Mechanical activation and thermal explosion in Ti-Ni and Nb-Si systems

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Abstract. Thermal explosion synthesis of previously mechanoactivated Ti-Ni and Nb-Si systems is studied experimentally. Thermal explosion in previously mechanoactivated Ti-Ni and Nb-Si systems is theoretically described at the macroscopic level. Preliminary mechanical activation is found to accelerate the synthesis of the reaction product. The thermokinetic and thermophysical constants of the process are determined by the inverse problem method using experimental data.

1. Introduction
At present, there are many methods to produce synthesized materials, but most of them require significant energy costs and are characterized by a multistage production process. This problem particularly concerns a number of low-energy systems, the internal energy of which is insufficient for conducting qualitative self-propagating high-temperature synthesis (SHS). Therefore, the development of methods of controlling the synthesis of materials to obtain products with required physical and chemical characteristics is the most important scientific problem of modern materials science.

Mechanical activation (MA) of reactive substances can be referred to the most effective method of controlling chemical conversions, which significantly expands the possibilities of materials synthesis [1, 2]. During MA, the particles of reagents are "pumped" with additional (excess) energy, substances are ground and an interphase surface is formed [3, 4]. These factors reduce the activation barrier of the chemical reaction and accelerate the synthesis of the final product.

The separation of the stages of mechanical excitation and chemical conversion is of particular interest, when the mixture is activated at the first stage, and the chemical conversion is initiated outside the mechanoreactor at the second stage. This two-stage process is effective for conducting SHS [5].

This paper investigates two-stage mechanochemical synthesis in Ti-Ni and Nb-Si systems using the experimental data [6, 7].

2. Procedure

2.1. Experiment
A powder mixture of Ti+Ni 55.06 wt% (stoichiometry 1:1) was mechanically activated in a M-3 planetary mill with a power rating of 45g under argon. The powders of titanium (PTEM1) and nickel (PNE1) were used. The mass ratio of the powder to the balls was 1:5. The duration of MA for the
powder mixture of titanium and nickel was from 1 to 9 minutes. The total time of MA was composed of discrete periods of 30 seconds, between which there was a cooling period of 5 minutes.

The powder mixture 62.3 wt% Nb+37.7 wt% Si (stoichiometry of NbSi₂, silicon powders with a purity of 99.7% and niobium, TS: 48-4-334-75) was mechanically activated under argon in a planetary high-energy centrifugal mill with a capacity of 60g and water cooling. The MA time was varied from 1 to 60 minutes. The dispersity of powders was varied in the range: from 10 to 63 microns for niobium and from 40 to 400 microns for silicon. The mass ratio of the powder to grinding balls was 1:20. The mass of the mixture placed into the drums of the mill was 30g. Before MA, the walls of the steel drums and the 5mm diameter balls were preliminarily lined with a grinding material to prevent the appearance of iron on their surfaces.

After MA, the powder mixture was pressed into cylindrical samples which were obtained on a hydraulic press at a pressure from 4.0 to 16.0 MPa. The thermal explosion of the sample was conducted in a constant volume unit (V=5 L) under argon.

A cylindrical sample 15mm in diameter, 18±5 mm in height, pressed from a mechanically activated mixture with an initial porosity of 30%, was placed on a stand in the gradientless central section of the tubular furnace. A thermocouple was placed near the sample, the readings of which were fixed by KSP-4. The furnace was protected with a molybdenum shield.

The structure and composition of activated powder mixtures and synthesis products were studied by scanning electron microscopy (Philips SEM515) and optical metallography (Axiovert200M).

2.2. Equations of mathematical model

To provide the uniform temperature distribution in the sample, the equations of energy conservation and chemical conversion, and the ratio for the excess energy can be written in the form:

\[
[c_2 + (1 - c_0) L_B (1 - \alpha) \delta(T - T_{LB})] \rho \frac{dT}{dt} = [Q_{A-B} + (1 - c_0) L_B e(T - T_{LB})] \rho \frac{da}{dt} - \rho \frac{df}{dt} + W_{A-B}, \quad (1)
\]

\[
\frac{da}{dt} = F(S) f(\alpha) k_{0 A-B} \exp \left[ -\frac{E_{A-B} - [c_0 f_A + (1 - c_0) f_B^0]}{RT} \right], \quad (2)
\]

\[
f = (1 - c_0)(1 - \alpha) f_B^0 + c_0 (1 - \alpha) f_A^0 + \alpha_0 f_F^0. \quad (3)
\]

