

The effect of various low-energy mechanical activation factors on the ignition temperature of the 3Ni+Al powder mixture

I.S. Polyakov^{1,2,}, O.V. Lapshin¹, E.N. Boyangin¹*

¹*Tomsk Scientific Center SB RAS, Tomsk, Russia*

²*Tomsk State University, Tomsk, Russia*

**plkv.ivan@mail.ru*

Abstract. The effect of preliminary low-energy mechanical activation (LEMA) of a 3Ni+Al powder mixture on the ignition temperature was studied by experimental and theoretical methods. Two modes of heating the specimen formed with activated powder mixture were used: the mode of continuous operation of the heating source and the mode of its shutdown when the set temperature was reached. The LEMA time ranged from 0 to 50 hours. The experimental data obtained were analyzed in terms of the macroscopic theory of mechanochemical synthesis. Special theoretical calculations were carried out separating the effects of defect formation and changes in the morphological structure of the reaction mixture due to grinding on its ignition temperature. An anomalous decrease of the critical ignition temperature in the preliminary activated 3Ni+Al powder mixture during the Ni₃Al intermetallic compound formation process was observed. It was found that the grinding of the components of the mixture with the formation of mechanocomposites leads to a significant decrease in the scale of heterogeneity, on which the diffusion transfer of reagents to the reaction zone is carried out. It was shown that early disconnection of the external heating source of the mechanically activated mixture does not prevent the chemical reaction in it in the thermal explosion mode.

Keywords: preliminary low-energy mechanical activation, Ni₃Al intermetallic compound, ball mill, thermal explosion.

1. Introduction

The grinding of substances is a stage of many technological processes. The most common grinding is in mills – various types of devices having a chamber inside which there are grinding bodies and the crushed material. The mechanical action that occurs during the grinding process not only reduces the particle size, but due to strong plastic deformations forms various kinds of structural defects. These processes together lead to a change in the free (excess) energy of the substance, thereby reducing the energy threshold for various physico-chemical transformations in it [1–3]. In particular, the energy stored during mechanical activation contributes to the implementation of high-temperature synthesis in weakly exothermic systems [4]. Among such systems, the Ni-Al system occupies a special place, on the basis of which synthesized chemical compounds and composite materials have high-strength, heat-resistant properties and can be used in high-capacity energy, as well as chemical, aviation and space industries [5].

In this paper, a study was conducted on the effect of various factors of preliminary low-energy mechanical activation (LEMA) on the ignition temperature of a mixture of 3Ni+Al.

2. Experimental procedure

The research used powders of aluminum (ASD-4, average particle size ~ 5 μm) and nickel (PNK-UT4, average particle size ~ 4 μm). Pre-mixing for 2 hours, followed by low-energy mechanical activation and grinding of the 3Ni+Al powder mixture was carried out in an IBMT-30 (HT Machinery, Japan-Taiwan) ball laboratory mill. Steel balls Ø25.4 mm in the amount of 15 pieces were used as shredders, the rotation speed of the drum was equal to 150 rpm. The weight of the powder mixture and the ratio of the mass of the balls to the mass of the mixture were, respectively, 50 g and 20:1.

To analyze the temperature dynamics as a result of a chemical reaction in a mechanically activated mixture, a thermometric research unit consisting of a reaction chamber, an electric furnace and an analog-to-digital converter was used. The activated powder mixture was compressed into a

cylindrical sample with a diameter of 10 mm and a length of 10 mm, the porosity of the sample was $\sim 30\%$. A powder sample with two 0.2 mm diameter tungsten-rhenium thermocouples pressed into it was installed in a quartz tubular electric furnace and heated at a constant speed. The sample was heated in two modes: continuous and with the shutdown of the nichrome spiral when the set temperature was reached. The readings from the thermocouples were recorded using an analog-to-digital converter LA-20USB (Rudnev-Shilyaev co.) and a personal computer. When measuring the temperature in the range from 0 to 2600 °C, the relative measurement error did not exceed 0.6%. The values of the thermokinetic parameters of the thermal explosion were determined from experimental thermograms after averaging the latter (five samples were prepared from powder mixtures of each composition).

