Micro hot-spot model of thermal explosion taking into account dielectric shell of sensitizing nanoparticle

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Abstract. The aim of this work is to modernize the micro hot-spot model of explosion decomposition laser initiation taking account optical and thermal properties of dielectric shell. The tasks are to modernize the micro hot-spot model of explosion decomposition taking into account the transparent dielectric shell of nanoparticle, which physical properties (complex refractive index, the coefficient of thermal conductivity) differ significantly from the properties of the material of nanoparticle nucleus; to calculate the efficiency factors of absorption and scattering of nanoparticles with the structure of the metal core – dielectric shell; to calculate the maximum temperature dependence on the radius of the nanoparticle at different thicknesses of the dielectric shell. Influence of oxide shell on the optical properties of the aluminium nanoparticles was studied in terms of Aden-Kerker and Mie theory for the spherical particle. It was shown that oxide shell changes drastically the optical properties of the nanoparticle, while the heating kinetics is influenced insignificantly.

1. Introduction

The explosion initiation with pulsed lasers is considered as a prospective substitution of electrical approaches of initiation. This way the substantial safety increasing could be achieved when one uses explosives with minimization of ecologic and industrial disasters’ risks. For that reason there are efforts in the direction of selectively sensitive explosives’ development having outstanding safety in transportation, storage, and handling [1-3]. The optical detonators based on primary explosive silver azide [4] were suggested. They are not utilized extensively because their threshold to electrical noises and heating is also low. The optical detonators based on secondary explosives seem to be more prospective providing the necessary diminishing of the laser initiation threshold. The sensibilisation of secondary explosives by doping with light absorbing nanoparticles was suggested in [5, 6] as well as synthesis of new materials [3, 7, 8]. The energy gain is achieved due to heating of nanoparticles with a thin layer of surrounding explosive substance that is a small part of the sample. As a result, the minimal energy density of pentaerythritol tetranitrate (PETN) initiation containing aluminum [5, 6], nickel [9] and cobalt [10] nanoparticles’ at the main wavelength of neodymium laser is more than 100 times lower than that of pure PETN pressed pellets. The micro hot-spot thermal explosion conception based on light absorption by nanoparticles in the volume of explosive was suggested for the silver and lead azide [11]. The prospective of optical detonators practical usage focused the interest of researchers on that model. The model was applied for secondary explosives in [6, 12]. The phase
transformation, light absorption and scattering including the calculation of nanoparticles’ and composites’ optical properties. As a result, it gave the opportunity not only to describe qualitatively and sometimes quantitatively the available experimental data on pulsed laser initiation (the critical energy density dependence on pulse duration) but also predict new effects such as wavelength value nanoparticles’ radius and sensitizing mass concentration influence on critical energy density of the laser pulse. The relevance of the continuing study of the micro hot-spot model has both fundamental and applied aspects. The fundamental relevance is concerned on the models’ of laser explosive initiation development. The applied aspects arise due to optical detonators’ optimization. The minimal critical energy densities of PETN laser initiation were determined for samples containing nanosized aluminum dopant. In terms of the model the real structure of aluminum nanoparticles is neglected. The nanoparticles are protected from oxidation by an oxide layer formed at the final stage of electrical explosion synthesis [12].

The aim of the work is modernization of micro hot spot model with account of optical and thermophysical properties of dielectric cover of the nanoparticles. The main tasks are (i) calculate the absorption and scattering efficiencies of nanoparticles having core-shell structure; (ii) modernize the model of thermal explosion [11] taking into account the nanoparticle’s cover; (iii) calculate the kinetics of explosion initiation and thermal field evolution in terms of the model. The model will be applied to the practically relevant composites PETN-aluminum nanoparticles for which the dependence of the critical energy density on the oxide content in nanoparticles was measured experimentally [2].

2. Optical properties

The influence of oxide cover on the optical properties of nanoparticles could be considered in terms of Aden-Kerker theory and Mie theory in the case of spherical particles. The thickness of the oxide layer was assumed to be uniform. The approaches of the optical properties of spherical nanoparticles with metal core-oxide shell structure were described in [13-15]. This model is fertile for describing of dielectric core – metal shell [16] and cage nanoparticles’ optical properties [17]. In the case of uncovered particles presented in [18, 19]. The value of the complex refractive index of aluminium core which is 0.96-8.07i at the main wavelength of neodymium laser was taken from [20], the refractive indexes of aluminum oxide and PETN are 1.762 and 1.54 respectively. In the ultraviolet range the shell refractive index could become a complex number, but it is a real number in the range of the main harmonics of the neodymium laser.

