The Effect of Electric Field on the Explosive Sensitivity of **Silver Azide**

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Abstract. The effect of a constant contactless electric field on the rate of a chemical reaction in silver azide is explored in this paper. The technology of growing and processing silver azide whiskers in the constant contactless electric field (field intensity was varied in the range from 10^{-3} V/m to 10^{0} V/m) allows supervising their explosive sensitivity, therefore, the results of experiments can be relevant for purposeful controlling the resistance of explosive materials. This paper is one of the first attempts to develop efficient methods to affect the explosive sensitivity of energy-related materials in a weak electric field (up to 10^{-3} V/m).

1. Introduction

Improvement of material resistance to the unsupervised outer factors is one of the most important problems in the present day materials science. This issue is particularly urgent for advancing the resistance of energy-related materials.

Silver azide is a traditional object of research into solid phase chemical reactions. Physical and chemical properties of silver azide are studied quite well [1]. Both slow and explosive decomposition are possible in this material after energy deposition. Silver azide crystals have a great practical value because they can be used as explosive materials with high initiating capacity [1, 2]. Silver azide is used in small-scale primers, in production of explosive materials, commercial cumulative charges, detonating cords, perforating systems, electric detonators, which are in use in oil and gas industries for perforating and pumping-in well sites, as well as in development geophysics as sensors of electromagnetic fields.

The outer energy deposition causes the decomposition process in silver azide crystals, including generation of non-balanced electrons and holes, their transfer to the crystal surface into reaction sites (RS) formed by edge dislocations and Cottrell atmosphere (containing positively charged particles), and a chain reaction in the reaction site as well [2-5].

We have found out in our research that the reactive capacity of silver azide crystals can be controlled efficiently via a contactless electric field [5-7].

The effect of electric field in the solid chemistry is traditionally considered in two aspects: injection and drift of charge carriers, disregarding the polarization. However, polarization depends on the spatial

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shift of the electron intensity in chemical agents, and it must have the most significant influence on the rate of a chemical reaction.

This paper presents the outcomes of research how the constant contactless electric field (field of polarization) affects explosive decomposition, initiated in silver azide whiskers by the laser pulse or the contact electric field in conditions of mono-polar injection of holes. The possibility to use for these purposes a weak electric field (up to 10^{-3} V/m), simulating real conditions of storage and transport of explosive materials, makes it possible to affect the long-term resistance of energy-rated materials under the action of unsupervised outer factors.

2. Technique of experiment

Experiments required the use of silver azide whiskers grown as described in [7]. Crystallization of silver azide in a weak constant contactless electric field (the field intensity was varied 10^{-3} V/m to 10^{0} V/m), as demonstrated by the outcomes of our experiments [6, 7], allows synthesizing chemically pure mono-disperse crystals with the low concentration of defects, which sizes can be modified via varying the intensity of crystallization field.

The samples were glued at both ends of a high electric resistant mica plate degreased preliminary by ethyl alcohol.

The direct experiment scheme "impact – response" was used for exploring the regularities of explosive decomposition. As a factor initiating explosive decomposition a constant contact electric field was used with intensity of 300 KV/m. The electric field was generated by sources of direct current. Gallium electric contacts were deposited under the microscope onto the most developed crystal face in the central part of the sample (010); the distance between electrodes was 1 μ m. The mode of monopolar injection of holes is activated in these conditions; the holes in the reaction sites force a chemical reaction. The specified electric field intensity makes it possible to observe a transition from the slow decomposition into the explosive one in silver azide whiskers within some minutes (360±20 s).

The explosive decomposition was also initiated by 200 µs to 20 ms pulse with 1070 nm wavelength (energy in the pulse up to 20 J), generated by the ytterbium quasi-continuous fiber laser. The exposure of initiation on the sample surface was identified by the pyroelectric head PE50BF-DIF-C and monitored according to the calibrated photodiode signal. We used only the central laser beam for initiation to support quite homogeneous distribution of actuation intensity over the sample surface [8]. The dispersion of initiating pulse energies did not exceed 3%. We selected one sample of a set to explore the kinetics of explosive decomposition; afterwards it was subjected to initiation by a low energy laser pulse. Unless it had exploded, the pulse energy was increased by 5% and the sample was initiated again. This procedure makes it possible to determine precisely an "own" initiation threshold of a sample in the set. A probabilistic curve of explosion was plotted down on the base of data obtained for approximately 30 crystals.

The explosive sensitivity was determined as explosion delay time. The explosion delay time is measured quite specifically due to the probabilistic character of explosive decomposition, in the area of small fields in particular. The explosion delay to be measured includes a probabilistic component and as the experiments revealed it depends on the "life history" of a sample. The explosion delay time at the intensity of the contact electric field 300 KV/m was accepted as a measurement standard (this field intensity corresponds to the average explosion delay 360 ± 20 s under the condition of 80-95 % explosion delay). At least 10 samples were examined for each point of experimental curves. The data of experiments were processed in Microsoft Excel.

The experimental facility shown in figure 1 was used for exploring the effect of a constant contactless electric field on the explosive sensitivity of silver azide whiskers. Polarization fields with the diverse configuration were used for the purpose of experiments (figure 1). The constant contactless electric field intensity was varied from 10^{-3} V/m to 10^{3} V/m.

