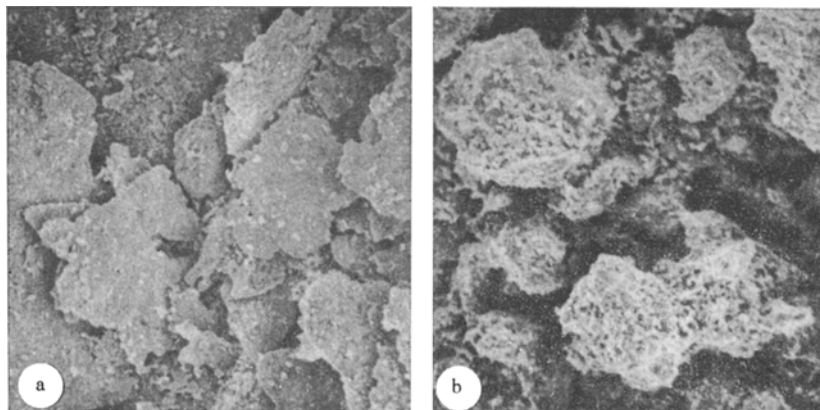


Fig. 4. Morphology of the particles of powder composite Ti–C before (a) and after the exoeffect (b).  $\times 150$ .

the critical heating rate and the specific power of the mill  $W_{sp}$ . The specific power of the mill required for EMS of a high-melting compound is determined experimentally. For titanium carbide with stoichiometry close to unity it is 2 W/g. Thus having experimentally determined the specific power of the mill required for EMS of titanium carbide, and using the data of the diagram (Fig. 2), we can calculate it for some other compound. For instance, in the synthesis of tungsten monocarbide  $W_{sp} = 37.4$  W/g, and in the synthesis of titanium diboride  $W_{sp} = 1.46$  W/g.

The authors of [4] established a correlation of the suitability of a system to EMS with the maximal temperatures of synthesis and the maximal melting point (of metal). It was shown that if the inequality  $T_{ad} > T_{mp}$  applies, the system is suitable for EMS.

The dependence of the delay time of synthesis of titanium carbide on the technological parameters and the composition of the charge (the specific power of the mill was 2 W/g) was investigated by the authors of [14]. When the particle size of titanium changed from 63 to 1600  $\mu\text{m}$  (the parameter  $x$ ), the delay time of EMS of titanium carbide was determined by the equation  $1.4x + 0.53y - 12.3 = 0$ . The influence of the diameter of the crushing balls, of the intensity and filling volume of the mechanical reactor vessel with balls for the delay time is described by the quadratic dependence  $y = ax^2 + bx + c$ . The addition of up to 50% metal (iron, nickel, cobalt) to the initial charge extended the delay time, and the mentioned dependence assumed the form  $ax - by + c = 0$ , and when the carbon content of the initial charge was raised from 9 to 20%, which delayed the synthesis of titanium carbide, the dependence had the form  $0.16x - 0.1y - 0.99 = 0$ . The addition of a certain amount of inert solvent or polymer (PMMA  $\geq 5\%$ ) to the initial charge, execution of the process in a certain medium (for the system titanium–activated carbon such a medium is argon) makes it possible to suppress EMS. Moreover, the above-mentioned factors reduce the heat content of the system, shift the thermal equilibrium to increased heat exchange with the environment, and thereby they prevent thermal explosion.

The thermograms of the system PT88N12–C in dependence on the medium of mechanical activation can be divided into three kinds (Fig. 1). Each of them corresponds to certain kinetics of forming titanium carbide [9]. For instance, mechanical activation in a medium of carbon dioxide led to the appearance of an endothermal effect on the thermogram (Fig. 1, curve 2), the formation of titanium carbide was effected by quasiexplosive kinetics [9]. When activation proceeded in a medium of oxygen, there were no thermal effects in the thermogram (curve 3), formation of the titanium carbide proceeded by S-shaped kinetics. Another way of changing the explosive nature of the formation of titanium carbide into an S-shaped nature was suggested in [4], specifically: stopping the process prior to EMS, holding, and subsequent activation.