The calculated in terms of Aden and Kerker theory dependencies of the absorption (solid line), extinction (dashed line), and scattering (dash-dot line) efficiencies on the radius of Al-Al$_2$O$_3$ at the oxide mass fraction 75% are shown on the figure 1. The ALEX aluminum nanoparticles were used in the experimental work [6, 21] whose average radius is 50 nm and the oxide content 10%. The mass fraction of the metallic aluminum decreases quickly from 90% achieved just after the synthesis to 75% and keep almost constant then. The dependences shown on the figure 1 are typical for metal nanoparticles. In the limit of small particles one distinguishes Rayleigh range where the absorption and scattering efficiencies increase with radius increasing. Then the maximum is observed with following slow decreasing of the efficiencies. At the same time, the difference between these curves and obtained for unoxidized nanoparticles are easily seen. The maximum values of absorption efficiency is 0.199 observed at radius 125.8 nm, extinction efficiency reaches maximum of 2.423 at $R=144.1$ nm and scattering maximum value is 2.240 seen at $R=145.4$ nm. The respective maximum values calculated in terms of Mie theory for unoxidized nanoparticles in several papers are 0.283 at $R=100.7$ nm for $Q_{abs}$, 3.379 at 117.4 nm for $Q_{ext}$, and 3.118 at $R=118.5$ nm for $Q_{sca}$. The decreasing of maximum absorption efficiency is 42% at the oxide mass fraction 25% accompanied by substantial optimal radius increasing. The difference in the optical properties of 50 nm nanoparticles calculated with taking into account and neglecting the oxide shell is important also. The oxide shell makes the absorption efficiency of that particles diminish from 0.109 to 0.047 that is higher than 2.3 times.

The calculated dependencies of the absorption (solid line), extinction (dashed line), and scattering (dash-dot line) efficiencies on the mass fraction of metallic aluminum in the range 0.10–0.95 at the
radius of core-shell Al-Al$_2$O$_3$ nanoparticles 50 nm is presented on the figure 2. The plot shows an unexpected feature. The absorption prevails over the scattering in the range of small cores’ radii meaning high fraction of the oxide. In the opposite range of low oxide fraction scattering prevails as for unoxidized nanoparticles. The dependencies of scattering and absorption efficiencies cross at the fraction value 0.765 that is close to oxide fraction in aluminum nanoparticles used as a dopant in the explosives utilized in optic detonators operated at the main (1064 nm) and second harmonics (532 nm) wavelengths of neodymium laser. The efficiency value at the cross point is 0.05.

![Figure 1](image1.png)  
**Figure 1.** The calculated dependencies of the absorption (solid line), extinction (dashed line), and scattering (dash-dot line) efficiencies on the radius of Al-Al$_2$O$_3$ at the oxide mass fraction 75%.

![Figure 2](image2.png)  
**Figure 2.** The calculated dependencies of the absorption (solid line), extinction (dashed line), and scattering (dash-dot line) efficiencies on the mass fraction of metallic aluminum in the range 0.10 – 0.95 at the radius of core-shell Al-Al$_2$O$_3$ nanoparticles 50 nm.

### 3. Heating kinetics

Let us discuss the heating of the nanoparticles with core-shell structure in the PETN matrix due to laser irradiation. In [20, 22] we showed that radiation transport is a fast process relatively to the thermal conduction and chemical exothermic reaction initiation. Thus, one is able to treat the radiative transfer as if it takes place at lower excitation energy densities or in inert matrices with close optic properties. For that reason, the model is suggested for the absorption efficiency value equal to 1, but one introduces additional factors concerned on the light absorption. Sometimes this factors could be determined experimentally ob the base of reflectance and transmittance of the sample.

The set of differential equations of the model take into account the metal core of the nanoparticle heating with laser pulse, conductive heat transport in oxide shell and PETN, and exothermic PETN decomposition. The self-sustained decomposition could be achieved if the laser pulse energy density is higher than the threshold one. The equation set is as follows:

$$
\frac{\partial T}{\partial t} = \alpha_{\text{PETN}} \left( \frac{\partial^2 T}{\partial x^2} + \frac{2}{x} \frac{\partial T}{\partial x} \right) + \frac{Q}{C} k \cdot n \cdot \exp \left( \frac{-E}{R g} \right), \quad x > R,
$$

$$
\frac{\partial T}{\partial t} = \alpha_{\text{Al}_2\text{O}_3} \left( \frac{\partial^2 T}{\partial x^2} + \frac{2}{x} \frac{\partial T}{\partial x} \right), \quad r < x < R,
$$

$$
\frac{\partial T}{\partial t} = \alpha_{\text{Al}} \left( \frac{\partial^2 T}{\partial x^2} + \frac{2}{x} \frac{\partial T}{\partial x} \right), \quad x < r.
$$

