The critical parameters of the thermal explosion micro hot-spot model dependence on the pulse duration

A V Kalenskii 1, A A Zvekov 2 and E V Galkina 1

1 Kemerovo State University, Kemerovo 650000, Krasnaya 6, Russia
2 Federal Research Center of Coal and Coal Chemistry SB RAS, Kemerovo 650000, Sovetsky av. 18, Russia

E-mail: kriger@kemsu.ru

Abstract. The dependencies of critical laser initiation energy density of pentaerythritol tetranitrate (PETN) – aluminum nanoparticles, PETN – cobalt nanoparticles and lead azide – lead nanoparticles on pulse duration were calculated in terms of the refined micro hot-spot model. It was shown that the absorption efficiency of the laser irradiation taken into account makes the initiation criterion change. According to the calculation results, the criterion in the limit of short pulses is energy density matching the experimental data. If the neodymium pulses duration is less than 50 ns, the radius of the nanoparticles with highest temperature changes insignificantly. The expression for the critical hot-spot temperature dependence on the pulse duration was derived. The conclusion was made that the model refining with nanoparticles absorption efficiency dependence on their radius is sufficient for the “small particles’ paradox” solution.

1. Introduction

It is essential to change the contemporary used initiation systems to optical ones in order to achieve substantial increasing of the blasting operations safety in the mining industry. In [1,2], the optic detonator stuffed with the primary explosive silver azide was developed but it did not get wide application because of its significant sensitivity to shock and electrical influences. A selectively sensitive to laser initiation composite based on secondary explosive PETN and metal nanoparticles was suggested in [3]. The minimal critical energy density of this explosive compound laser pulse initiation ($H$) is about 0.7 J/cm$^2$ [4], which we consider as an encouraging mark on the way of the selectively sensitive optic detonator development. The main processes leading to the explosion initiation are absorption of the laser irradiation by metal nanoparticles, their heating and ignition of the surrounding matrix close to the contact surface nanoparticle – explosive [4,5]. The micro hot-spot model of the explosion initiation with laser irradiation was suggested [6] for the math description of the processes. One of the model assumptions is independence of the nanoparticle absorption efficiency on its size. The absorption cross section was thought to be equal to the geometrical cross section [6]. The critical energy density calculations with pulse duration ($t_i$) variation were done in terms of the model. In the case of nanoparticles’ ensemble the radius of the mostly heated nanoparticle depends on the pulse duration as $t_i^{-1/2}$. At the same time, when the pulse duration diminishes, the calculated critical energy density decreases and tends to zero [6]. The experimental dependence $H(t_i)$ measured for lead azide pellets in the limit of the short pulses ($t_i<100$ ns) does not depend significantly on the pulse.
duration [6], on the contrary. The theoretical trend \( H \to 0 \), when \( t_i \to 0 \) meaning that the optimal nanoparticles are of the small size, was referred to as “the small particles’ paradox”.

The ‘small particles’ paradox” solution is essential for the physical substantiation of the micro hot-spot model. In [4,7], a modern variant of the model was proposed taking into account the dependence of the absorption efficiency \( (Q_{abs}) \) on the nanoparticles’ radius \( (R) \) and the wavelength, as well as the scattering properties of the nanoparticles. The aim of the present work is to calculate the critical parameters of the lead azide – lead, PETN – Al and PETN – Co composites laser initiation on the pulse duration on the pulse duration in terms of the refined micro hot-spot model keeping in mind the “small particles’ paradox” solution for the practically important explosives.

