Controlling Explosive Sensitivity of Energy-Related Materials by Means of Production and Processing in Electromagnetic Fields

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Abstract. The present work is one of the world first attempts to develop effective methods for controlling explosive sensitivity of energy-related materials with the help of weak electric (up to 1 mV/cm) and magnetic (0.001 T) fields. The resulting experimental data can be used for purposeful alternation of explosive materials reactivity, which is of great practical importance. The proposed technology of producing and processing materials in a weak electric field allows forecasting long-term stability of these materials under various energy impacts.

Introduction

Modern constructional materials are often subjected to extreme impacts (separate or combined action of electro-magnetic fields, laser radiation, light, temperature) which cause various physical and chemical transformations in the materials and making their application areas limited. From the range of impacts, great interest is attracted by electro-magnetic fields of uncontrolled origin (different manifestations of static electricity, radiation from powerful electric and radio devices, other man-made radiation sources). The impact of such radiations on explosive materials can initiate quickly developing processes in them and cause fires and explosions. Due to that, it is important to develop effective methods of controlling explosive sensibility and stability of energy-related materials. Among other areas such control is greatly demanded by coal industry.

This research is one of the world first attempts to develop effective methods of controlling explosive sensitivity of initiating explosives (on the example of silver azide whiskers) using the technology of production and processing of energy-related materials in superweak electric (up to 1 mV / cm) and magnetic (up to 0.001 T) fields. The resulting experimental data can be used for purposeful alternation of explosive reactivity which is of great practical importance.

Silver azide whiskers were chosen as a test object for this research. They represent a traditional model object used to create a theory of fast reactions in solids. Under the influence of external factors of different nature they are capable to undergo irreversible transformations generating inert end products (molecular nitrogen and metal), which can be easily analyzed by conventional physical and chemical methods. Physicochemical properties of silver azide have been studied in detail, the band
structure and the parameters of the crystal lattice have been determined [1-4]. There are two practically significant applications of silver azide whiskers: they serve as explosives with high initiating ability [1, 5], and as sensitive sensors measuring very low electric and magnetic fields.

Technology of inorganics crystallization in weak electric fields suggested in [6-8] allowed obtaining samples with improved performance (monodispersity, the minimum number of defects, increased shelf life, the size controlled by varying the electric field in crystallization, etc.). Samples of silver azide obtained at automated installation for synthesis and crystallization described in [7] contain the minimum number of defects. The content of impurities of positive metal ions Zn$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Al$^{3+}$, Pb$^{2+}$, assessed by atomic emission and X-ray fluorescence analysis methods, makes up 2 • 10$^{-5}$ mole percent in average; dislocation density determined by etch pits [9] is 2 • 10$^{2}$ cm$^{-2}$ in average.

The results of our studies [10] showed that the process of solid-phase decomposition of silver azide can be effectively controlled by a non-contact electric field. Thus, this research focuses on application of weak electromagnetic fields simulating real conditions of storage and transportation of explosives and on development of technology to control sensitivity of energy-related materials.

**Experimental technique**

Crystallization in a weak non-contact electric field was carried out by the method described in [6] at the apparatus shown in Fig. 1.

![Fig. 1. Installation for crystallization in the electric field](image)

Fig. 1. Installation for crystallization in the electric field: 1. power supply; 2. switch of the voltage adjustment range; 3. block of the voltage divider; 4. electrodes; 5. crystallizer; 6. grounded shield housing.

The crystallizer is a cylindrical weighing bottle partially filled with a solution of the corresponding salt. To increase the reliability of the experimental results $n$ crystallizers were connected to various steps of a voltage divider (Scheme $n = 4$). An element of 1.5V is used as the power supply. It provides a weak constant non-contact electric field without additional hardware and eliminates interferences. As seen in Figure 1, the proposed apparatus allows varying the voltage of the electric field in the experimental cell in the range from 10$^5$ to 10$^6$ (from 10$^5$ V to 10$^3$ V when switched on via resistance R5=1.1 MMOhm, and from 10$^3$ V to 10$^6$ V when switched on via resistance R6 = 1.1 GOhm). The voltage divider unit includes a serially connected resistances R1 = 2.2 kOhm, R2 = 20kOhm, R3 =
200kOhm, \( R_4 = 2\text{mOhm} \) with terminals at each stage. Crystallization in the electric field was carried out until the solvent completely evaporated (evaporation rate was 0.407 g / 24h at the temperature of \( 23 \pm 2 ^\circ\text{C} \)).

Figure 2 shows the technology of producing samples in a weak magnetic field. The weighing bottle with a solution of silver azide was placed in a uniform and non-uniform magnetic field. The gradient of the magnetic field was created by permanent magnets. Thus assembled structures were mounted in a grounded shield housing. Magnetic field distribution was measured by milliteslametre in points at the distance of 0.5 cm (instrument error at the measurement area of 200 mT was about \( \pm 2\% \)).

![Fig. 2. Installation diagram for crystallization in a uniform (a) and non-uniform (b) magnetic fields](image)  
1 - crystallizer; 2 - permanent magnets; 3 - microscope eyepiece; 4 - grounded shield housing.

