

The Size Effects and Before-Threshold Behavior of Solid-Phase Chain Reactions

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Abstract – In this work a new kind of size effect of solid-phase chain reaction proposed in [1] is experimentally proved. The diffusion constant and the mobility of electron excitations–chain carriers are experimentally determined under conditions of explosive decomposition. The existence of before-threshold behavior of the process is theoretically grounded and is experimentally proved. The regularities of the reaction transition from extinction mode to self-acceleration mode under increase of external pulse intensity have been studied.

1. Introduction

The chain character of heavy metal azide (HMA) explosive decomposition is proved theoretically and experimentally, but for all that in literature there does not exist a common opinion on the nature of main stages of the process. The size effect investigation, i.e. dependence of the explosive decomposition initiation critical parameters on the size of the sample is an effective method of the chain mechanism identification [2]. The main difficulties in identifying the chain generation and propagation elemental stages concern as well the fact that the regularities of self-acceleration modes of explosive decomposition were investigated only. To identify the mechanism of solid-phase chain reaction the investigation of size effects, before-threshold behavior kinetics and the regularities of the reaction transition from extinction mode to self-acceleration mode under increase of external pulse intensity is especially actual.

The convenient subject for investigation of these effects is HMA relating to energetic materials, i.e. substances decomposed with evolving significant energy [3,4]. Therefore, they can be subject to all known kinds of solid-phase decomposition both under stationary external effects and self-sustaining reaction owing to the energy evolved during decomposition.

2. The dependence of initiation critical energy of explosive decomposition by pulse radiation on the size of the sample

Typically, gas dynamic and thermal relaxation of the sample [5] are considered as the reasons of the dependence of explosive decomposition initiation parameters on the size of the sample.

In the work [1] a new feature of the increase of critical energy density (H_c) of HMA explosion initiation by pulse radiation characteristic of the solid-phase chain reactions has been proposed. In accordance with the model it is bound up with the

increased rate of electron-hole pairs (breaking chain stage) on crystal surface in comparison with the bulk recombination. It results in increase H_c if the sample size is comparable with the free path of electron excitations – chain carriers. The proposed model is a solid-state analogue of the dependence of explosion initiation critical parameters on vessel dimensions of gas-phase reaction [2].

Let us consider the effect of laser 20 ns pulse radiation on silver azide microcrystal. Taking into account the influence of surface on the reaction propagation the kinetics of the process will be described by the system of integro-differential equations [1]:

$$\begin{cases} dp/dt = G(t) - 2k_2 p^2 - k_r p + 3k_1 \beta A + D \Delta p, \\ dA/dt = k_2 p^2 - k_1 A, \\ dN_2/dt = 3k_1 A, \quad D \frac{dp}{dx} \Big|_{x=0, x=l} = sp, \\ \beta \beta = (L - p - 1,5[N_2] - 2A)/L; \end{cases} \quad (1)$$

where p , A , N_2 are concentrations of holes, N_6 complexes and molecular nitrogen in the bulk of the crystal; k_2 , k_1 , k_r are constants of generation, N_6 complex destruction and $e-h$ pair recombination rates in the bulk of the crystal; D is the diffusion constant of holes; $s=5 \cdot 10^5$ cm/s is the rate of surface recombination in silver azide crystals; sp is a boundary condition taking into account the recombination rate of charge carriers on the surface; β is the coefficient taking into account anion expenditure during the reaction; L is Loshmidt number.

The dependence of initiation energy critical density on the size of the crystal under short pulses is formulated as:

$$H_c = \left[\frac{k_r^*}{k_2} + 2 \cdot \frac{(k_r^*)^2}{k_2 \cdot k_1} \right] \cdot \frac{E}{\alpha} \quad (2)$$

where $k_r^* = k_r + \pi^2 D / r^2$ is the effective constant of the recombination rate with the account for inhibitory influence of the surface; E is the average energy of one $e.h.$ pair generation; α is the effective absorption coefficient.

In the work [1] it is shown that H_c increase will reveal itself in the most effective way in the size range of the crystal

$$r_1 = \pi \left(\frac{6D^2}{k_1 k_2 L} \right)^{1/4} \leq r \leq r_2 = 2 \sqrt{\frac{\pi^2 D}{k_r}} \quad (3)$$

with the reaction constants estimated in [1] these values are $r_1=1 \mu\text{m}$, $r_2=20 \mu\text{m}$.