After appropriate processing, the information was obtained in the form of a time-temperature table or graph for each working channel. The sampling rate was 10000 Hz. Next, the received thermograms were decrypted using special software. The thermogram was used to determine the ignition temperature, maximum temperature and total synthesis time.

3. Results and Discussion

We believe that at the low-energy mechanical activation stage, the degree of β_i defectiveness occurring in the components of the mixture is proportional to the broadening of the X-ray diffraction reflex lines and can be calculated using the formula [6]

$$\beta_i = \frac{I_i}{P_i} [1 - \exp(-P_i t_a)], \quad (1)$$

I_i, P_i – kinetic constants determining the rates of accumulation and relaxation of defects (and with them excess energies) in the components of the mixture ($I = Ni, Al$); $\beta_i = (B_i - B_{i0})/B_{i0}$ – the degree of structural imperfections in the component; B_{i0}, B_i – broadening of X-ray diffraction reflexes in component i before and after mechanical activation; t_a – mechanical activation time.

Dynamics of the increase in the reaction surface s at the stage of agglomerate formation in a powder mixture during machining, we described by the ratio [6]

$$s \approx s_m - (s_m - s_0) e^{-\gamma t}, \quad (2)$$

s_0 – the size of the specific surface area of particles in the initial period of mechanical activation; s_m – the maximum achievable value of the specific surface area of the reagent particles during grinding; the coefficient γ characterizes the constant of the grinding rate.

We believe that after the grinding limit is reached, with a further extension of the machining, the structure of the mixture is transformed and consists not of agglomerates, but layered mechanocomposites. Moreover, since the limit value of s_m is asymptotic, we will conditionally assume the limit value of s_{m1} , which is close to s_m and can be achieved during machining. To find the value of the reaction layer in the mechanocomposite during machining, you can use the following ratio

$$r = \begin{cases} r_{m1} - r_0 Y \ln\left(\frac{t}{t_{m1}}\right), n = 1, t < t_c, \\ r_{m1} - \frac{r_0 K}{(1-n)} \left(\frac{1}{t^{n-1}} - \frac{1}{t_{m1}^{n-1}}\right), n \neq 1, t < t_c, \\ r_c, t \geq t_c \end{cases} \quad (3)$$

$r_0 = 1/s_0$; Y – constant that determines the rate of formation of layered mechanocomposites; n – degree indicator; r – the thickness of the reaction layer in a mechanocomposite consisting of adjacent layers of Ni and Al reagents; $r_{m1} = l/s_{m1}$, t_{m1} – time to reach the size r_{m1} ; t_c – time to reach the final size r_c .

The mathematical formulation of the problem of mechanochemical synthesis from a pre-mechanoactivated mixture consists of a system of the following basic equations [6]

– chemical transformation in the case when the reaction proceeds in a kinetic mode (homogeneous model)

$$\frac{d\eta}{dt} = F_c K_0 \exp\left[-\frac{U}{R(T+273)}\right], \quad (4)$$

– chemical interaction limited by diffusion (heterogeneous model)

$$\frac{d\eta}{dt} = F^2 k_0 \exp\left[-\frac{E}{R(T+273)}\right] f(\eta), \quad (5)$$

– the thermal balance required to calculate the rate of temperature change in a sample compressed from a mechanoactivated 3Ni+Al composition

$$\left[1 + (1-c_0) \frac{L}{c} (1-\eta) \delta(T-T_L)\right] \frac{dT}{dt} = \frac{Q'}{c} \frac{d\eta}{dt} - \frac{a_\varphi}{c} \frac{d\varphi}{dt} + W - \Psi(T-T_0). \quad (6)$$

