

Propagation of the Chain Reaction Wave along the Silver Azide Crystal

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Abstract – In this work the new mechanism of branching-chain reaction wave propagation along the silver azide crystal is formulated and mathematical simulation of generation and propagation of the reaction wave initiated by the pulse radiation along the silver azide crystal is carried out. Several variants of the chain reaction initiation are being considered: electron-hole pair generation in the subsurface area of the crystal, hot-spot irradiation, homogeneous excitation. Calculations were carried out with various distributions of breaking chain center concentration along the crystal. The chain reaction wave propagation along the crystal is sufficiently close to the experimental values and is two orders of magnitude more than the diffusion and heat transfer rates.

1. Introduction

Processes of chemical reaction wave propagation are investigated by the humanity from the times immemorial. Now there exist two main mechanisms of the reaction propagation:

- detonation (shock wave initiates chemical reaction that proceeds with evolving of energy sustaining shock wave);
- "normal" propagation of exothermal process (activation of the non-reacting layer is realized through slow processes of diffusion, thermal conduction or convection).

The propagation rate of detonation wave front is defined by sound velocity in the medium and equates ~ 5 km/s for solids. The movement of exothermal reaction front is defined by processes of diffusion and thermal conduction with the typical velocity for solids \sim m/s.

The propagation rate of heavy metal azide (HMA) explosive decomposition initiated by the pulse radiation was experimentally determined by several groups of authors and equates ~ 1 km/s, which is 5 times less than the rate of the detonation wave. From the equation estimating the reaction propagation rate $v = \sqrt{2D/t}$ it follows that the estimation of the carrier diffusion coefficient $D \sim 1000$ cm²/s, which corresponds to $\mu = 40000$ cm²/(V s) and is 4 orders of magnitude more than the experimental mobility of electronic carriers in silver azide that was determined in the studies on photoconduction and Hall effect [1]. Therefore, existing mechanisms cannot explain the

reaction propagation rate observed in HMA. The objective of this work is to formulate a new mechanism of the branching-chain reaction wave propagation along the silver azide crystal and mathematical simulation of propagation along the silver azide crystal of the reaction wave initiated by pulse radiation.

The proposed mechanism is based on the following experimentally approved facts:

- explosive decomposition initiation of HMA crystals by pulse (~ 20 ns) radiation is the result of the branching-chain reaction propagation in the crystal [2];
 - electron-excited atom particles on the crystal surface can nonradiatively transfer their energy through sufficiently large distances (significantly larger than a lattice constant) with the generation of electron excitations in the bulk of solids.
- Chemical energy of heterogenous reactions can be efficiently transferred to the electrons of a solid and markedly disturb the electron subsystem equilibrium of the crystal. The electron channel of the chemical energy utilization is shown in:
- high values of the accommodation coefficient of vibrationally excited molecules on pure surfaces of metals and semiconductors and virtual independence of the single-quantum vibrational relaxation rate on a sample temperature;
 - the crystal luminescence;
 - electronic and ionic emission;
 - other non-equilibrium effects [3].

The fundamental distinction between detonation and accommodation mechanisms of the reaction propagation consists in the following: in the first case excitation transfers to the reaction area through ionic subsystem while in the second case excitation transfers through electronic subsystem.

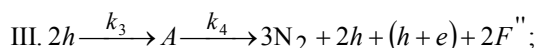
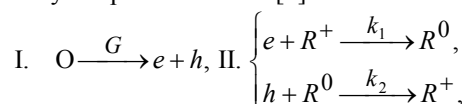
In the work [4] a comparative estimation of silver azide explosive decomposition initiation critical energy dependence on a sample size and radiation zone diameter was carried out. It is shown that the dependence of the critical initiation energy on a sample size is defined by reagent diffusion onto the crystal surface and their fast recombination there. The calculated values of the diffusion constant (0.3 cm²/s) and the rate constants of electron-hole bulk recombination ($2.4 \cdot 10^6$ s⁻¹) under explosion conditions practically coincide with the ones determined earlier in photoconduction and Hall effect studies [1]. It is shown that

silver azide explosive decomposition initiation critical energy dependence on radiation zone diameter may be defined by nonradiative transfer through distance r_0 of electronic excitations of reaction products (molecular nitrogen) to crystal lattice with generation of 3–4 electron-hole pairs providing the carrier multiplication and branching-chain reaction propagation [4]. The space-time characteristics of the reaction energy transfer to silver azide crystal lattice have been estimated. It is shown that the experimental rate of the energy transfer from the reaction area is two orders of magnitude more than the rates of reagent diffusion and thermal discharge of the sample.

