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Mechanical Activation Methods in Inorganic Materials Science

E. G. AVVAKUMOV

*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia**E-mail: ega@academ.org*

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Abstract

Many branches of science and technology need new materials. Different methods are used to obtain them. In particular, one of the promising methods used both at the stage of preparation for the thermal synthesis of materials and as an independent method is the mechanical activation of solids. Research carried out by domestic and foreign scientific organisations is devoted to the development of fundamental principles of mechanochemical technologies. This review summarises and formulates some patterns of mechanochemical reactions, such as the reactions of hydrated compounds and mechanically stimulated solid-phase thermal reactions, and indicates the most effective ways of their use. Examples of the synthesis of materials with valuable properties for use in modern technology are presented.

Keywords: thermodynamic and kinetic laws of mechanochemical reactions, synthesis in mixtures of hydrated compounds, mechanically stimulated solid-phase synthesis

INTRODUCTION

The synthesis of materials possessing practically significant properties is currently one of the urgent problems. A disadvantage of commonly used solid-phase thermal synthesis is in low reaction rates, because they are limited by the rates of diffusion processes, which occur with noticeable effects only at a high temperature. To accelerate synthesis, new physical methods are involved, and at present the method moving to the forefront is mechanical activation based on the treatment of solid mixtures in grinding and activating devices. The joint mechanical treatment of solid mixtures involves their grinding, and they are subjected to plastic deformations. Mass transfer processes are accelerated, and the components are mixed at the atomic level, which provides an acceleration of the chemical interaction between the solid reagents.

The materials of the highest interest for modern materials science are those possessing unique characteristics, such as a high melting point, low thermal expansion coefficient, high hardness and resistance to wear, high conductivity or high resistance, piezo- or pyroelectric properties, etc. Many of the listed properties are characteristic of simple and complex oxides and the compounds of transition metals with carbon, nitrogen, boron, sulphur. The present work summarises the methods of obtaining the indicated compounds with the help of mechanical activation. To choose the most optimal routes for the implementation of this method, its new versions have been proposed, taking into account the chemical properties of reagents and energy effects of chemical reactions that proceed under the effect of mechanical activation, in particular **soft mechanochemical synthesis**, implying the use of hydrated compounds as initial components, and **mechani-**

cally stimulated exothermal solid-phase synthesis. The prospects of using soft mechanochemical method for the synthesis of materials are described in review [1]. However, since then, new works contributing to the development of this method have been published. The present work should be considered as a continuation of the above-indicated review. The published articles are so numerous that many essential works can inevitably be omitted. The author hopes that the main ideas and notions will be understandable to the readers despite the indicated shortcoming.

THERMODYNAMIC AND KINETIC ASPECTS OF MECHANOCHEMICAL REACTIONS

By present, the syntheses of a large number of compounds have been carried out, some regularities of mechanochemical processes have been established, and their mechanisms have been studied. These studies are summarised in a series of reviews and monographs [2–9].

Before passing to the description of specific works, some general regularities typical not only for mechanochemical reactions but also for other chemical processes are to be considered.

The probability for chemical reactions to occur is determined by thermodynamic calculation of the difference of isobaric-isothermal potentials (free Gibbs energy changes, ΔG) for final products (ΔG_{fin}) and initial reagents (ΔG_{in}).

$$\Delta G_{\text{reaction}} = \sum \Delta G_{\text{fin}} - \sum \Delta G_{\text{in}} \quad (1)$$

A reaction proceeds spontaneously in the direction towards a decrease in the free energy, that is, in the forward direction if $\Delta G_{\text{reaction}} < 0$ and in the reverse direction if $\Delta G_{\text{reaction}} > 0$.

The formation of products occurs mainly in the systems with the negative values of the thermodynamic potential. The same is true for mechanochemical reactions. For instance, we have studied the reduction of tin dioxide by aluminium, silicon, tungsten, and carbon, and demonstrated a direct correlation between the thermodynamic potentials of reactions and the dynamics of dioxide reduction under the conditions of mechanical activation [7, 9].

One of the fruitful ideas of modern chemistry is the concept of element electronegativity. Its conclusions are successfully employed in the diverse areas of chemistry [10, 11]. The electronegativity (X) of an atom is the value characterising the relative ability of an atom in the molecule to acquire a negative charge. According to Mul-

liken [12], electronegativity can be measured as a sum of ionisation potential and electron affinity of an atom. Another, more complicated method to determine electronegativity was proposed by Pauling [13]. He established a connection between the difference of atomic electronegativities in AB molecule and the thermal effect (Q) of AB formation from atoms A and B:

$$X_A - X_B = 0.208 \sqrt{Q} \quad (2)$$

In elaborating this concept, it was proposed to characterise molecules using the average orbital electronegativity (X_{av}) of a compound [13]:

$$X_{\text{av}} = (\sum n_i X_i) / \sum n_i \quad (3)$$

where n_i is the number of atoms in the compound, X_i is atom electronegativity, according to Mulliken [12].