The following designations are accepted in (4)–(6): t – time; T – temperature, °C; $\eta = d/r_e$ – the depth of chemical transformation, d – the width of the zone of the formed product in the unit cell of the size r_e (the rate of chemical transformation at $\eta \leq r_c/r_e$ is determined by the equation (1), but when $\eta > r_c/r_e$ – with equation (2)); $F = r/r_0$; $F_c = r_0/r_c$ – function value F at $r = r_c$; $k_0 = D_0/r_0$ – pre-exposure; D_0 – the preexponent in the diffusion coefficient $D(T) = D_0 \exp[-E/R(T+273)]$; $f(\eta)$ – kinetic law; K_0 – the preexponent in the temperature-dependent chemical reaction constant $K(T) = K_0 \exp[-U/R(T+273)]$; R – universal gas constant; T – temperature, °C; $E = E_0 - a_E [c_0 \beta_{Ni} + (1-c_0) \beta_{Al} e(T-T_L)]$ – diffusion activation energy, taking into account the influence of excess energies contained in activated components; T_L – melting point Al in °C; a_E – coefficient; c_0 – the mass fraction of nickel in the powder mixture; $U = U_0 - a_E [c_0 \beta_{Ni} + (1-c_0) \beta_{Al} e(T-T_L)]$ – the activation energy of a chemical reaction; E_0 , U_0 – activation energy without mechanical activation; $c = c_0 c_{Ni} + (1-c_0) c_{Al}$, c_{Ni} , c_{Al} – the heat capacity of the reaction sample, nickel and aluminum; $Q' = Q + (1-c_0) L e(T-T_L)$; Q – the thermal effect of the reaction from the formation of an intermetallic compound Ni₃Al; L – heat of melting Al; $\varphi = (1-\eta) [c_0 \varphi_{Ni} + (1-c_0) \varphi_{Al}]$ – the amount of excess energy contained in a unit volume of the activated reacting mixture; a_φ – a coefficient that determines the part of the stored excess energy that is spent on heating the sample during its relaxation; $\varphi_{Ni} = K_{Ni} \beta_{Ni}$, $\varphi_{Al} = K_{Al} \beta_{Al} [1 - e(T-T_L)]$ – excess energies contained in Ni and Al components; K_{Ni} , K_{Al} – coefficients; T_0 – ambient temperature; W – the rate of inert heating of the sample due to an external source; $\Psi = \chi S / [V(1-p)]$ – a complex characterizing the heat exchange of a sample with the environment; χ – the actual heat transfer coefficient of the sample with the environment; $S = \pi D H + \pi D^2 / 2$, $V = \pi D^2 H / 4$ – surface area and volume of the sample; H , D – length and diameter of the sample; p – porosity of the sample.

The Heaviside function $e(T-T_L)$, located at the β_{Al} parameter, characterizes the phase transition in low-melting aluminum: at $T < T_L$, the function $e = 0$, at $T \geq T_L$, the function $e = 1$.

The phase transition due to the possible melting of aluminum in (6) is characterized by the Dirac delta function

$$\delta(T - T_L) = \begin{cases} 0, & T \neq T_L \\ \infty, & T = T_L \end{cases}.$$

We assume that the amount of excess energy φ_i stored in structural defects is proportional to the degree of defect of component i

$$\varphi_{Ni} = K_{Ni} \beta_{Ni}, \varphi_{Al} = K_{Al} \beta_{Al} [1 - e(T - T_L)], \quad (7)$$

K_i – the proportionality coefficient.

In addition to the known tabular values of thermophysical and chemical parameters ($c_0 = 0.87$, $c_{Ni} = 500$ J/kg·K, $c_{Al} = 900$ J/kg·K, $L = 10750$ J/kg, $R = 8.31$ J/mole·K), The constants of formal chemical kinetics were used in the work, established by solving the inverse problem of thermal explosion in a pre-mechanically activated system 3Ni–Al [6]: $I_{Al} = 0.026$ h⁻¹, $P_{Al} = 0.12$ h⁻¹, $I_{Ni} = 0.23$ h⁻¹, $P_{Ni} = 0.35$ h⁻¹, $W = 3.15$ °C/sec, $\Psi = 0.00357$ sec⁻¹, $E_0 = 24 \cdot 10^4$ J/mole, $k_0 = 2.5 \cdot 10^{12}$ sec⁻¹, $a_E = 57420$ J/mole, $Q = 5 \cdot 10^5$ J/kg.