In (1)–(3): \( c_A, c_B = c_B^0 + L_B \delta(T - T_{LB}) \) are the heat capacities of components \( A \) and \( B \); \( c_B^0 \) is the heat capacity of component \( B \), independent of the phase transition; \( t \) is the time; \( T \) is the temperature; \( T_{LB} \), \( L_B \) are the temperature and melting heat of heat of \( B \); \( c_2 = c_0 e^{T_{LB}} + (1 - c_0) c_B^0 \); \( c_0 \) is the mass concentration of \( A \) in the powder mixture and the reaction product (stoichiometric mixture); \( \rho = c_0 \rho_A e^{T_{LB}} (1 - c_0) \rho_B \) is the density of the mixture; \( W_{A-B} \) is the rate of heating by an external source of energy; \( \alpha \) is the chemical conversion degree defined as the mass fraction of the product in the reactive mixture; \( k_{0 A-B} \) is the pre-exponential factor; \( E_{A-B} \) is the activation energy of chemical reaction; \( R \) is the universal gas constant; \( \alpha_0 \) is the amount of the converted substance after MA; \( \rho_A, \rho_B \) are the density of components \( A \) and \( B \); \( Q \) is the thermal effect of reaction; \( f(\alpha) \) is the kinetic law;

\[
\delta(T - T_{LB}) = \begin{cases} 0, & T \neq T_{LB} \\ \infty, & T = T_{LB} \end{cases}
\]

is the Dirac delta function; \( \varphi_f = I_{A-B}, \varphi_f = I_{A-B} \rho_A, \varphi_f = \varphi_f \alpha_0 \alpha \) is the amount of excess energy stored in reagents \( A, B \) and product \( F \); \( \varphi_f = I_{A-B} \rho_A \rho_B / 2 \) is the amount of excess energy stored in the product during MA; \( \varphi_f \) is total excess energy in the system; \( F(S) = K_{A-B} \mu_A \mu_B / S^2 \) is the value of the interphase surface formed during MA; \( \mu_A, \mu_B \) are the initial volume fractions of reagents \( A \) and \( B \) in the powder mixture; \( t_0 \) is the time of mechanical activation; \( I_{A-B} \) is the accumulation rate constant of excess energy in the reagents and the product during MA; \( K_{A-B} \) is the coefficient of agglomeration of the initial particles of reagents into mechanocomposites during MA.

Initial conditions:
3. Results and discussion
The conducted studies showed that the preliminary mechanically activated mixture did not contain reaction products. This is seen in figure 1 that depicts the X-ray diffraction pattern of a powder mixture of titanium and nickel after MA for 5 minutes. The X-ray diffraction pattern shows only the peaks of the initial components. Earlier, it was also found in [8] that there were no chemical reactions in the Ti+Ni powder mixture in the investigated time range of preliminary MA.

\[ t = t_a, \quad T = T_0, \quad \alpha = \alpha_0, \quad \varphi_A = \varphi_{A,0}, \quad \varphi_B = \varphi_{B,0}, \quad \varphi_F = \varphi_{F,0}, \quad (4) \]

Figure 1. X-ray diffraction pattern of the Ti + Ni powder stoichiometric mixture after MA for 5 min.

Figure 2. Ignition temperature (1) and the maximum synthesis temperature (2) as a function of the time of preliminary MA of the Ti + Ni initial powder mixture.

Figure 2 shows the ignition temperature of the mixture (curve 1) and the maximum synthesis temperature of intermetallide (curve 2) as a function of the time of preliminary MA during the further thermal explosion. The increase in the time of MA leads to the decrease in the values of ignition temperatures with a variation in the values during MA for 4–6 min. A similar jump in the values is also observed for the maximum synthesis temperatures. Moreover, increasing the activation time of the initial mixture, the quantity first increases sharply, and then remains practically constant.

Figure 3 shows the X-ray diffraction patterns of the synthesized product after thermal explosion of the Ti+Ni powder mixture for different times of preliminary MA. It can be concluded that during synthesis the activated components interact completely with the formation of the TiNi stoichiometric phase. In addition, the reaction product also contains TiNi3 and Ti2Ni phases.

