INITIATION OF EXPLOSION OF PENTAERYTHRITOL TETRANITRATE BY PULSES OF THE FIRST AND SECOND HARMONICS OF A NEODYMIUM LASER

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It is shown that during initiation of explosion of pentaerythritol tetranitrate (PETN) by the second harmonic of a laser, the primary process of energy absorption is ionization of PETN molecules by the mechanism of two-photon absorption. Possibility of regulating the PETN sensitivity by adding nickel nanoparticles to laser irradiation is established.

Keywords: energetic materials, laser, explosion, nanoparticles.

The mechanism of explosive decomposition of high-energy materials exposed to laser pulses has not yet been interpreted unambiguously. The key problem in the initial stage of radiation interaction with an explosive is a mechanism of energy absorption in the sample. The widespread viewpoint is that with increasing laser pulse energy density H to values H^* less than the critical value H_{cr}, free electric charge carriers arise in the zone exposed to laser radiation as a result of ionization of defective crystal regions [1]. This leads to a nonlinear growth of the absorption, multiplication of free charge carriers by the avalanche mechanism, and excitation of optical breakdown whose threshold H^* is determined by the threshold of crater formation [2]. In [3, 4] the thickness of the layer of the surface breakdown was indicated to be 30–80 μm. It should be noted that the above-enumerated works and many other works (for example, see [5, 6]) used the first harmonic of a neodymium laser (1.06 μm) operating in the Q-switch mode. No systematic investigations of a dependence of explosive decomposition threshold on the radiation wavelength were performed.

PETN and its mixtures with nanodimensional Al (100 nm) and Ni (280 nm) particles were investigated. A Nd^{3+}:YAG laser operating in the Q-switch mode at the fundamental frequency ($\lambda = 1064$ nm) and at the second harmonic ($\lambda = 532$ nm) with pulse duration at half maximum of 12 ns, maximum pulse energy at the fundamental frequency of 1.5 J, and intensity distribution over the beam cross section close to rectangular one was used. In the first series of experiments, a dependence of the PETN explosion probability P on the laser pulse energy density H was investigated. Our experiments at the fundamental laser frequency demonstrated that no PETN explosion was observed under our experimental conditions with maximum possible energy density $H = 30$ J/cm^2. Moreover, when the diameter of the irradiation zone was halved ($d \approx 1.25$ mm), an energy density of 120 J/cm^2 was attained, and the same result was obtained. Thus, under conditions of our experiment the critical energy density corresponding to a 50% probability of explosion was $H_{cr} > 120$ J/cm^2. With further decrease in the irradiation zone diameter $d < 1$ mm, H_{cr} increased because of the size effect [1]; therefore, measurements at smaller light beam diameters were not performed.

At the second harmonic of laser radiation, a possibility of initiation of the PETN explosion was established. A dependence of the sample explosion probability on the energy density of the initiating pulse was measured. At fixed energy density, 10 samples were subsequently irradiated, and the explosion probability was determined. The critical energy density was $H_{cr} = 12.3$ J/cm^2. Thus, the initiation threshold of PETN with the density $\rho \approx 1.73$ g/cm^3 by the
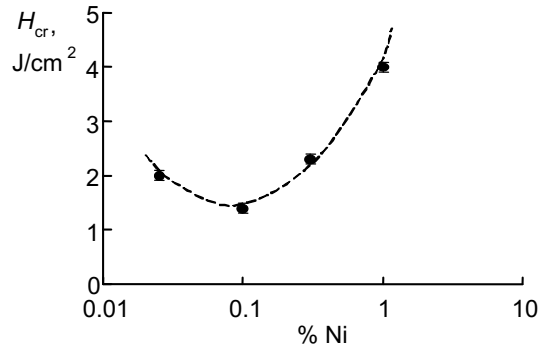
Fig. 1. Dependence of the threshold of initiation of explosive decomposition on the nickel particle content in the sample.

second harmonic of the laser was by more than an order of magnitude lower than by the first harmonic! This result allows us to doubt that at least for the second harmonic of the laser, the initial stage of explosion initiation was caused by ionization of defective regions of the sample, heating of free charge carriers, and avalanche ionization and optical breakdown, as suggested in [1, 2] for the first harmonic of the laser.