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Figure 1. Experimental facility for exploring the explosive decomposition of silver azide samples in: a) a longitudinal contactless electric field, its electric-field vector overlaps with the crystallographic direction [001]; b) and c) a cross contactless electric field, its electric-field vector overlaps with the crystallographic directions [010] and [100].

3. Results and Discussion

The samples of silver azide synthesized via crystallization in the electric field are needle-like habit crystals. Simple forms of a pinacoid $\{010\}$ and a rhombic prism $\{110\}$ are recorded on the explored samples. A combined type of forms $\{010\}+m\{110\}$ is typical of whiskers synthesized this way. Observing the growth of crystals in the process of crystallization, it was revealed that the silver azide whiskers grow from the top in the direction [001] with the developed face (010) and a side face (110) (see figure 2a). No volume damages seen by the optical microscope were found on the whiskers grown in the electric field, they are optically transparent with perfect faceting (figure 2b).



Figure 2. a) crystallographic faces of a silver azide whisker and b) general view of a crystal

The concentration of basic impurities (Fe, Si, Ca, Mg, Al, Na) in the synthesized crystals did not exceed 10^{16} cm⁻³. The defect structure of the crystals under consideration was analyzed by the X-ray fluorescence method (JEOL JSM-6390 LA, integrated with REM-RMA (PЭM-PMA) was used for the purpose of the research) and by atomic emission spectrometry (atomic emission spectrometer with inductively coupled plasma iCAP 6500). The density of dislocations in the crystals grown in a weak contactless electric field was determined by the method of etching pits [9] and averaged to $2 \cdot 10^2$ cm⁻².

Having analyzed the explosive decomposition of samples in conditions of laser initiation, we revealed that the crystals grown in the contactless electric field are the most suitable ones for interpretation of experimental results. The crystals grown in the electric field have a narrow probabilistic curve – the width of interval with the most probable explosion divided by the critical energy density does not exceed 0.05; the rate of reaction propagation in the crystal is constant; the obtained kinetic curves are smooth without any pips, therefore, the number of samples per each experimental point can be reduced.

The experimental results into the effect of a contactless electric field (polarization field) of diverse configuration on the explosive sensitivity of silver azide whiskers are provided in figure 3. The straight line in figure 3 represents the explosive sensitivity of crystals without a field of polarization.

The explosive sensitivity of the samples goes down sharply, as one can see in figure 3, simultaneously with the decreasing intensity of the contactless electric field. For instance, the intensity of the contactless electric field below 10^{-2} V/m is in line with the explosion delay time over $6 \cdot 10^3$ s. We should note that without any regards to mutual configuration of electric fields, in particular in zones with the intensity below 10^{-3} V/m, the curves nearly overlap when passing through the extremum.

As the chemical reaction in the anion sub-lattice of silver azide progresses till a quite stable semiproduct N_6 [5, 10] is formed in the sample, the study of its formation in the contactless electric field helps to realize how a field of polarization affects the solid phase decomposition of silver azide whiskers. Furthermore, the dependence of relative dielectric permittivity vs. intensity of the constant contactless electric field was assessed by the method proposed in [11].

The dependences of relative dielectric permittivity ($\epsilon_{\kappa p}$), explosive sensitivity (figure 4, curve 2), and specific volume N₆ (figure 4, curve 3) on intensity of a constant contactless electric field (longitudinal contactless electric field in figure 1a) are presented in figure 4.



Figure 3. Explosive sensitivity of silver azide vs. intensity of the effecting contactless: 1, 3 - cross electric field, its vector of intensity overlaps with the crystallographic directions [010] and [100], respectively; 2 - longitudinal electric field, its vector of intensity overlaps with the crystallographic direction [001].

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Figure 4. Relative dielectric permittivity $\varepsilon_{\kappa p}$ (1), explosive sensitivity of silver azide crystals (2) and relative volume of semi-product lg β (3) vs. logarithm of intensity of the constant contactless electric field

The experiments revealed that the amount of the formed semi-product in the contactless electric field drops significantly (the logarithm of the semi-product specific volume averages to 6 m provided that there is no electric field). It is worth noting that the field influences on the amount N_6 in the whole range of its intensity. Therefore, it implies the importance of the effecting field for formation of the semi-product in the process of solid phase decomposition of silver azide crystals.

Considering the intensity of the contactless electric field ranging from 10^{0} V/m to 10^{3} V/m and the relative dielectric permittivity, an assumption can be made that the mechanism of effecting contactless electric field is a combined one and depends on types of polarization: dipolar orientational, ionic, and electronic ones. However, the effecting electric field seems to be relevant only for the change in electron density in atoms provided that the intensity of polarization field does not exceed 10^{-2} V/m, as a consequence, the semi-product of solid phase decomposition of silver azide whiskers is formed slower. Thus, a weak (below 10^{-2} V/m) contactless electric field influences the rate of chemical reaction due to the electron density of reacting particles drifting along the vector of the electric field intensity, as a result, overlapping of electron clouds is less probable in the course of chemical bound formation. To sum up, polarization in the constant contactless field can be viewed as a method to control the explosive sensitivity of silver azide crystals.

4. Conclusion

The technology of growing and processing silver azide whiskers in the constant contactless field (in the specified range of field intensity) allows controlling their explosive sensitivity, as a result, making it possible to use the obtained experimental data for purposeful supervising the resistance of explosive materials. We note that the time till explosion of samples depends directly on the intensity of the constant contactless electric and magnetic fields in the course of crystallization and on the number of reaction sites in the sample.

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