MA in the niobium-silicon system differs from the titanium-nickel system in that during the first minutes of MA the heterogeneous particles actively interact and form niobium silicide phases. After 2 minutes of MA the NbSi2, Nb5Si3, Nb5Si2 phases are detected. This powder system is低-energy and is incapable of initiation of SHS without any preliminary MA. The determined MA time interval that is required to conduct SHS in the thermal explosion mode was from 2 to 28 minutes. Figure 4 shows the characteristic temperatures during thermal explosion. Synthesis reactions can develop both in the liquid and solid phase, depending on the time of preliminary MA.

The increase in the ignition temperature with increasing the time of MA is caused by the decrease in the reactivity of the initial powder mixture due to the initial conversion of the substance at the stage of mechanical activation. When a smaller number of pure components start chemical interaction, the temperature of the mixture does not reach high values.
According to the XRD data, after the thermal explosion of the Nb-Si preliminary mechanically activated mixture, the formation of both multiphase and single-phase (NbSi₂) products is observed depending on the time of preliminary MA.

![Figure 3.](image1)

**Figure 3.** X-ray diffraction pattern of TiNi intermetallide (synthesis product) after 2 (a), and 9 (b) minutes of preliminary MA. ● - TiNi, ■ - TiNi₃.

![Figure 4.](image2)

**Figure 4.** The maximum temperature of reaction (Δ) and the temperature of thermal explosion (○) as a function of the mechanical activation time. (a) reaction of thermal explosion in liquid phase, (b) reaction of thermal explosion in solid phase.

4. Estimation of the Kinetic Parameter Constants

The values of the initial parameters used in the theoretical calculations were taken from [9, 10]:

\( c_{\text{Ni}}=462 \text{ J/kg} \cdot \text{K}, \quad c_{\text{Ti}}=524 \text{ J/kg} \cdot \text{K}, \quad c_{\text{Nb}}=263 \text{ J/kg} \cdot \text{K}, \quad c_{\text{Si}}=719.9 \text{ J/kg} \cdot \text{K}, \quad a_{\text{Ti}}=47.87, \quad a_{\text{Ni}}=58.7, \quad a_{\text{Nb}}=92.9, \quad a_{\text{Si}}=28.08, \quad \rho_{\text{Ti}}=4500 \text{ kg/m}^3, \quad \rho_{\text{Ni}}=8900 \text{ kg/m}^3, \quad \rho_{\text{Nb}}=8570 \text{ kg/m}^3, \quad \rho_{\text{Si}}=2330 \text{ kg/m}^3, \quad T_{\text{LSi}}=1688 \text{ K}, \quad L_{\text{Si}}=1.8 \times 10^9 \text{ J/kg}, \quad \mu_{0\text{Ti}}=0.61, \quad \mu_{0\text{Ni}}=0.39, \quad \mu_{0\text{Nb}}=0.3, \quad \mu_{0\text{Si}}=0.7, \quad c_0=0.62. \)

The rate of heating of the powder sample:

\( W'_{\text{Ti-Ni}}=W_{\text{Ti-Ni}}/(c_{\text{2p}})=619.6 \text{ K/min}, \quad W'_{\text{Nb-Si}}=W_{\text{Nb-Si}}/(c_{\text{2p}})=898 \text{ K/min}. \)

The initial temperature is \( T_0=300 \text{ K}. \)

The kinetic parameters \( I_{A,B}, \quad K_{A,B}, k_{A,B}, \quad E_{A,B} \) and \( Q_{A,B} \) characterizing the process of two-stage mechanochemical synthesis in the Ti-Ni and Nb-Si systems were determined using the experimental data.
data and the phenomenological equations (1)–(4) by the inverse problem method. For this purpose, equation (1) was integrated and written in the form:

\[ \Delta T = T_m - T_i \cong (1 - \alpha_0) \left( \frac{Q_{A+B} + I_{A+B}I_t}{c} \right) \cdot \frac{Q_{A+B} + I_{A+B}I_t}{c} \cdot \left( \frac{1}{c} \right). \]  (5)

\( T_m \) is the maximum synthesis temperature, \( T_i \) is the ignition temperature of the mixture. To obtain the relation (1), the chemical conversion during the inert heating of the mixture (up to \( T_i \)) was neglected. It is assumed that during synthesis, the contribution from an external energy source can be neglected.