For lack of precise parameter values U_0 and K_0 , let's take the following values of chemical constants for a homogeneous model and a reaction occurring in a kinetic mode: $U_0 = 55 \cdot 10^3$ J/mole, $K_0 = 4.9$ sec⁻¹. U_0 and K parameter values were found in [7] using experimental data on the kinetics of phase formation (the time of appearance of intermetallides) at the thin boundary of nickel-aluminum contact, given in [8, 9]. Initial conditions for a mathematical model of the stage of mechanochemical synthesis:

$$t = 0: T = T_0, \eta = 0, \beta_{Ni} = \beta_{Ni}(t_a), \beta_{Al} = \beta_{Al}(t_a), F = F(t_a). \quad (8)$$

Fig. 1 shows the theoretical dependence of the ignition temperature T_1^* of a 3Ni+Al powder mixture pre-mechanically activated in a low-energy mill (curve 1). It can be seen that with increasing mechanical activation time, the ignition temperature decreases. However, when the minimum size of the reaction layer is reached, the ignition temperature practically ceases to change. It can be stated that the numerical calculation of the ignition temperature corresponds well to the experimental data (circles).

Let's evaluate the contribution of each of the mechanical activation factors to the ignition temperature of the mixture. To do this, we will carry out special theoretical calculations separating the effect of defect formation and changes in the morphological structure of the mixture due to grinding on the ignition temperature.

Line 2 in the figure characterizes the dependence of the ignition temperature T_2^* on the time of LEMA, which contributes to the accumulation of defects without morphological changes due to the grinding of the components of the mixture. Here, the magnitude of the degree of defect β_i varies in calculations, and the value F^{-1} characterizing the heterogeneity of the mixture is a constant and is equal to 1.

Line 3 expresses the dependence of the ignition temperature T_3^* on the time of LEMA, which determines the degree of morphological changes in the mixture without taking into account defect formation. In this case, $\beta_i = 0$ is assumed in the equations for calculating the synthesis process, and the heterogeneity of the mixture F^{-1} varies.

It can be seen that with relatively short machining times, defect formation processes are dominant and more effectively contribute to reducing the ignition temperature. At the same time, for this period of machining, the maximum difference between the values T_2^* and T_3^* does not exceed 100 °C.

Calculations show that under conditions of prolonged mechanical processing, morphological changes in the mixture that occurred due to the grinding of components make a more significant

contribution to the intensification of subsequent synthesis than the accumulation of defects. During this period, the maximum difference between the values T_2^* and T_3^* reaches 300–350 °C.

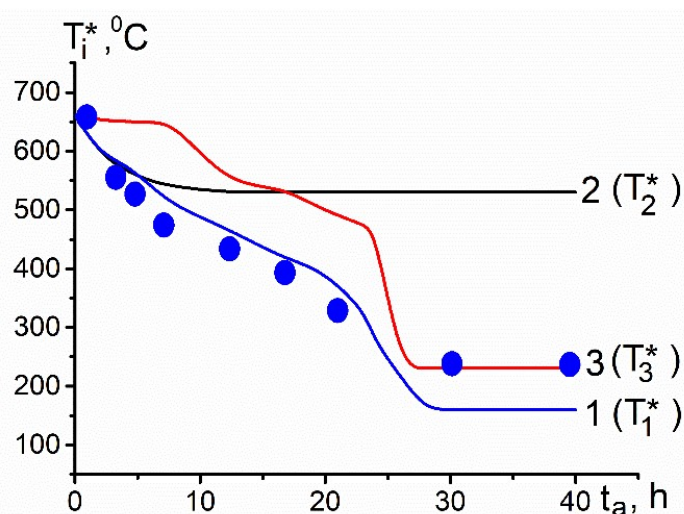


Fig. 1. Theoretical (1–3) and experimental (circles) dependences of the ignition temperature of the pre-activated 3Ni+Al powder mixture on the time of HMA: true (1), without taking into account morphological changes and taking into account defect formation (2), without taking into account defect formation and taking into account morphological changes (3).

