Effect of the Heating Stage on Ignition Conditions of a Nickel-Aluminum Powder Mixture

O. V. Lapshin¹ and V. E. Ovcharenko¹

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In the mathematical model of high-temperature synthesis of an intermetallide compound with the nucleation process at the interface of different components taken into account, the ignition conditions of the initial powder mixture of pure elements by Semenov’s mechanism may be violated.

A common drawback of the known mathematical models of exothermic transformation of a powder mixture of pure elements to an intermetallide compound in the combustion regime is neglect of the process of formation of a reaction surface between heterogeneous components at the stage of ignition. It is extremely difficult to register experimentally the chemical reaction of formation of new phases at this stage of interaction of the initial components. The moment of interface formation is the starting point of the stage of intense transformation of the initial powder mixture to intermetallide products, which can be registered experimentally [1–4]. The intensity of phase transformations is largely determined by the state of the reacting surface. It was shown [5, 6] that the process of nucleation of the intermetallide phase in a nickel-aluminum powder mixture can have a significant effect on the duration and temperature of ignition of the initial powder mixture. A detailed analysis of this problem for the case of heating of a powder mixture by an external source is given in the present paper.

The equation of the thermal balance of the initial powder mixture of pure elements at the stage of its ignition for low completeness of transformation with uniform heating of the sample by an external source of energy can be written in the following form:

\[
\frac{dT}{dt} = \frac{Qd}{V} \frac{D_0}{r_0^2} \exp \left( - \frac{E}{RT} \right) + \frac{W S}{V} \frac{\alpha S_p (T - T_0)}{V},
\]

\(T(0) = T_0.\)

Here \(V, S, \) and \(S_p\) are the volume, cross-sectional area, and surface area of the sample, respectively, \(C_v\) and \(\rho\) are the volume heat capacity and density of the mixture, respectively, \(T\) is the temperature of the mixture, \(T_0\) is the initial temperature of the mixture equal to the ambient temperature, \(t\) is the time, \(\alpha\) is the heat-transfer coefficient, \(Q\) is the thermal effect of the reaction, \(D_0\) is the preexponent, \(E\) is the activation energy of formation of the intermetallide compound, \(R\) is the gas constant, \(r_0\) is the dispersity of the powder medium, and \(W\) is the power of the heating source.

Assuming the Frank-Kamenetskii parameter \(\beta = RT_0/E\) to be small, we rewrite Eq. (1) in dimensionless variables:

\[
\frac{d\theta}{d\tau} = \exp \theta + q - \omega \theta, \quad \theta(0) = 0.
\]

Here

\[\theta = \frac{E(T - T_0)}{RT_0^2}, \quad \tau = \frac{t}{t^*}, \quad \omega = \frac{\alpha S_p t^*}{VC_v},\]

are the dimensionless temperature, time, and heat-transfer coefficient, respectively.

¹Institute of Strength Physics
and Material Science, Siberian Division,
Russian Academy of Sciences, Tomsk 634055.
\[ t^* = \frac{C_vRT_0^2 \exp(E/RT_0)r_0}{QpD_0E} \]
is the characteristic time of the process, and
\[ q = \frac{WSEt^*}{VRT_0^2C_v} \]
is the dimensionless power of the heating source.

The critical conditions of ignition of this power mixture may be written in the form \[ \frac{d}{d\theta} \frac{d\theta}{d\tau} = 0, \quad -\frac{d\theta}{d\tau} = 0 \] or
\[ q = \omega(\ln \omega - 1), \quad \theta_{\text{ign}} = 1 + q/\omega = \ln \omega, \]
where \( \theta_{\text{ign}} \) is the critical temperature of ignition.

According to Semenov [8], if the heating parameters of a powder mixture are higher than the critical values, the ignition temperature may be assumed to be the temperature of equal heat influx from internal and external sources. In this case, we have
\[ \exp \theta_{\text{ign}} = q - \omega \theta_{\text{ign}}, \]
where \( \theta_{\text{ign}} \) is the ignition temperature.