2. Micro hot-spot model

Let us consider the thermal explosion initiation model in the system comprising nanoparticles in the explosive material matrix heated with laser irradiation. The equations describing the conductive heat transport in the composite coupled with the chemical decomposition of the explosive material are as follows [4-7]:

\[
\frac{\partial T}{\partial t} = \alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{2}{x} \frac{\partial T}{\partial x} \right) + k_0 \frac{nQ}{c} \exp \left( -\frac{E}{k_B T} \right)， \quad x > R,
\]

\[
\frac{\partial n}{\partial t} = -k_0 n \exp \left( -\frac{E}{k_B T} \right)， \quad x > R, \quad (1)
\]

\[
\frac{\partial T}{\partial t} = \alpha_M \left( \frac{\partial^2 T}{\partial x^2} + \frac{2}{x} \frac{\partial T}{\partial x} \right)， \quad \frac{\partial T}{\partial t} = 0, \quad n_0 = 0, \quad x < R,
\]

the boundary condition at the surface \( x = R \) are

\[
J - c_M \alpha_M \frac{\partial T}{\partial x} \bigg|_{x \to R^-} + c \alpha \frac{\partial T}{\partial x} \bigg|_{x \to R^+} = 0
\]

where \( T \) is temperature, \( E \) is decomposition activation energy, and \( k_0 \) is preexponential factor, \( Q \) is heat released with the decomposition of a cubic centimetre of the explosive, \( \alpha \) and \( \alpha_M \) are thermal diffusivities and nanoparticle materials, \( R \) is nanoparticle’s radius, \( c \) and \( c_M \) are the volumetric heat capacity of the matrix and inclusion material, \( n \) is the share of undecomposed explosive, and \( J(t) \) is the absorbed density of the laser pulse radiation power. For the simulation, the following parameters were used: \( c = 2.22 \text{ J/(cm}^3\text{K)} \), \( \alpha = 1.1 \cdot 10^{-3} \text{ cm}^2\text{s}^{-1} \), \( E = 165 \text{ kJ/mole} \), \( k_0 = 1.2 \cdot 10^{15} \text{ s}^{-1} \), \( Q = 9.64 \text{ kJ/cm}^3 \) for PETN; \( E = 152 \text{ kJ/mole} \), \( Q = 7.42 \text{ kJ/cm}^3 \), \( k_0 = 1 \cdot 10^{13} \text{ s}^{-1} \), \( c = 2.48 \text{ J/(cm}^3\text{K)} \) for lead azide; \( c_M = 3.74 \text{ J/(cm}^3\text{K)} \), \( \alpha_M = 0.267 \text{ cm}^2\text{s}^{-1} \) for cobalt; \( c_M = 1.46 \text{ J/(cm}^3\text{K)} \), \( \alpha_M = 0.241 \text{ cm}^2\text{s}^{-1} \) for lead and \( c_M = 2.43 \text{ J/(cm}^3\text{K)} \), \( \alpha_M = 0.973 \text{ cm}^2\text{s}^{-1} \) [4-8]. The dependence of the laser pulse radiation power on time is close to the normal distribution function [9]. Taking the maximum intensity of the pulse as a reference time position, we obtain for value \( J(t) \) the expression [10]:

\[
J(t) = \sqrt{\frac{\pi}{2}} \cdot Q_{abs} R^2 k_i \cdot H_0 \cdot \exp \left( -k_i t_i^2 \right) \quad (3)
\]

where \( k_i \) is the effective constant corresponding to the pulse full width at half maximum \( t_i \) as \( k_i = 2(ln2)^{1/2} t_i \text{s}^{-1} \), \( Q_{abs} \) is nanoparticle absorption efficiency equal to the ration of the absorption cross section and the geometrical cross section \((\pi R^2)\). The additional multiplicative constants in equation (3) are used to norm the integral of \( J(t) \) over entire time axis to the value \( Q_{abs} H_0 \).

In the initial variant of the laser initiation micro hot-spot model, it was assumed that \( Q_{abs} = 1 \) and it does not depend on the nanoparticles’ size. In the refined model, we used Mie theory for the spherical nanoparticle absorption efficiency with radius \( R \) calculation [7,11] that gave us the \( Q_{abs}(R) \) dependence. The critical parameters of the explosion initiation were determined solving the model.
equations (1)-(3) on the variable step mesh according to the approach thoroughly described elsewhere [5]. The ordinary differential equation set obtained after the dividing of the space into cells was solved by the Runge — Kutta method of 1–5 orders with a variable time step. A relative error at the integration step did not exceed $10^{-12}$, whereas the integral relative error estimated by the precision of the energy conservation law fulfilment did not exceed $2.5\cdot10^{-6}$.

