Features of mechanochemical synthesis in the system of solid reagent – active gas

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Abstract. Different modes of mechanochemical synthesis of titanium nitride are found based on the developed mathematical model and experimental data. Approximate analytical formulas are obtained for estimating the characteristics of mechanochemical synthesis during its different stages.

1. Introduction
Mechanical activation (MA) is an effective method for stimulating chemical reactions and expanding the possibilities for the synthesis of inorganic materials [1-3]. For example, MA can be used to synthesize low-energy compositions which practically do not burn under the typical conditions of synthesis.

During the MA process, reagents are significantly dispersed and the area of interphase contact increases, which leads to the formation of a new highly defect structure that is characterized by the increased excess energy. The presence of excess energy increases the chemical activity of the system.

The purpose of this work is an experimental and theoretical study of mechanochemical synthesis initiated by thermal explosion in a binary heterogeneous system of «titanium-nitrogen» to find different modes of this process.

The one- and two-stage mechanochemical synthesis of titanium nitride was considered in the work. In the first case, the heterogeneous system «titanium-nitrogen» was used to study the chemical transformation of initial reagents into the final product directly in the mechanoactivator.

In the second case, the «titanium-nitrogen» system was used to study two-stage mechanochemical synthesis. At the first stage, the activation of reagents was conducted in the mechanoreactor, and at the second stage a chemical compound was synthesized in the thermal explosion mode.

In the work the experiments were conducted to develop the mathematical models of processes. The diagrams of initial parameters determining the process were constructed to describe the different modes of thermal explosion in the mechanically activated mixture. The results obtained can be used to predict the behavior of the system after MA and optimize the mechanochemical synthesis of titanium nitride for obtaining a product with required properties and a structure.

2. Procedure

2.1. Grinding and mechanical activation of the powder mixture.
The mechanical activation and grinding of titanium powder (PTS) was conducted in a planetary mill M-3 (45g) under extra-pure 1st grade nitrogen (GOST 9293-74). The volume of steel drums was
1000 cm³, the initial pressure of nitrogen in the drum was 2 \times 10^5 \text{ Pa}, and the diameter of steel balls was 0.3-0.4 cm. The weight of the powder and the ball-to-powder mass ratio were 10 g and 20:1, respectively. The duration of mechanical activation was varied in the range of 0.5-6 minutes. In each case, only fresh titanium powder was used. At specified moments of time the mill was stopped to measure the pressure of nitrogen in the drum using the manometer MT6.184, the nitrogen content in the products and the broadening of X-ray reflections of titanium and titanium nitride.

The specific surface of titanium powders was determined after MA of different durations by the gas-adsorption method. Morphology of the powders was studied by scanning electron microscopy (Phillips SEM 515 and EDAX).

2.2. Synthesis of the mechanically activated mixture in the thermal explosion mode.

A setup for thermal studies, consisting of a reaction chamber, an electric furnace, and an electronic potentiometer KSP-4, was used to analyze the dynamics of temperature during the interaction of mechanically activated titanium with nitrogen. Activated powder with a mass of 3-3.5 g was poured into the cups made of steel thin mesh and pressed by hand to obtain a porosity of 60-65%. The cup with a powder and a tungsten-rhenium thermocouple 100 microns in diameter was placed in a tubular electric furnace, the reaction chamber of which was filled with nitrogen and heated at a constant rate of 360–380 degrees/min to the temperature of thermal explosion. The thermocouple data were recorded using an electronic potentiometer KSP-4. The thermogram determined the ignition temperature and the maximum synthesis temperature.

To study the relaxation of excess energy, mechanically activated titanium powder was pressed in the cylinders with a diameter of 1 cm and a height of 1 cm, which were annealed in a vacuum electric furnace in the temperature range of 200-14000ºC for 1 hour at each temperature.

The phase composition of the final products and the conditional values of accumulated and relaxed excess energy were studied by X-ray diffraction. The chemical composition of the final products was determined by the Kjeldahl method.

3. Mathematical model

For a mathematical description of the mechanochemical synthesis of titanium nitride, we use the methodology and basic equations given in [4]. In addition, we accept the assumptions as follows:

- difference in the density of the initial mixture and the product is neglected;
- heat release from the grinding device and the relaxation of excess energy in the mechanically activated and synthesized mixture is insignificant.