The proposed mechanism of the explosive decomposition propagation consists in the following:

- a local initiating effect induces excitation of electronic subsystem of the crystal and the start of the branching-chain reaction,
- excited reaction products at their deactivation generate two electron-hole pairs on site of the reaction (electrons are localized on the generated anionic vacancies) and one electron-hole pair in vicinity r_0 to the reaction site,
- while the chain reaction progresses up to maximal rate the concentration of electron-hole pairs in unirradiated part of the crystal becomes sufficient for transition of the reaction to a self-accelerating mode and the start of the reaction in adjacent areas.

The bimolecular model is the most probable model of silver azide explosive decomposition initiated by the pulse radiation [1]:

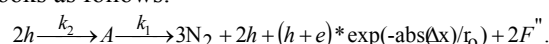


where R^0 , R^+ are recombination centers in various charging states, $2F''$ is the complex of two anionic vacancies with three molecules of nitrogen located there.

The first stage is generation of electron-hole pairs by external radiation. The second stage is recombination of electron-hole pairs on the bulk and surface local centers; with that the carrier recombination rate is limited by the hole capture on the neutral center $V_r \approx k_r p$ [1]. The third stage is interaction of two holes localized in adjacent sites of the crystal lattice with the generation of the intermediate complex A (N_6), consequent destruction of the complex and generation of molecular nitrogen (N_2) and center $2F''$ with evolving energy used for carrier generation. This is the stage of the chain propagation.

The work [2], along with diffusion and heat transmission mechanisms says about the existence of the mechanism of chemical energy fast transfer from the reaction area into the unirradiative part of the crystal. In this case the stage of the chain propagation

looks as follows:



where $r_0 \sim 50 \mu\text{m}$ (the area size of the reaction energy absorption) is experimentally determined.

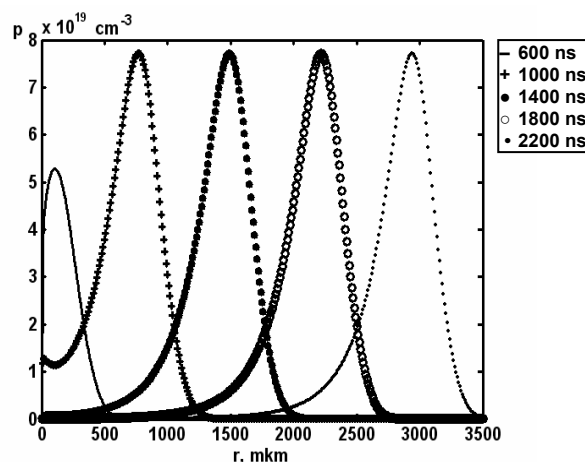


Fig. 1. Propagation of chain reaction front of explosive decomposition along silver azide crystal

The mathematical simulation of the branching-chain reaction propagation along the 3500 μm sized crystal (Fig. 1) with initiation by the laser pulse radiation in the intrinsic region of the absorption $\alpha=10^5 \text{cm}^{-1}$ is carried out in a one-dimensional approximation; the rate of the chain propagation along the crystal is determined depending on the constants of the model k_r , k_1 , k_2 .

One of the model parameters varied and the other two were constant and equal:

- under change k_r $k_1=3 \cdot 10^7$, $k_2=0.5 \cdot 10^{-11}$;
- under change k_1 $k_r=1 \cdot 10^7$, $k_2=0.5 \cdot 10^{-11}$;
- under change k_2 $k_1=3 \cdot 10^7$, $k_r=1 \cdot 10^7$.

The equation for the reaction propagation rate along the crystal is obtained analytically depending on the constants of the model:

$$V = \frac{x(1) \cdot k_1 \cdot k_2}{(1 + x(3) \cdot k_r / k_1) \cdot (k_1 + k_2 \cdot x(2))}, \quad (1)$$

where $x(1)$, $x(2)$, $x(3)$ are fitting parameters equating $5.05 \cdot 10^{16}$, $1.87 \cdot 10^{19}$, 2.95 , respectively.

The reaction rates calculated by the numerical integration of differential equation system and by the equation (1) differ by less than 1–2%.

Several variants of the chain reaction initiation have been considered: electron-hole pair generation in the subsurface crystal area; hot-spot irradiation; homogeneous excitation. Calculations were carried out at various distributions along the crystal of the breaking chain center concentration.