It is sometimes difficult to calculate the free Gibbs energy for reactions in two- and multi-component systems because of the lack of reference data. The authors of [14, 15] established a clear correlation between $\Delta G_{\text{reaction}}$ and ΔX calculated according to the equation

$$\Delta X = \sum X_{\text{fin}} - \sum X_{\text{in}} \quad (4)$$

where X_{fin} and X_{in} are electronegativities of the final and initial compounds in the reaction, respectively.

Electronegativity values are tabulated for almost all elements of the Mendeleev's periodic table, and calculation of average orbital electronegativities does not involve any special problems. For this reason, equation (4) can be used to assess the probability of reactions to proceed in the mixtures of solids in the case if thermodynamic data for these mixtures are unavailable or unknown, instead of equation (1) for the free Gibbs energy of the reaction. The indicated equation (4) does not contradict with equation (1), because according to the definition of electronegativity formulated by Pauling, it is connected with the thermal effect of molecule formation from atoms.

The probability of the synthesis of compounds during mechanical activation of the mixtures of solids depends not only on the Gibbs energy difference between the final products and initial reagents but also on some other factors, in particular on the difference of reagent hardness values [7]. The higher is plasticity of the components of a solid-phase reaction, the better is contact between particles and the higher is synthesis rate. A correlation between the rate of a solid-phase reaction and the sizes of reacting particles has been

also established: the smaller is size, the higher is reaction rate [8].

The mechanical energy supplied to the mixtures is transformed into other kinds of energy, among which the major ones are thermal energy and the energy accumulated by the material. The thermal component represents losses as a rule, while the energy accumulated by the material can be used in the reaction process. Initial reagents are transformed into final products as a result of the interaction between elastic strains and chemical forces. Elastic stresses cause an increase in the internal energy of reagents. Consequently, the thermodynamic parameters of initial reagents, intermediates and final products differ from the standard values, which leads to differences in equilibrium constants and enthalpies of reactions.

It is generally thought that among two main thermodynamic factors of mechanical action, namely temperature and pressure, pressure is the most significant one. Under its action, shear stresses arise in the solids, and the work output by elastic stresses is spent to overcome the energy barrier that separates the initial and final states in elementary acts. Therefore, kinetic parameters are changed, and an additional contribution to reaction enthalpy is made.

The rate of interaction ($d\alpha/dt$) in the mixtures of solids is determined by the area of contacting regions, depending on the energy of mechanical action and the mechanical characteristics of solids:

$$d\alpha/dt = K_m x S_n \quad (5)$$

where K_m is the constant characterising the probability of reaction to proceed under the specific conditions of mechanical action; x is the probability of contact between solid particles; S_n is the area of contact between particles [9].

The initial stages of mechanical activation involve grinding of all the components in the mixture to equal extents. The hardness of hydrated compounds is 3–4 times lower than that of non-hydrated ones, so grinding proceeds at a higher rate. In addition, some amount of water is released from hydrated compounds due to their partial dehydration. In agreement with the Rehbinder effect, their hardness decreases, and grinding accelerates. Fine particles combine to form globules [16].

The reason for aggregation is the transition of the substance to the state of plastic flow, and this state is responsible for the acceleration of chemical interaction. It follows from the reported data

that the conditions necessary for the activation of solids are to involve the plastic flow of solid reagents arising as soon as possible. This can be achieved either by enhancing the mechanical parameters (loading rate, device power, etc.) or by involving smaller reagent particles, which will be able to pass into the state of plastic flow immediately during activation.

According to the above-described information, the rate of a solid-phase reaction proceeding in the grinding devices can be expressed in terms of the law of mass action through equation

$$d\alpha/dt = K_m x S_n (1 - \alpha) (1 - e\alpha) \quad (6)$$

where K_m is an energy-related constant characterising the value of mechanical action in the device used for grinding that does not depend on treatment time; e is the coefficient that takes into account the deviation of mixture composition from the stoichiometry, $e = c/l$ (where c is the stoichiometric coefficient, l is the molar ratio of A to B in the initial mixture).

In the case when specific surface is linearly dependent on grinding time at the initial stages of grinding (that is, $S_n = kt$), where k is grinding constant from the equation of grinding kinetics $S_n = S_m(1 - e^{-kt})$, integration of the equation gives

$$\alpha/(1 - \alpha) = Kt^2 \quad (7)$$

where $K = K_m x S_m$.

As indicated above [16], fine particles form globules in which the particles are bound with each other and are in permanent contact, then it may be accepted that S_n is a constant value and remains unchanged during treatment. Taking this into account, we obtain the equation

$$\alpha/(1 - \alpha) = Kt \quad (8)$$

which is similar to the equation of a bimolecular reaction, but the physical sense of constant K differs from that in the molecular kinetic theory of chemical reactions. The indicated equation provides a satisfactory description of the experimental data in the case of high mechanical load. Clarification of the physical sense of constant K and its quantitative characteristics is the subject of a number of publications [17, 18].