Taking into account the above assumptions, the mechanochemical synthesis in the Ti-N system will be described by the system of phenomenological equations as follows:

- grinding that determines the change in the specific surface of particles

\[
\frac{dS}{dt} = (1 - \alpha_\mu)(S_m - S)k - \frac{S}{(1 - \alpha_\mu)} \frac{da}{dt}, \quad (1)
\]

- dynamics of excess energy in the titanium particles and the reaction product

\[
\frac{d\varphi}{dt} = \Delta(1 - \alpha_\mu) - \varphi_y \exp \left( - \frac{U - \varphi}{RT} \right), \quad (2)
\]

\[
\frac{d\varphi_F}{dt} = \Delta(1 - \alpha_\mu) - \varphi_y \exp \left( - \frac{U - \varphi_F}{RT} \right) - \frac{\varphi_F}{\alpha} \frac{da}{dt}, \quad (3)
\]

- pressure of nitrogen in the mill chamber

\[
p = \frac{\rho_g}{M_g} RT, \quad (4)
\]
- chemical conversion

\[ \frac{da}{dt} = K(T) \left( \frac{p}{p^*} \right)^{\varepsilon} f(\alpha) F(S), \quad (5) \]

- heat balance

\[ \sum \frac{dT}{dt} = \frac{Q}{c} \frac{da}{dt} + J_i, \quad (6) \]

The parameter \( \Sigma \) in (6) can be determined as follows. For the first stage of mechanochemical synthesis (mechanoactivation and grinding): \( \Sigma = 1 + c_m \rho_m/(\chi_0 \alpha_p) \), for the second stage of mechanochemical synthesis: \( \Sigma = 1 \).

Initial conditions for the first stage of mechanochemical synthesis

\[ t = 0: S = S_0, \varphi = 0, T = T_0, \ p = p_0, \ \alpha = 0; \quad (7) \]

for the second stage of mechanochemical synthesis

\[ t = 0: S = S_a, \ \varphi = \varphi_a, T = T_0, \ p = p_0, \ \alpha = \alpha_a; \quad (8) \]

In (1)-(8) the parameters and variables are used as follows: \( t \) is the time; \( T_0, T \) are the initial and current temperature; \( \alpha \) is the mechanochemical conversion degree defined as the product-to-mixture mass ratio; \( \varphi \) is the gas pressure in the mill chamber; \( p^* \) is the normal pressure; \( R \) is the universal gas constant; \( M_g \) is the molecular weight of gas; \( \rho_g \) is the gas density; \( S_0, S \) are the initial and current specific surface of titanium; \( \rho_m \) is the maximum specific surface of titanium achieved during grinding; \( k \) is the coefficient characterizing the grinding rate of the powder mixture; \( \chi_0 \) is the initial volume fraction of the powder mixture in the mill chamber; \( \mu \) is the mass fraction of gas in the reaction product; \( \Delta = bW/(\chi_0 V) \) is the constant characterizing the accumulation rate of excess energy in the mixture; \( W \) is the mill capacity; \( V \) is the volume of the mill chamber; \( b \) is the coefficient of proportionality; \( \varphi, \varphi_F \) are the amount of excess energy in titanium and in the reaction product, which are identical with the relative broadening of the peaks of X-ray diffraction; \( Y, U \) are the pre-exponential factor and the activation energy of the relaxation of excess energy; \( K(T) = k_0 \exp[-(E-Y\varphi)/RT] \) is the constant of the chemical reaction rate; \( k_0 \) is the pre-exponential factor; \( E \) is the activation energy of chemical reaction; \( g \) is the exponent; \( \gamma \) is the coefficient characterizing the effect of excess energy on the activation energy \( E \); \( f(\alpha) \) is the kinetic law (in our case, the reaction in the diffusion approximation through the product layer, therefore \( f(\alpha) = 1/\alpha \)); \( F(S) = S/S_0 \) is the function of the reaction surface, \( Q \) is the thermal effect of reaction, \( v_m, v_W \) are the volume fractions of grinding bodies and walls of the mill chamber, \( c_m, \rho_m \) are the heat capacity and density of the mill; \( c, \rho \) are the heat capacity and density of titanium; \( J \) is the external heating rate of the powder mixture at the first stage of mechanochemistry \((i=1)\) due to the operation of the mill, and at the second stage of mechanochemistry \((i=2)\) due to heating in the electric furnace; \( S_a, \varphi_a, \alpha_a \) are the values of the parameters of \( S, \varphi \) and \( \alpha \) by the time of the completion of mechanoactivation \( t_a \).

To solve the formulated problem (1)-(7), the initial parameters are used as follows [5, 6]: \( E = 141510 \) J/mol, \( Y = 36564 \) J/mol, \( Q = 3.5 \times 10^5 \) J/kg, \( c = 528 \) J/(kg K), \( c_m = 500 \) J/(kg K), \( \rho_m = 7800 \) kg/m\(^3\), \( g = 45 \) min\(^{-1}\), \( U = 42000 \) J/mol, \( J_0 = 0 \), \( J_0 = 360 \) K/min, \( \gamma = 1 \), \( M_g = 2.8 \times 10^3 \) kg/mol, \( \mu = 0.23 \), \( \Delta^* = 21.6 \) min\(^{-1}\). The value \( \Delta^* \) determines the accumulation rate of excess energy during the mechanoactivation of titanium at \( \chi_0 = 0.0037 \) [5]. We assume that for an arbitrary \( \chi_0 \) the constant of the accumulation rate of excess energy can be found from the relation

\[ \Delta = \frac{\Delta^* \cdot 0.0037}{\chi_0}. \]
4. Discussion

Figure 1 shows the dynamics of the specific surface of particles as a function of the time of mechanical activation in the titanium-nitrogen system. The solid line denotes the theoretical calculation, the symbol ● denotes the experimental points, and the dashed line is the spline curve fitting to the experimental points. It can be seen that, as grinding proceeds, an intensive increase in the theoretical value \( S \) is observed. Then, when the system reaches the limit of grinding, the specific surface of the particles remains practically unchanged.