Simulation of silver azide crystal initiation from the surface allowed to define a functional dependence of the reaction propagation rate along the crystal on the constants of the model (k_r , k_1 , k_2). The value of the rate is obtained ($\sim 1 \text{ km/s}$) and well conforms with the experiment [3].

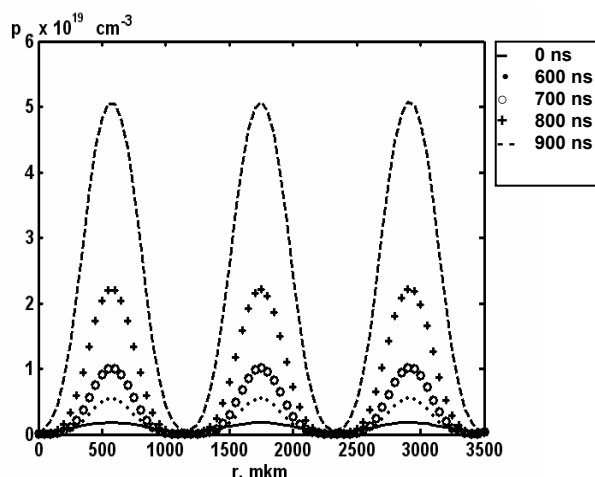


Fig. 2. Distribution of reagent concentration along crystal in 0, 600, 700, 800 and 900 ns

The task of hot-spot generation of the reaction (with initiation through narrow slits) is considered at a homogenous distribution of the recombination center concentration. At the first phase after the finishing pulse is absorbed, a fast (~ 10) decrease of the reagent concentration used for complex A generation is observed. In the sequel an increase of the reagent concentration up to the maximal value determined by transition of the branching-chain reaction to singular mode as a result of the sample decomposition takes place owing to the reaction propagation. Duration of the acceleration stage and corresponding effective constant is defined by the exceeding initiation energy density and changes within a wide range. In Fig. 2 the reagent concentrations along the crystal are shown in 0, 600, 700, 800 and 900 ns practically at the threshold initiation energy density (the concentration of generated electron-hole pairs). Two localized holes (N_3) are used for formation of the intermediate complex A (N_6); in the result of destruction two holes generate in the reaction area, and one hole generates in vicinity r_0 to the reaction area, and this induces "sharpening" of the reagent distribution peak and slow increase of the reagent concentration in the unirradiative region. While the reagent concentration exceeds $\sim 10^{20}$, electron-hole pair concentration in adjacent areas exceeds a critical value and there starts the reaction acceleration.

Then the reagent concentration decrease begins as the result of the significant decomposition of the sample in the region of irradiation. Outside the region of irradiation an electron-hole pair concentration increases in this moment. In Fig. 3 the reagent concentrations along the crystal are present in 1000, 1100 and 1200 ns. The reaction propagation along the crys-

tal comes with the constant rate and amplitude until the reaction areas "feel" each other. Maximal concentration of the reagents in the center of the unirradiative region and propagation rate of the reaction on this site significantly increase. This effect is analogous to the well known "superadiabatic burning" when temperature in epicenter between hot-spots of ignition is several times higher than the one of the adiabatic threshold.

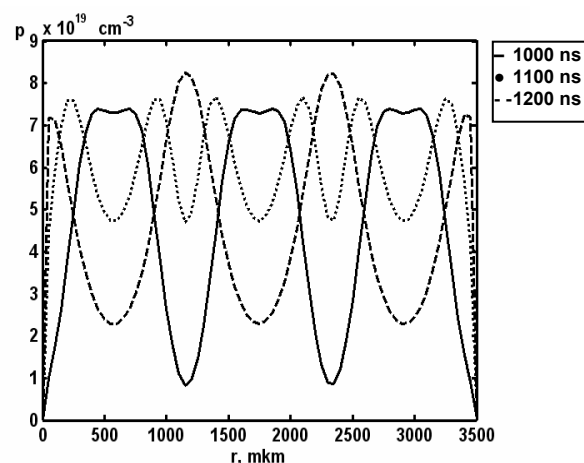


Fig. 3. Distribution of reagent concentration along crystal in 1000, 1100 and 1200 ns

This effect shows up when the reaction initiation is realized homogeneously and the concentration of breakage or propagation centers is distributed non-uniformly. In concordance with the experiment [4] after the increase of energy density of the initiating pulse the reaction is localized with formation of one first, then two, three, etc. hot-spots of initiation (where the concentration of the recombination centers is found to be accidentally lowered).

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