$$\text{Figure 1.} \text{ The calculated dependencies of the PETN-Co laser initiation critical energy density on pulse duration assuming that } Q_{\text{abs}} = 1. \text{ The Co nanoparticles’ radii for each curve are listed on the legend, 1 is the envelop curve.}$$

3. Results and discussion

Figure 1 shows the calculated dependencies of the critical (minimal) energy density of PETN – cobalt nanoparticles composite laser initiation ($H$) assuming $Q_{\text{abs}} = 1$. The pulse duration was varied in the range 0.1 – 50 ns while the curves were calculated for the radii values 10, 20, 30, 40, 50 and 75 nm. At each pulse duration there is a particle with the optimal radius ($R_{\text{min}}$). Its heating to the maximal temperature leads to the self-accelerating reaction hot-spot formation at the minimal laser pulse energy density ($H$). In the case of nanoparticles ensemble with continuous size distribution, at every pulse duration there is a minimal critical energy density for the entire ensemble $H(t_i)$ presented in figure 1, curve 1. This curve is an envelope curve in the geometrical sense for the dependencies calculated at different radius values. Matching the results of the paper [6] one sees that as the pulse duration decreases the critical energy density of the explosion initiation for the nanoparticles of different size ensemble (envelope) also decreases with the trend $H \to 0$ in the limit $t_i \to 0$. Ignoring the objective laws of the light absorption gives 17-fold critical energy density decrease (from 154 to 8.9 mJ/cm$^2$) with the pulse duration decreasing from 100 to 0.1 ns. The $R_{\text{min}}$ decreases from 140 to 5 nm (almost 30-fold decrease) which is significantly more pronounced than the corresponding diminishing of the critical energy density in this range of pulse durations. The possible pulse duration diminishing gives, obviously, the following decrease of the critical energy density of the explosion initiation.

The dependence of the light absorption efficiency of cobalt nanoparticles in PETN matrix (refractive index of PETN is 1.54) at a wavelength of 1064 nm was calculated using Mie theory in [8]. The applicability of Mie theory for the metal nanoparticles absorption efficiency calculation was proven in [11]. The maximum in $Q_{\text{abs}}(R)$ curve with height 1.26 was observed at the radius value
$R_m = 98$ nm. At the radii range $R > R_m$, the absorption efficiency slightly decreases with oscillations. The $Q_{\text{abs}}(R)$ dependence is similar to that calculated for the nanoparticles of aluminum, silver, copper, nickel and some other metals in PETN [7, 11-15].

Let us consider the influence of the absorption efficiency dependence on the nanoparticles radius in the limit of short laser pulses. The corresponding calculated dependencies of the laser initiation explosion critical energy density for the cobalt nanoparticles radii 10, 20, 30, 40, 50 and 75 nm on the pulse duration is shown in figure 2. The relative positions of the curves calculated for different radii are affected by both the absorption efficiency and pulse duration. The absorption efficiency value makes the curves calculated for different radii to shift upward if the $Q_{\text{abs}}(R) < 1$ and downward in the opposite case. As a consequence, the envelope curve $H(t)$, which has the same meaning as in figure 1, tends to the positive constant in the limit of short pulses. The minimal critical energy density decreases only 3-fold with pulse duration decreasing from 100 to 0.1 ns, giving contrast with the case $Q_{\text{abs}}(R) = 1$. The radius of the most heated nanoparticle keeps almost constant equal to 85 nm governed by the dependence $Q_{\text{abs}}(R)$ in the limit of short pulses. Thus, the absorption efficiency dependence on the nanoparticles radius in the limit of short pulses introduced into the model is sufficient to solve the "small particles’ paradox". In the opposite limit of pulses with high durations, the nanoparticles with relatively higher radii are heated most. In this limit, the absorption efficiency dependence on the radius is weak, so the critical energy density of the laser pulse dependence on the pulse duration is close to $t^{0.4}$.

![Figure 2](image_url)

**Figure 2.** The calculated dependencies of the PETN-Co laser initiation critical energy density on pulse duration with $Q_{\text{abs}}(R)$ calculated in terms of Mie theory. The Co nanoparticles’ radii for each curve are listed on the legend, 1 is the envelop curve.