If the crystal size is $r > (2-3) r_2 \approx 50 \mu\text{m}$ the initiation energy critical density practically coincides with the bulk density $H_c=H_o$. If $r \leq 1 \mu\text{m}$ H_c increases more than 10^3 times that practically corresponds to the total ionization of anionic sublattice. Finally, the branching-chain reaction is not realized and microcrystals are decomposed without explosion.

The experimental investigation of $H_c(r)$ dependence on the size of the crystals is carried out in the apparatus described in [5].

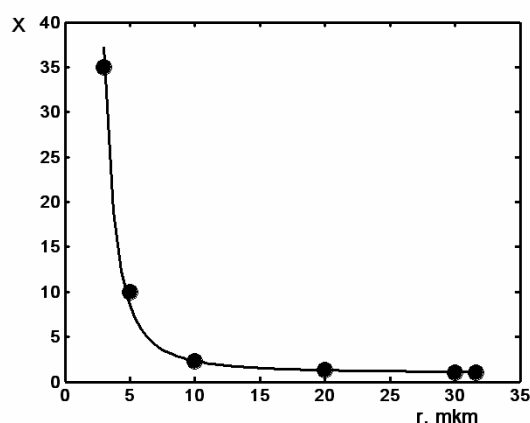


Fig. 1. The calculated and experimental dependence's of critical energy density upon sample size (2)

The results are presented in Fig. 1. From these results it follows that according to [1] H_c increases more than 30 times if the crystal size decreases from 35 to 3 μm and tends to H_o if the crystal size increases. After the effect of pulse radiation the large crystals ($r > 50 \mu\text{m}$) either explode over exceeding initiation threshold or experience no visual changes (including flash of light emission). The microcrystals sized $r \leq 1 \mu\text{m}$ cannot be initiated up to the energy density $H \geq 10 \text{ dyne/cm}^2$. Under these H there realize reactions of degenerate explosion at which the microcrystals are practically decomposed entirely under pulse duration, but the stage of exponential increase of the reagent concentration is absent.

In Fig. 1 the experimental and calculated from the equation (2) dependences of the explosion initiation energy critical density on the sizes of silver azide microcrystals are shown. The comparison with the experiment has allowed to determine the parameters $k_r = 1,6 * 10^6 \text{ s}^{-1}$ and $k_1 = 6,2 * 10^7 \text{ s}^{-1}$ for silver azide microcrystals which do not sufficiently differ from the values obtained in [1] while studying other experimental explosive characteristics in silver azide.

Thus, the experimental results confirm the viewpoint [1] that the breaking chain stage is the recombination of electron excitations. High rate of this stage on the surface of the crystal is one of the main

reasons for H_c increase if the sample sizes are comparable with the free path of electron excitations.

The obtained results also allow the estimation of the mobility (diffusion constant) of electron excitations directly during explosive decomposition. The calculations were carried out with the diffusion constant of holes $D = 0.25 \text{ cm}^2/\text{s}$ which corresponds to their experimental mobility $\mu \approx 10 \text{ cm}^2/\text{V s}$ @ $T = 400^\circ\text{K}$ [6]. In the work [7] it is shown that the main mechanism of electron scattering under these temperatures is their scattering on longitudinal optical phonons:

$$\mu(T) \sim T^{-1/2}, \quad D = kT/e * \mu, \quad D(T) \sim T^{1/2}$$

Thus, the diffusion constant should not sharply increase under temperature rise during explosive decomposition.

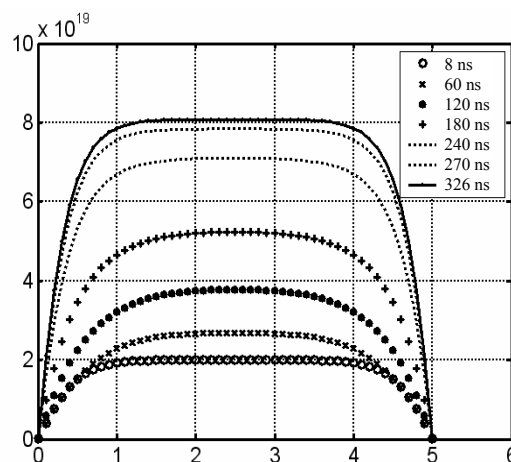


Fig. 2. The calculated kinetics of distribution of reagents concentration in microcrystal along crystal in 8, 60, 120, 180, 240, 270 and 326 ns

The close coincidence calculated at $D=0.25 \text{ cm}^2/\text{s}$ and experimental values $H_c(r)$ indicate firstly that the mobility (diffusion constant) of electron excitations during explosion decomposition slightly differs from the values determined with use of Hall effect and secondly that the temperature rise is not the first cause of HMA explosive decomposition.