In general, analyzing the figure, it can be stated that line 3, which determines the ignition of the mixture due to morphological changes, is more close to the true ignition temperature T_1^* from the time of the LEMA represented by curve 1. Moreover, during the period of 20–25 h LEMA, the most significant morphological changes in the mixture should occur, which, in fact, entails it represents an abnormal decrease in the ignition temperature. According to the mathematical model presented above, this decrease in T_1^* is due to the fact that during this period the structure of the mixture with a heterogeneity scale of F^{-1} is replaced by a structure with a heterogeneity scale of F_c^{-1} , and the activation energy of the chemical interaction that can be realized in such structures is replaced with a value of E by the value of U .

4. Conclusion

Thus, based on the results of the study, we assume that the abnormal decrease in the ignition temperature of the 3Ni+Al powder mixture is caused by morphological changes due to low-energy mechanical activation. These changes, first of all, do not affect the energy, but the kinetic parameters of the subsequent synthesis. The grinding of the components of the mixture with the formation of mechanocomposites leads to a significant decrease in the scale of heterogeneity (parameter F^{-1}), at which the diffusion transfer of reagents to the reaction zone is carried out. This increases the number of reaction micro-foci in the mixture, which will help to reduce the initiation temperature of the subsequent reaction.

However, a qualitative leap in the intensification of the reactivity of the mixture occurs when the heterogeneity scale of the extremely small F_c^{-1} size is reached, in which the subsequent synthesis reaction will be determined not by diffusion with high activation energy E , but by boundary kinetics, i.e. directly by chemical processes with low activation energy U , which do not require the cost of mass transfer of reagents. In other words, low-energy mechanical activation, although it practically does not explicitly store excess energy in the substance, but allows you to move from structures with a large diffusion path to germinal structures ready for rapid conversion of the charge of the initial components into the product of a new phase.

5. References

- [1] L. Takacs, The historical development of mechanochemistry, *Chem. Soc. Rev.*, vol. **42**, 7649, 2013; doi: 10.1039/C2CS35442J
- [2] A.S. Rogachev, Mechanical activation of heterogeneous exothermic reactions in powder mixtures, *Russ. Chem. Rev.*, vol. **88**, 875, 2019; doi:10.1070/RCR4884
- [3] O.V. Lapshin, E.V. Boldyreva, and V.V. Boldyrev, Role of mixing and milling in mechanochemistry synthesis (review), *Russ. J. Inorg. Chem.*, vol. **66**, 433, 2021; doi: 10.1134/S0036023621030116
- [4] Kh. Nazaretyan, S. Aydinyan, H. Kirakosyan, D. Moskovskikh, A. Nepapushev, K. Kuskov, M. Tumanyan, A. Zargaryan, R. Traksmay, and S. Kharatyan, AlCo-rich AlCoNiFe and AlCoNiFeCr high entropy alloys: Synthesis and interaction pathway at high heating rates, *Journal of Alloys and Compounds*, vol. **931**, 167589, 2023; doi: 10.1016/j.jallcom.2022.167589
- [5] M.A. Korchagin, Thermal explosion in mechanically activated low-calorific-value compositions, *Combust. Explos. Shock Waves*, vol. **51**, 578, 2015; doi: 10.1134/S0010508215050093
- [6] O.V. Lapshin, E.N. Boyangin, Macrokinetics of thermal explosion in a 3Ni-Al system mechanically activated in a low-energy mill, *Journal of Alloys and Compounds*, vol. **948**, 169790, 2023; doi: 10.1016/j.jallcom.2023.169790
- [7] O.V. Lapshin, V.E. Ovcharenko, A mathematical model of high-temperature synthesis of the intermetallic compound Ni₃Al during ignition, *Combust. Explos. Shock Waves*, vol. **32**, 158, 1996; doi: 10.1007/BF02097085
- [8] V.I. Itin and Yu.S. Naiborodenko, *High-Temperature Synthesis of Intermetallic Compounds*, Tomsk: Tomsk Univ., 1989.
- [9] Yu.S. Naiborodenko, V.I. Itin, B.P. Belozerov, and V.P. Ushakov, Phases and reactive-diffusion kinetics for mixed Al-Ni powders, *Soviet Physics Journal*, vol. **16**, 1511, 1973; doi: 10.1007/BF00889952