Thus, the regularities of the EMS of high-melting compounds are very variegated. With the aid of the above-mentioned parameters we can control the process, ensure a stable reaction, or else we can suppress it or change to a different kinetic regime. On the whole the established regularities of processes of mechanical activation are based on ensuring the start of a spontaneously proceeding exothermal reaction.

It was established [2-15] that the composition of high-melting compounds forming in mechanochemical synthesis depends on a number of factors: the temperature of the synthesis, the type of phase diagram metal–nonmetal, the composition of the medium of mechanical activation, the kinetics of formation of the compounds.

During EMS a considerable amount of heat is liberated, and consequently the temperature becomes very high. Calculation of  $T_{ad}$  shows that in the reaction zone the reagents may be in different states of aggregation (solid and liquid-phase, gaseous). Moreover, thanks to the specifics of the method, the final product is cooled fairly rapidly, and that also makes its mark on the structure formation.

The authors of [7, 12] examined the case of formation of the phase composition of compounds when  $T_{mp}^i \leq T_{ad} \leq T_{mp}^j$ ,  $T_{mp}^i \leq T_{ad} \leq T_{bp}^j$ , where  $T_{mp}^i$  is the melting point of the  $i$ -component;  $T_{bp}^j$  is the boiling point of the  $j$ -component. It was established that at the instant of reduction of boron anhydride by magnesium the temperature is high enough for the final products to evaporate [12]. Subsequent quenching of the reaction products prevents oxidation of the boron. This brings about a higher yield of amorphous boron from boron anhydride than with the SHS process. Of particular interest are publications reporting on investigations of the structure formation of powders of cast alloys. Most high-melting compounds form eutectic with metals. Because of the high temperatures accompanying the synthesis of high-melting compounds (for TiC  $T_{ad} = 3281^\circ\text{K}$ ) in the presence of the solvent metal, conditions for the crystallization of the high-melting compound in the metallic matrix are created. When the titanium carbide was nonstoichiometric composition, the structure of the alloy corresponds to triphase equilibrium  $\text{TiC}_{1-x} + \text{Ni}_3\text{Ti} + \text{Ni}$ , and when the composition is stoichiometric, it corresponds to the biphasic equilibrium  $\text{TiC} + \text{Ni}$  [3].

The correlation between the phase diagram of metal–nonmetal and the composition of a high-melting compound was established in [15]. It was shown that with EMS of high-melting compounds that melt incongruently and that also have a line of stoichiometry coinciding with the narrow region of homogeneity or passing outside the region, it is extremely difficult or altogether impossible to obtain single-phase products. For each actual case its conditions of synthesis have to be chosen. For instance, if the yield of tungsten monocarbide from the composition  $\text{WO}_3 + \text{Mg} + \text{C}$  is to be increased, hydrogen or hydrocarbons have to be present. The latter are a kind of carrier of carbon to tungsten particles. The formation of the phase composition of the final product in the system  $\text{B}_2\text{O} + \text{Mg} + \text{Ti}$  is determined solely by the magnesium-thermal reaction [15]. Depending on the titanium content of the initial composite, the final product consists of the phases  $\text{TiB}_2 + \text{MgO}$  or  $\text{TiB}_2 + \text{MgO} + \text{Ti}$ . Other titanium borides do not form. If the line of stoichiometry passes inside the region or coincides with one of the boundaries of the phase diagram, there are no particular difficulties in obtaining single-phase products by EMS (TiC, ZrC, HfC, ZrB<sub>2</sub>, TiB<sub>2</sub>, Ti<sub>3</sub>Si<sub>3</sub>, etc.).

It was established [9] that the composition and properties of a high-melting compound change in dependence on the kinetics of its formation. For instance, in EMS of titanium carbide accompanied by the appearance of an exoeffect on the thermogram, the content of free carbon and its specific surface change jumpwise whereas when the process is carried out along the S-shaped kinetic curve it proceeds smoothly (Fig. 3).

The morphology of particles of powdered composite  $\text{Ti} + \text{C}$  is shown in Fig. 4. Before the exothermal effect the particles had lamellar shape; after the synthesis they became oval with a highly developed surface. When titanium carbide forms according to S-shaped kinetics, the morphology of the powder particles changes in a different way: with longer time of mechanical activation the amount of particles with "spongy" shape increases.

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