3. Before-threshold behavior of silver azide chain explosive decomposition

The realized consideration allows to predict theoretically and to detect experimentally a new before-threshold behavior of the chain reaction propagation. This behavior is observed under irradiation of the microcrystals sized $r_2 < r < r_2$ by pulses with the energy density $H_o < H(r) < H_c(r)$.

It results in that the reaction after beginning in the bulk of the crystal goes out owing to the diffusion of electron excitations on the crystal surface where breaking chain reaction appears more expressive. At the increasing pulse energy density and the condition $H(r) \geq H_c(r)$ the reaction transforms from extinction mode to self-acceleration mode resulting in the explosion of the

sample. In the system "MATLAB" the software package was developed for mathematical modeling of the kinetics of solid-phase chain reactions in silver azide. The package allows to solve numerically the system of 1500–2000 integro-differential equations. The obtained solution allows visualizing the image of the reaction propagation at any moment and at any point of the crystal. Fig. 2 and 3 present the results of the reagent space distribution calculation in silver azide microcrystals sized $5\mu\text{m}$ at different points of time. The initial rate of electron-hole pair generation is taken the same for the whole bulk of the sample. Fast decrease of hole concentration owing to N_6 complex generation is realized directly after the pulse finishing. In subsurface areas a faster decrease of hole concentration is realized owing to the high recombination rate on the crystal surface. The following growth of reagent concentrations, especially in the central part of the crystal, is bound up with the multiplication of electron excitations during chain reaction (Fig. 2). The maximal concentration is achieved in 326 ns, then the decrease of the reagent concentrations is realized owing to the sample burnout (Fig. 3).

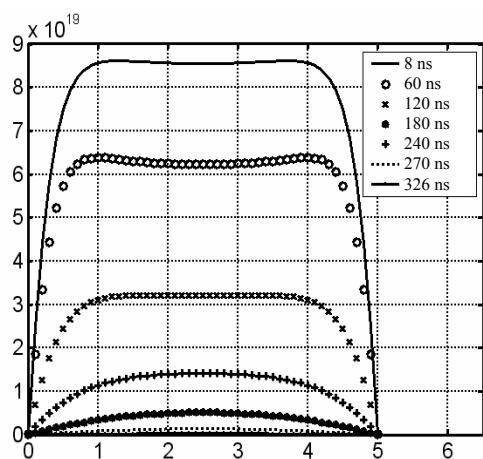


Fig. 3. The calculated kinetics of distribution of reagents concentration in microcrystal along crystal in 326, 440, 550, 660, 770, 880 and 1000 ns

The before-threshold behavior was detected under irradiation of the microcrystals having $r \sim 5\mu\text{m}$ size. From Fig. 1 it follows that the initiation energy critical density of the crystals of this size increases nearly 10 times in comparison with the large crystals. It is shown that the irradiation of microcrystals with energy density less than the critical density causes flash appearance and visual darkening of the sample. Explosion of the sample does not occur though. At the exceeding critical energy density the reaction transforms to self-acceleration mode resulting in the explosion of the sample. In Fig. 4. showed the experimental dependence of the maximum luminescence of silver azide microcrystal pulse energy density.

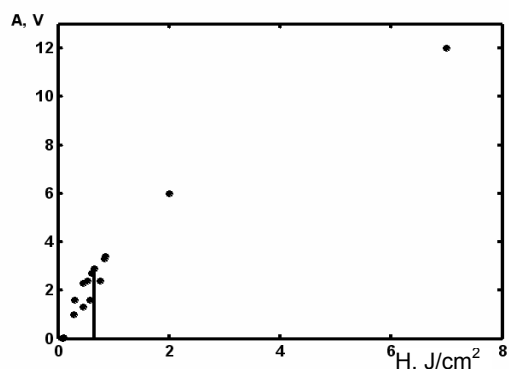


Fig. 4. The experimental dependence of the maximum luminescence of silver azide microcrystal pulse energy density. The line is the explosion decomposition

4. Conclusion

Thus, the investigation of the size effects under initiation of silver azide explosive decomposition enabled:

- to prove experimentally a new kind of the size effect of solid-phase chain reaction proposed earlier;
- to estimate diffusion constant and mobility of holes during explosive decomposition;
- to prove experimentally and to ground theoretically the existence of before-threshold behavior of solid-phase chain reactions.

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