Indeed, the critical electric field strength of dielectric crystal breakdown by electromagnetic radiation within the context of avalanche ionization theory can be described by the expression [7]

$$E_{cr}(\omega) = E(0)\sqrt{1 + \omega^2 \tau^2} \ ,$$

where $E(0)$ is the static electric field of the breakdown, ω is the laser radiation frequency, and τ is the relaxation time of the charge carrier pulse. From this expression it follows that the increase in ω must lead to an increase in $E_{cr}(\omega)$. In dielectric crystals $\tau \geq 10^{-15}$ s; therefore, the situation with $\omega^2 \tau^2 << 1$ can be observed. In this case, $E_{cr}(\omega) = E(0)$. If $\omega^2 \tau^2 \geq 1$, $E_{cr}(\omega) > E(0)$. Since $H_{cr} \sim E_{cr}^2$, than $H_{cr}(\omega_2) \geq H(\omega_1)$ for the mechanism of avalanche ionization and optical breakdown. In our experiment, the reverse situation was observed. We assumed that when the samples were initiated by the second harmonic of the laser, the ionization of the PETN molecules proceeded by the mechanism of two-photon absorption. Indeed, the edge of the fundamental absorption band in the measured absorption spectra of PETN crystals was observed at photon energies $E_f \geq 3.5$ eV. If the probability of two-photon absorption is high, than the energy $2E(\omega_2) = 4.66$ eV will be sufficient for ionization.

For the model of two-photon absorption the primary absorbed energy was spent completely on the ionization of the medium, i.e., the situation was analogous to the case of electron-beam initiation studied in [8, 9]. This suggests that the PETN initiation by the second harmonic of the laser, by analogy with the electron-beam initiation, has the following stages: ionization of the medium, thermalization and recombination of electronic excitations, and exothermic decomposition of ionized PETN molecules most likely in the vicinities of structural defects. As a result, a shock wave was formed and propagated through the crystal that finally led to sample explosion by the impact-wave mechanism by analogy with the electron-beam mechanism [9]. In [10] it was demonstrated that it is easy to initiate explosion by the first harmonic of a neodymium glass lasers when PETN samples were doped with Al nanoparticles.

In the present work, we experimentally investigate the dependence of the probability of explosion of PETN samples containing 0.025, 0.1, 0.3, and 1% Ni (by weight) on the initiating pulse energy density. From the results shown in Fig. 1 it can be seen that the optimal concentration at which the sensitivity to laser radiation is maximum is ~0.1%, and the explosive decomposition threshold is $H_{cr} = (1.4 \pm 0.05)$ J/cm^2.

Under analogous conditions we carried out the experiment with an optimum aluminum particle concentration of 0.1% by weight determined in [10]. It appeared that H_{cr} obtained in the present work for samples doped with Al was by 20% smaller than the result presented in [10] and was $H_{cr} = (1.15 \pm 0.05)$ J/cm^2. This result can be due to different parameters of the neodymium glass laser ($\lambda = 1.06$ μm and $\tau = 20$ ns) used in [10].
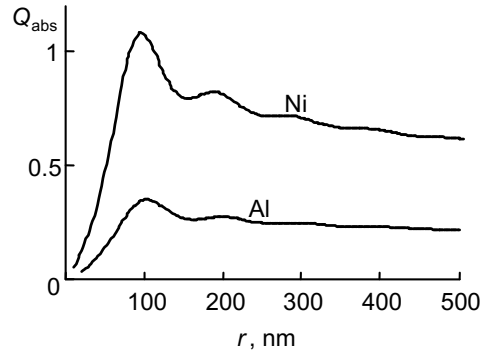
Fig. 2. Dependence of the light absorption efficiency factor Q_{abs} on the radius of inclusions in the PETN matrix.

We now discuss the results within the framework of the model of thermal explosion microcenter initiation upon exposure to laser radiation assuming that metal nanoparticles absorbing laser radiation are heated and form hot spots – centers of chemical decomposition – that caused explosion when the laser energy density reached the H_{cr} value. In [11] the model was suggested and the light absorption efficiency factor Q_{abs} was calculated for metal particles incorporated in the PETN matrix depending on the particle sizes. According to [11],

$$Q_{abs} = \sigma/\sigma_g \,, \tag{1}$$

where σ is the true light absorption cross section and σ_g is the geometrical absorption cross section of the inclusion.