The critical hot-spot temperature is another crucial parameter along with critical energy density, which dependence on the pulse duration may give an insight in the critical conditions of the self-accelerating reaction initiation. For that reason we performed the calculations of the hot-spot temperature on pulse duration at the critical energy density values for the aluminium nanoparticles with $R = 100$ nm in PETN matrix. Anticipating the analytical expression for that dependence, the model (1)-(3) reduction to the Nikolay Semenov’s model of thermal explosion [16] was done. Let us consider a metal nanoparticle and a surrounding heated layer with thickness $h$ assuming that they have the same
temperature as a ‘reactor’. The matrix contacting this heated layer could be considered as thermal reservoir for the system cooling.

In terms of these assumptions, the effective heat released after the total explosive consumption inside the ‘reactor’ is

$$\dot{Q} = \frac{V}{CV+C_mV_m} \cdot Q,$$

where $V$ is volume of the explosive’s heated layer with thickness $h$, $V_m$ is the nanoparticle volume. The denominator in (4) corresponds to the ‘reactors’ effective heat capacity. The ‘reactors’ temperature augmentation concerned on the explosive decomposition is read as

$$\frac{dT}{dt} = \frac{V}{CV+C_mV_m} \cdot Qk_0 \exp\left(\frac{-E}{k_B T}\right) \approx \frac{4\pi Rh(R+h)}{CV+C_mV_m} \cdot Qk_0 \exp\left(\frac{-E}{k_BT}\right).$$

(5)

The heat transferred from the ‘reactor’ to the matrix in a time unit is equal to the heat integrated flux on its boundary. The temperature gradient could be estimated as the difference of the ‘reactor’ temperature and that of the medium divided by the heated layer thickness. Thus, the temperature diminishing term concerned on the heat conduction is as follows

$$\frac{dT}{dt} = \alpha C \cdot \frac{T-T_0}{h} \cdot \frac{4\pi(R+h)^2}{CV+C_mV_m}.$$  

(6)

Now the task (1)-(3) could be approximately reduced to the Semenov’s thermal explosion model using equations (5) and (6) as

$$\frac{dT}{dt} = D \cdot \left[\exp\left(\frac{-E}{k_BT}\right) - \frac{\alpha C}{k_0Q} \cdot \frac{R+h}{Rh^2} (T-T_0)\right],$$

(7)

where $D = \frac{4\pi k_0 Q h R (R+h)}{CV+C_mV_m}$. The critical conditions of the reaction initiation for that task is

$$\begin{cases} \frac{dT^*}{dt} = D \cdot \left[\exp\left(\frac{-E}{k_BT}\right) - \frac{\alpha C}{k_0Q} \cdot \frac{R+h}{Rh^2} (T^*-T_0)\right] = 0, \\ \frac{d^2T^*}{dt^2} > 0. \end{cases}$$

(8)

Where the first line in the equation set (8) we used to derive the dependence of the hot-spot critical temperature on the pulse duration introducing though $h$ value. Assume that one knows the critical temperatures at one of the pulse duration values. Introducing the difference in critical hot-spot temperatures $\delta T = T^*-T_1$, applying the Frank-Kamenetskii approximation [16] and neglecting the small $\delta T$ value in the second term, one arrives at the expression:

$$T^* = 2T_1 + \frac{k_BT_1^2}{E} \cdot F(h),$$

(9)

where $F(h) = \ln\left[\frac{\alpha C}{k_0Q} \cdot \frac{R+h}{Rh^2} (T_1-T_0)\right]$. The thickness of the reacting (heated) layer was estimated as $h = (2\alpha/k_i)^{0.5}$. The dependence of the critical hot-spot temperature calculated using the model (1)-(3) on the $F(h)$ function is shown in figure 3. The calculations with equation (9) were done using the preliminary calculated critical temperature at the pulse duration full width at half maximum 7 ns. The corresponding results are presented in figure 3 as well. The obtained slope coefficient and the intercept
on the critical temperature axis match the linear approximation of the results calculated with the full model (1)-(3) with precision 2 and 4%, respectively.