Assuming that the point of ignition of the powder mixture is determined by the equality of the heat inputs from external and internal sources, the following relation can be obtained from equations (1) and (2):

\[
\frac{Q_{A+B} + I_{A+B}t_a}{c} \cdot k_{0,A+B} \cdot \frac{I_c^2}{2} \cdot k_{0,A+B} \cdot \exp \left( \frac{-E_{A+B} + I_{A+B}t_a}{RT_i} \right) = W_{A+B}. \]  (6)

Relations (5) and (6) were transformed into equations of straight lines with coordinates \( X-Y \):

\[ Y = \frac{Q_{A+B} + I_{A+B}}{c} \cdot X, \]  (7)

\[ Y = \ln \left( k_{A+B} \cdot k_{0,A+B} \right) \cdot E_{A+B} \cdot X. \]  (8)

\( \ln (7): \ X = t_a \) and \( Y = \Delta T \) \( 1 - \alpha_0 \), in (8): \( X = \frac{1}{RT_i} \) and

\[ Y = \ln \left( \frac{2c_cW_{A+B}}{Q_{A+B} + I_{A+B}I_t} \cdot \frac{k_{0,A+B}^2}{c} \cdot \exp \left( \frac{-I_{A+B}t_a}{RT_i} \right) \right). \]

Figures 2, 3 show the experimental data that were processed by the method of least squares. The parameter \( Q_{A+B} \) was determined at the point of intersection of the straight line (7) with the \( Y \)-axis, and the value \( I_{A+B} \) was determined from the slope of the straight line to the \( X \)-axis. Similarly, using the straight line (8), the parameters \( k_{A+B}k_{0,A+B} \) and \( E_{A+B} \) were determined. As a result, the thermophysical and thermokinetic constants characterizing the mechanochemical synthesis in the Ti-Ni and Nb-Si systems were calculated: \( Q_{Ti-Ni} = 99758 \) J/kg, \( Q_{Nb-Si} = 770000 \) J/kg, \( E_{Ti-Ni} = 107360.5 \) J/mol, \( E_{Nb-Ni} = 132214.3 \) J/mol, \( K_{Ti-Ni}k_{0,Ti-Ni} = 2.5 \times 10^5 \times 1 / \text{min}^3 \), \( K_{Nb-Si}k_{0,Nb-Si} = 2.5 \times 10^6 \times 1 / \text{min}^3 \), \( I_{Ti-Ni} = 43400.7 \) J/(kg-min), \( I_{Nb-Si} = 42000 \) J/(kg-min).

5. Conclusion

Two-stage mechanochemical synthesis was experimentally studied in the Ti-Ni and Nb-Si systems. The results have shown that preliminary mechanical activation intensifies chemical conversions at the second stage of synthesis, increases the thermal effect from the synthesis reaction in the Ti-Ni system, and contributes to the change of the thermal explosion mode to the solid-phase mode in the Nb-Si system.

Thermophysical and thermokinetic constants characterizing the process of two-stage mechanochemical synthesis of titanium niobium and niobium silicide were determined by the inverse problem method using the experimental data and the mathematical model.

References
[1] Butyagin Yu P 1994 Russ. Chem. Rev. 63 965
[2] Boldyrev V V 2004 RFBR Information Bulletin 37 38
[3] Korchagin M A, Grigorieva E F, Barinova A P and Lyakhov N Z 2004 Dokl. AN. SSSR. 372 40
[4] Bernard F and Gaffet E 2001 Intern. J. Self-Propagating High-Temperature Synth. 10 109
[5] Merzhanov A G 2000 Solid-flame combustion (Chernogolovka: ISMAN)
[6] Shkoda O A and Lapshin O V 2016 Russ. Phys. J. 59 1231
[7] Shkoda O A and Terekhova O G 2016 Int. J. of Self-Propagating High Temperature Synth. 25 14
[8] Kasatsky N G and Shkoda O A 2012 Physics and Chemistry of Material Treatment 5 71
[9] Babichev A P, Babushkina N A, Bratkovsky A M et al 1991 Physical Quantities: Reference Book, ed by Grigorieva I S and Meylihova E Z. (Energoatomizdat, Moscow, Russia)
[10] Smithells C J 1980 Metals. Reference Book (Metallurgy, Moscow, Russia)