![Figure 1. Specific surface of the titanium particles as a function of the time of MA.](image)

It should be noted that the experimental value of \( S \) as a function of the MA time is not monotonous. First, under the conditions of MA, the specific surface of the mixture increases, i.e. the powder of titanium is ground. Increasing the time of grinding to 5 min, the specific surface of powder decreases due to the agglomeration of powder particles and then increases again. The values of the parameters \( S_m \) and \( k \) used in (1) were found by processing the experimental data by the inverse problem method from the analytical relation that expresses the specific surface during the grinding of titanium as a function of the time of mechanoactivation:

\[
S \approx S_m \left[ 1 - \left( 1 - \frac{S_0}{S_m} \right) e^{-kt} \right]. \tag{9}
\]

Relation (9) was obtained by integrating (1) under the assumption that the chemical reaction has a negligible effect on the final particle size of the solid particles. Then, \( S_m = 1.2 \times 10^6 \text{ m}^{-1} \), \( k = 0.81 \text{ min}^{-1} \).

Assuming that the temperature of the system changes slightly (since \( Q/(c\Sigma) \approx 1.5 \)) at the stage of mechanoactivation of the titanium powder and integrating (5) with allowance for (2) and (9), we finally find an approximate dependence of the degree of chemical conversion on time during the grinding of titanium in a mill:

\[
\alpha \approx 2 \left( \frac{p_o}{p_i} \right)^\frac{g}{2} \frac{S_m}{S_0} \frac{RT_0}{Y\Delta} k_o \exp \left( -\frac{E}{RT_0} \right) \left[ \exp \left( \frac{Y\Delta}{RT_0} \right) - 1 \right]. \tag{10}
\]

The value \( \alpha \) calculated using formula (10) is the upper limit of this parameter.

From (10) it is possible to determine the minimum time of mechanoactivation \( t_{a*} \) required for the complete conversion of the reagents into the reaction product at the stage of MA \((\alpha=1)\):

\[
t_{a*} = \frac{RT_0}{Y\Delta} \ln \left[ 1 + \frac{1}{2} \left( \frac{p_o}{p_i} \right)^g \frac{S_0}{S_m} \frac{RT_0}{Y\Delta} \exp \left( \frac{E}{RT_0} \right) \right]. \tag{11}
\]

The diagram obtained by solving the system (1)–(8) and determining the different modes of the mechanochemical synthesis of titanium nitride is shown in figure 2. Regions I and II are separated by...
the line that is a locus of points \((t_a, \Delta)\) corresponding to the critical conditions of thermal explosion in an energy-intensive mill.

In Region I, the parameters of the mill operation \(t_a\) and \(\Delta\) exceed the critical parameters. In this case, the mode of one-stage mechanochemical synthesis takes place, when titanium nitride is synthesized at the stage of MA. Here \(t_a > t_a^*\), the final product is a powder mixture of small-sized titanium nitride particles with a highly defect internal structure (figure 3a).

**Figure 2.** Diagram of different modes of mechanochemical synthesis of nitride in the Ti–N system.

Region II shown in figure 2 corresponds to the mode of two-stage mechanochemical synthesis. Under these conditions at the MA stage, titanium powder is ground and activated under nitrogen without chemical interaction between the reagents \((t_a < t_a^*)\). The synthesis of titanium nitride under nitrogen occurs outside the mechanoreactor, at the stage of heating a sample formed from a powder mixture of activated titanium. In this case, preliminary MA will intensify the chemical conversion at the stage of TiN synthesis. The final reaction product obtained is a compact uniform material with a normalized (defect-free) structure (figure 3b).

**Figure 3.** Photos of the final product obtained by the one-stage (a) and two-stage (b) mechanochemical synthesis of titanium nitride.

5. **Conclusion**

1. A mathematical phenomenological model describing the mechanochemical synthesis of titanium nitride in the macroscopic approximation was proposed.
2. Based on the experimental data obtained and the mathematical model developed, the inverse problem was solved to determine the parameters for the grinding of titanium powder in an energy-intensive mill.
3. The diagram of the modes of one-stage and two-stage mechanochemical synthesis in the Ti–N system was constructed, which allow a final product to be obtained with different properties and structure.
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