The curves $Q_{abs}(r)$ calculated for Al and Ni inclusions in the PETN matrix at a wavelength of 1064 nm are shown in Fig. 2. As can be seen from Fig. 2, the light absorption efficiency factor for Ni is much higher than for Al. In particular, in the distribution maximum for the Al nanoparticles $Q_{abs} = 0.19$ and for Ni nanoparticles $Q_{abs} = 0.82$, that is, the light absorption by Ni is much more effective; however, $H_{cr}(Al) < H_{cr}(Ni)$. It seems likely that to compare the efficiency of light absorption by various inclusions, it is necessary to consider directly the absorption coefficient K rather than Q_{abs}. If σ is the photon absorption cross section of metal inclusions and n is the inclusion concentration in the sample, for the light absorption coefficient of the sample we can write the expression

$$K = \sigma n \,. \tag{2}$$

Let us derive an expression for K for the formulated problem. From Eq. (1) it follows that

$$\sigma = Q_{abs}\, \sigma_g = Q_{abs}\pi r^2. \tag{3}$$

By analogy with [11], we consider that particles are spherical. The inclusion concentration can be calculated from the formula [12]

$$n = \frac{1}{V_d}\frac{\rho_0}{\rho_d}\frac{\chi}{\left[1-\chi\left(1-\dfrac{\rho_0}{\rho_d}\right)\right]}\,, \tag{4}$$

where V_d is the inclusion volume, ρ_0 is the sample density, ρ_d is the density of the inclusion particle, and χ is the mass fraction of the added inclusion.

In our experiments, the minimum threshold of explosive decomposition for Al and Ni additives was $\chi = 0.1\%$ by weight or $\chi = 10^{-3}$. Provided that particles are spherical and that the second term in the square bracket of Eq. (4) is small, we derive
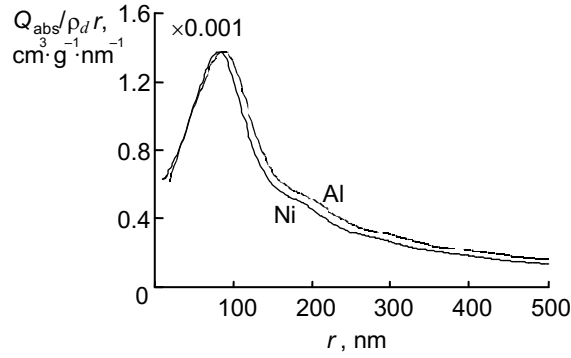
Fig. 3. Dependence of $Q_{abs}/r\rho_d$ on the radius of inclusions in the PETN matrix.

$$n = \frac{3}{4\pi r^3} \frac{\rho_0}{\rho_d} \chi. \tag{5}$$

The concentration estimated at $\rho_0 = 1.73$ g/cm^3, $\chi = 10^{-3}$, $\rho_d = 2.7$ g/cm^3, and $r = 50$ nm for Al was $n_{Al} \approx 10^{12}$ cm^{-3}. At $\rho = 8.9$ g/cm^3 and $r = 140$ nm for Ni, it was $n_{Ni} \approx 5 \cdot 10^{10}$ cm^{-3}. From these values under assumption of uniform particle distribution over the sample, we obtain that at H_{cr}^{min}, inclusions are in both cases at the distance from each other $R \approx 10d$.

From Eqs. (1)–(3) and (5), we derive the following expression for K:

$$K = \frac{3}{4} \chi \frac{\rho_0}{\rho_d} \frac{Q_{abc}(r)}{r}. \tag{6}$$

Thus, the dependence of K on the particle sizes is determined by the ratio $Q_{abs}/r\rho_d$ shown in Fig. 3. Under conditions of our experiment, taking into account that $\chi_{Ni} \approx \chi_{Al}$, we obtain

$$\frac{K_1}{K_2} = \frac{\rho_2}{\rho_1} \frac{Q_1 r_2}{r_1 Q_2}. \tag{7}$$

Subscripts 1 and 2 refer to Al and Ni, respectively. Using $\rho_2 = 8.9$ g/cm^3, $\rho_1 = 2.7$ g/cm^3, and $Q_{abs}/\rho_d r$ from Fig. 3 for the particle sizes in the distribution maxima ($r_1 = 50$ nm and $r_2 = 140$ nm), we obtain $K_1/K_2 \approx 1.6$, that is, the absorption coefficient of inclusions of Al nanoparticles is greater than of Ni inclusions.

For the examined model, a lower ignition threshold must correspond to a higher absorption coefficient. From our experiment it follows that $H_{cr}(Ni)/H_{cr}(Al) = 1.2$. This is in qualitative agreement with the suggested model. For more exact estimations, a number of factors should be considered: particle size distribution, presence of an oxide film, temperature of heating of an individual particle, deviation from the spherical shape, etc. This requires further theoretical consideration.

From the model presented here it follows that for further experiments to choose metals providing the least H_{cr} value, $Q_{abs}(r)/r\rho_d$ must be calculated, its maximum value must be chosen, nanoparticles with the corresponding sizes must be synthesized, and experiments on the determination of the mass fraction χ of the additive providing the least H_{cr} value must be performed.

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