\[ T^*, K \]

\[ F(t) \]

**Figure 3.** The dependence of the critical temperature on the pulse duration in the coordinates of equation (9).

4. **Comparison with experimental data**

The critical energy density values were experimentally measured for lead azide with pulse duration variation. Figure 4 shows the dependencies of the critical laser pulse energy densities on the pulse duration calculated in the case of lead azide containing lead nanoparticles. The calculations were done for the radii values 30 nm (1), 50 nm (2), 100 nm (3) and 300 nm (4) using the dependence \( Q_{abs}(R) \) obtained previously using Mie theory. As in the case of the PETN-Co system, the absorption efficiency values affects the \( H(t) \) curves positions shifting them upward when \( Q_{abs} < 1 \). The values for the lead nanoparticles radii 10, 30 and 50 nm inside the lead azide matrix are 0.089, 0.333 and 0.755 respectively [7]. It is evident that critical energy density increases because of \( Q_{abs} \) influence for the nanoparticles’ with radius 50 nm by 33% and by 200% (3-fold) for the nanoparticles with \( R = 30 \) nm. As a consequence, the envelope curve \( H(t) \) tends to the constant limit in the short pulses case. This theoretical result is the direct consequence of the light interaction with metal nanoparticles features. The experimental dependence corrected with the illuminance increasing factor 12 (as in [17]) is presented also in figure 4. One sees that when the pulse duration diminishes, the experimental critical energy density values decrease in the range \( t_i > 200 \) ns, but tend to a constant limit in the range \( t_i < 100 \) ns. The theoretical envelope curve for the nanoparticles ensemble shows the critical energy density decreasing with \( t_i \) diminishing the range of long pulses with trend to a limit in the case of short pulses matching the experimental data well.

In the lead nanoparticles in the lead azide matrix case, the radius of the nanoparticle that heated most in the limit \( t_i \rightarrow 0 \) is 64 nm at the wavelength 1064 nm. This value is slightly lower than the radius of the nanoparticle that absorbs laser irradiation most effectively. Thus, the hot-spot formation at the threshold conditions occurs on the nanoparticles with radius \( R_{max} \) that is not zero. At a wavelength of 1064 nm, the dependencies of the optimal nanoparticle radius calculated assuming \( Q_{abs} = 1 \) and using the dependence \( Q_{abs}(R) \) obtained with Mie theory cross at the pulse duration of 12 ns and \( R_{m} = 74 \) nm.
At shorter pulses the optimal radius is determined by the optic properties of the nanoparticles, at longer – by the heat conduction effects mostly.

Decreasing of the absorption efficiency in the limit $R \to 0$ is typical for every metal. It means that the introduction of the absorption efficiency factor into the hot-spot model of laser initiation is sufficient for the “small particle’s paradox” solution.

![Figure 4](image_url)

**Figure 4.** The dependence of the lead azide containing lead nanoparticles critical energy density of the laser pulse on the pulse duration calculated for nanoparticles’ radii 30 (1), 50 (2), 100 (3) and 300 nm (4) using $Q_{\text{abs}}(R)$ values obtained with Mie theory; 5 is envelop curve for the nanoparticles ensemble; 6 is experimental data [6] corrected with illuminance increasing factor 12.

### 5. Conclusion

In terms of the refined micro hot-spot model, the dependencies of critical laser initiation energy density of pentaerythritol tetranitrate (PETN) – aluminum nanoparticles, PETN – cobalt nanoparticles and lead azide – lead nanoparticles on pulse duration were calculated. It was shown that the absorption efficiency of the laser irradiation taken into account makes the initiation criterion change. According to the calculation results, the criterion in the limit of short pulses is energy density matching the experimental data. In the case of cobalt nanoparticles, the optimal nanoparticle radius in the short pulse limit tends to 85 nm. It was concluded that the model refining with nanoparticles absorption efficiency dependence on their radius is sufficient for the “small particles’ paradox” solution. This work was supported by Ministry of Education and Science of the Russian Federation (governmental project No. 2014/64).

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