(1)
where $T$ is temperature, $n$ is relative concentration of the explosive that decreases during the reaction from 1 to 0, $\alpha_{\text{PETN}}=1.1 \times 10^3 \text{cm}^2 \text{s}^{-1}$, $\alpha_{\text{AlO}_2}=0.136 \text{cm}^2 \text{s}^{-1}$ and $\alpha_{\text{Al}}=0.97 \text{cm}^2 \text{s}^{-1}$ are temperature diffusivities of PETN, alumina, and aluminum, $R$ is molar gas constant, $E=165 \text{ kJ/(mole-K)}$, $k_0=1.2 \times 10^{16} \text{ s}^{-1}$ and $Q=9.64 \text{ kJ/cm}^3$ are activation energy, pre-exponent factor, and exothermic effect of PETN decomposition respectively. The conditions on the boundary PETN-Al$_2$O$_3$ reflect simple energy conservation, while at the boundary Al$_2$O$_3$-Al the conditions contains additional term $J$ for laser pulse absorption:

$$J - C_{\text{Al}} \alpha_{\text{Al}} \frac{\partial T}{\partial x} \bigg|_{R=0} - C_{\text{AlO}_2} \alpha_{\text{AlO}_2} \frac{\partial T}{\partial x} \bigg|_{R=+0} = 0,$$

$$-C_{\text{PETN}} \alpha_{\text{PETN}} \frac{\partial T}{\partial x} \bigg|_{R=-0} = 0$$

where $C_{\text{Al}}=2.7 \text{ J/(cm}^3 \text{K)}$, $C_{\text{AlO}_2}=2.8 \text{ J/(cm}^3 \text{K)}$, and $C_{\text{PETN}}=2.22 \text{ J/(cm}^3 \text{K)}$ are volumetric heat capacities of aluminum, alumina, and PETN. $J(t)$ is absorbed by metal core power density (in W/cm$^2$) of laser pulse. We used the first-type conditions $T=T_0=300 \text{ K}$ on the boundary of the considered system that is nanoparticle, oxide shell, and PETN layer with thickness $7R$. This model is a new modernization of the suggested in [11] model of lead azide explosion initiation adopted in [20, 22] for PETN containing metal nanosized dopant explosion initiated with laser pulse. This model is a kind of micro hot spot model. It has something in common with models of low-temperature ignition of coal particles in air flow [23], ignition of covered explosives by laser beam [24], ignition of combustible substance with heated particle being a limited heat source [25, 26], sintering of materials by laser beam [27], ignition of materials by local heating [28, 29]. In the experiments of interest the laser power density is close to normal distribution function:

$$J(t) = k_H \cdot R^2 \cdot \exp(-k_H r^2)/(\sqrt{\pi} \cdot r^2),$$

where $k_H=2(\ln2)^{1/2}/t_i$ is parameter describing the full width at half maximum of the pulse ($t_i$), $H$ is pulse energy density, the ratio of nanoparticles’ and core radii squares takes into account the energy absorption by metal core while it is calculated for entire nanoparticle.

The nanoparticle’s heating due to laser pulse absorption with consequent PETN heating was modelled by equation system (1)–(3) numerical solution on the non-uniform stationary grid taking into account the two boundary conditions (2). The methods are described thoroughly in [19]. The figure 3 shows the temperature kinetics on the boundary PETN-Al$_2$O$_3$ and on the distance 10 nm inside the PETN matrix. The absorption efficiency was 1 and the energy density was 20 mJ/cm$^2$. As in terms of the model neglecting the oxide shell there is a critical energy density of the laser pulse, which is the lowest energy density making the surrounding PETN decompose entirely almost instantly. The main regularities of this process are similar to arising in the model neglecting oxide shell discussed in [9, 20, 22]. The energy density 20 mJ/cm$^2$ is lower than the critical value for radii of nanoparticles between 10 and 120 nm. The maximum temperature value is achieved during the pulse at 5 ns after power maximum. The temperature decreases then, which is accompanied by the reaction hot spot expanding.

The optimal radius of the nanoparticle provides the lowest critical energy density. Thus it could be evaluated by critical energy density calculation with radius variation. On the other hand, the optimal radius coincides with the radius of the most heated nanoparticle in the under threshold conditions. On the figure 4 the dependence of the maximum temperature on the nanoparticle’s radius at absorption efficiency equal to 1 and energy density 20 mJ/cm$^2$ is presented. In the case of aluminum nanoparticles the optimal radius is 60 nm, which is slightly higher than the average radius of the nanoparticles used in the experimental works [4, 5, 11]. The respective temperature at the maximum point is 905 K. It is worth to note that the oxide shell does not influence the optimal radius. Alumina’s density is denser than aluminum, so the nanoparticle with overall radius 50 nm has oxide layer of 3.3 nm. The temperature diffusivity of the oxide is lower than that of aluminum, but is about 100 times higher than...
of PETN. Thus, we are able to conclude that oxide shell influences significantly the optical properties of the aluminum nanoparticles with radius 50 nm, while thermophysical processes initiated by laser pulse keep almost the same.

![Figure 3. Temperature kinetics on the boundary PETN-Al nanoparticle having radius 50 nm (solid line) and at the distance 10 nm from that boundary in the PETN matrix. The calculations were done at the absorption efficiency value 1 and energy density of the pulse 20 mJ/cm².](image)

![Figure 4. The calculated dependence of the maximum heating temperature on the nanoparticles’ radius at absorption efficiency equal to 1, aluminium core mass fraction 75% and energy density 20 mJ/cm².](image)

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