APPLICATION OF SOFT MECHANOCHEMICAL SYNTHESIS FOR OBTAINING THE MATERIALS

Initial components for soft mechanochemical synthesis are the compounds containing hydroxide groups and bound water: hydroxides and solid

acids, basic and acid salts, crystal hydrates, etc. [6]. The hardness of these compounds is 3–4 times lower than the hardness of anhydrous ones, which makes it possible to decrease the level of mechanical load during activation. The product formed in the course of mechanical activation can be in the crystal or X-ray amorphous state. For the latter one, thermal treatment at rather low temperatures is required.

The features and advantages of this method for different reactions have been considered previously in [19]. It is determined on the basis of the entire set of results obtained that the difference in the acid-base properties of compounds plays a significant part in these reactions. The larger is this difference, the higher is reaction rate and the depth of conversion. One of the products of reactions in the mixtures of hydrated compounds is water. Thermodynamically favourable reactions are those in which a minimal amount of water is participating.

A good example of the high efficiency of the method is given by the data reported in [20], related to the soft mechanochemical synthesis of calcium molybdate from the crystal hydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$.

Crystal CaMoO_4 is formed after mixture activation in a VM-4 vibratory mill for 5 min and does not require thermal treatment. Without activation, a similar product is formed after annealing at a temperature of 650 °C.

At present, ceramic materials based on ZrO_2 – Al_2O_3 find broad application in various areas of technology due to a unique combination of the physicochemical characteristics of this system: high chemical and thermal stability, as well as lower inclination to low-temperature degradation, on the one hand, and commercial availability on the other hand. Zirconium oxide (ZrO_2) intended for mixed corundum ceramics, stabilised with 3 % yttrium, was obtained in the finely dispersed state by the soft mechanochemical synthesis. This ensured the formation of high-quality mixed ZrO_2 – Al_2O_3 ceramics [21].

This method was also used by the authors of [22] to obtain the solid solution of zircon (ZrSiO_4) with cerium.

The synthesis of aluminium-magnesium and aluminium-nickel spinel was implemented successfully by the soft mechanochemical method as described in [23].

The issues related to the synthesis of catalyst supports, in particular using the soft mechanochemical synthesis, are the subject of review [24].

MECHANICALLY STIMULATED EXOTHERMAL SOLID-PHASE SYNTHESIS

Another method allowing a substantial decrease in energy consumption for mechanical activation is based on using the heat of exothermal reactions between the reagents. This contribution is substantially higher than thermal heating due to the transition of mechanical energy into thermal. The exothermal heat effect manifests itself in most of mechanochemical reactions and leads to the acceleration of chemical interaction. Sometimes it exhibits explosive behaviour, which places it in close quarters with the method of self-propagating high-temperature synthesis, however, the method of reaction initiation is different.

Processes based on exothermal reactions, in particular the reduction of oxides with metal reducing agents, have been used for practical purposes (aluminothermy, magnesiothermy) for a long time. They are also successfully used at present to obtain fine metal powders from the mixtures of metal oxides with magnesium under the action of mechanical activation [25].

Mechanically stimulated exothermal solid-phase synthesis (explosive mechanochemical synthesis) has come into use not long ago. Nevertheless, its application is becoming increasingly extensive. For instance, some results on the synthesis of the carbides of transition metals using this method were described in monograph [7], and the authors who obtained those results can be recognised as the pioneers of this direction. Though the method is named explosive, an explosion not always can be recorded in grinding devices. Reagent mixtures are placed in tightly closed reactors into energy-intensive mills (vibratory or eccentric), with the possibility to adjust vibration frequency. The carbides of B, W, V, Ti, Ta, Zr, Hf were synthesised using these mills [7].

Some carbides and composites based on these carbides have been successfully synthesised recently using this method [26].

A new approach to obtaining refractory materials was implemented as described in [8, 27] for the synthesis of tungsten carbide as an example. This approach is based on the use of exothermal reduction of tungsten (VI) oxide by metal reducing agents (aluminium or magnesium). For this purpose, a ternary mixture $\text{WO}_3 + \text{C} + \text{Al}$ (or Mg) is subjected to mechanical activation. As a result, tungsten carbide is formed, along with a metal oxide, which is removed from the mixture through dissolution in an acid.

Mechanical activation is a promising method also for use at the stage of mixture preparation for self-propagating high-temperature synthesis. For instance, the authors of [28–30] used this method to make ceramics based on the borides of transition metals with melting points around 4000 °C.

CONCLUSION

On the basis of the review of the presented results, it is possible to outline the routes for the most efficient application of mechanical activation to obtain materials with valuable properties. This is achieved in the case if the duration of mechanical activation is minimal, and subsequent thermal treatment is carried out at the minimal temperature sufficient for product crystallisation. It is promising to use exothermal effects to accelerate the reduction of oxides by metals. The heat released during this interaction is consumed for the acceleration of target reaction, while the formed metal is in the fine dispersed state and possesses increased reactivity, which also promotes acceleration of the synthesis of target product.

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