We now consider the effect of nucleation of a new phase at the stage of ignition on the ignition temperature of the initial powder mixture.

According to [9, 10], the equation for the growth of the new phase nucleus is
\[ \frac{d\varphi}{d\theta} = K \exp \left(-\frac{U}{RT} \right), \]
where \( \varphi = \delta/\delta^* \) is the relative size of the nucleus, \( \delta \) and \( \delta^* \) are the current and critical sizes of the nucleus, respectively, \( K \) is the preexponent, and \( U \) is the activation energy of nucleation. In dimensionless parameters, this equation has the form
\[ \frac{d\varphi}{d\tau} = k \exp \sigma \theta, \]
where \( \sigma = U/E \) and \( k = Kt^* \exp(-U/RT_0) \).

Since the heat release of the nucleation reaction of the intermetallic phase may be assumed to be negligibly small [3], we assume that the temperature of the powder mixture at the stage of nucleation increases only due to its heating by an external source of energy. Taking into account the nucleation process of the intermetallic phase, Eq. (2) acquires the form
\[ \frac{d\theta}{d\tau} = q - \omega \theta \quad \text{for } \varphi < 1, \]
\[ \frac{d\theta}{d\tau} = \exp \theta + q - \omega \theta \quad \text{for } \varphi \geq 1 \]
with the initial condition \( \theta(0) = 0 \).

Replacing the time derivative in Eq. (7) by the temperature derivative, we have
\[ \frac{d\varphi}{d\theta} = \frac{k \exp \sigma \theta}{q - \omega \theta}. \]
From here, we obtain
\[ \varphi = \int \frac{\exp \sigma \psi}{q - \omega \psi} \, d\psi, \]
where \( \psi \) is the integration parameter.

The condition of termination of the process of nucleation of a new phase (\( \varphi = 1 \)) is the equality
\[ 1 = \int \frac{\exp \sigma \psi}{q - \omega \psi} \, d\psi, \]
where \( \theta_z \) is the final temperature of nucleation.

Using the Laplace principle of the greatest parameter [11] and assuming that \( \theta_z \gg 0 \), we can rewrite Eq. (10) in the form
\[ 1 = \frac{k \exp \sigma \theta_z}{\sigma(q - \omega \theta_z)}. \]

We consider two situations: \( \theta_z < \theta_{\text{ign}} \) and \( \theta_z > \theta_{\text{ign}} \).

In the first case, the actual ignition temperature \( \theta_f \) equals the value of \( \theta_{\text{ign}} \) determined by formula (5). The ignition of the system follows Semenov’s mechanism. It is also obvious that \( \theta_z \) cannot be higher than the temperature \( \theta_h = q/\omega \), for which the absolute values of the rates of heat input and output are identical under conditions of the absence of internal sources of heat release in the powder system. Therefore, we have \( \theta_z < \theta_h \). On the other hand, the critical ignition temperature is higher than the temperature \( \theta_h \) and, hence, than the final temperature of nucleation, i.e., \( \theta_{\text{ign}} > \theta_z \). The latter means that the process of nucleation does not affect the critical conditions of ignition of the powder mixture.

In the second case, for \( \theta_z > \theta_{\text{ign}} \), ignition by Semenov’s mechanism does not occur. The actual temperature of ignition \( \theta_f \) here is equal to the final temperature of nucleation, since it is exactly at this temperature that internal heat-release sources begin to “operate,” intense growth of the intermetallic phase begins, and the breakdown of thermal equilibrium occurs.

It can be easily shown that the functions
\[ y_1(\theta) = \frac{k \exp \sigma \theta}{\sigma(q - \omega \theta)}, \quad y_2(\theta) = \frac{\exp \theta}{q - \omega \theta} \]
are increasing for \( \theta < \theta_h \). Since \( y_2(\theta_{\text{ign}}) = 1 \), then the inequality \( y_2(\theta_z) < 1 \) is satisfied for \( \theta_z < \theta_{\text{ign}} \). After simple transformations, we obtain