The crystallization process was observed through the microscope, "Biolam" (ocular zoom \( \times 120 \)), photo and video shooting were performed.

Control of the defect structure of the materials was carried out by X-ray fluorescence (research was conducted at the installation JEOL JSM-6390 LA, combined PMA-SEM) and atomic emission (using atomic emission spectrometer with inductively coupled plasma iCAP 6500) analysis methods.

Since in silver azide whiskers, reaction regions (RR) coincide with dislocations emergences, the study of dislocation structure of crystals was carried out by etching holes method \[8\]. Contrasting etch pits were obtained by etching the crystals in 10\% aqueous solution of sodium thiosulfate. Individual edge dislocations runs, local and overall dislocation density of the samples were measured using an optical microscope.

The test samples were stuck at both ends onto a mica substrate pre-defatted with ethanol with the help of BF-6 glue which has high electrical resistance.

Explosive sensitivity of the samples was determined as the explosion delay time at which the explosion of the sample can be registered judging by a flash or audible signal with 50\% confidence. To study the decomposition patterns we used a scheme of direct experiment: exposure - response. The explosive decomposition of silver azide whiskers was initiated in two ways:

1. by an impulse of solid-state YAG: Nd\(^{3+}\) laser LDPL10M 10 ns in duration at a wavelength of 1064 nm (impulse energy being up to 1.1J) and by an impulse of ytterbium quasi-continuous laser from 200 ms to 20 ms fiber in duration at a wavelength of 1070 nm (pulse energy being up to 20J) \[4,10\]. Initiating exposure on the surface of the sample was determined using a pyroelectric head PE50BF-DIF-C (OphirPhotonics) and controlled by a signal of calibrated photodiode. A luminescence signal was recorded using a photomultiplier Hamamatsu H11526-20-NN. It provided a time reference of the signal moment caused by the sample explosion with the initiating laser impulse. It also allowed assessing the luminescence signal increase rate and recording the time when the luminescence caused by the explosion products arose. Only the central part of the laser beam was used to initiate the explosion ensuring a sufficiently homogeneous distribution of the excitation intensity on the sample surface. The spread of initiating impulse energies did not exceed 3\%. Approximation of the
Experimental data was performed based on the dependence of explosion probability on initiation exposure within micromodel of chain reaction of energy-related materials explosive decomposition proposed in [11].

2. by constant contact electric field. The electric field 300 kV/m in strength was created using the DC power supply (Fig. 3). The test samples were stuck at both ends onto a mica substrate pre-defatted with ethanol with the help of BF-6 glue which has high electrical resistance. Gallium was used for electrical contacts (inter-electrode distance being 1 mm). Under these conditions monopolar injection of holes which promote a chemical reaction in reaction sites takes place [9].

![Fig. 3. Experimental setup for the investigation of explosive sensitivity in electric-field decomposition: 1 - power supply; 2 - crystal; 3 - gallium contacts; 4 - mica substrate.](image)

Explosive sensitivity was defined as an explosion delay time. Measuring the explosion delay time has a number of features due to a probabilistic nature of the explosive decomposition especially at low strength areas. The measured value of the explosion delay time contains a probabilistic component, and experiments have shown that it depends on a sample biography. Explosion delay time at contact electric field intensity of 300 kV/m is adopted as a reference value (this field intensity corresponds to the explosion delay time of 360 ± 20 on average with the probability of 80-95%).

Application of the technology of energy-related materials treatment in noncontact electric field for controlling the reactivity of the materials on the example of silver azide whisker is analyzed in paper [9]. Figure 4 shows an experimental installation for a research into explosive sensitivity of silver azide samples in the non-contact electric field of different spatial configurations in a wide range of electric field strengths from $10^{-3}$ V/m to $10^4$ V/m.

![Fig. 4. An experimental installation for a research into explosive decomposition of silver azide samples: a) in the longitudinal non-contact electric field, its intensity vector coinciding with the](image)
crystallographic direction [001]; b) and c) in cross the non-contact electric field, its intensity vector coincides with the crystallographic directions [010] and [100]; 1 - ATM crystal, 2 - mica substrate, 3 - gallium contacts, 4 - electrodes.

**Results and Discussion**

Dependence of explosion probability after laser initiation with the above characteristics on the initiation exposure showed that silver azide whiskers grown in the electric field have higher initiation threshold (approximately 50% higher than control samples grown without the field) (Fig. 5). Furthermore, the exposure threshold value increases with increasing intensity of non-contact electric and magnetic fields during crystallization.

![Fig. 5. Dependence of explosion probability (P) of initiation exposure (H) of silver azide samples grown at different electric field intensities during crystallization: curve 1 - 10^{-4} V / m; curve 2 - 10^{-3} V / m; curve 3 - 10^{-1} V / m; Curve 4 - without the field.](image)

To analyze the explosive luminescence of silver azide whiskers we determined the time passed from exposure to the laser impulse to luminescence peak caused by the explosive decomposition for each batch of samples. Within each batch an average time and standard deviation (S) were calculated. Mathematical results of oscillogram processing are summarized in Table 1.

| Electric field intensity during crystallization of (E, V / m) | 0    | 10^{-3} | 10^{-2} | 10^{-1} | 10^0 |
|-------------------------------------------------------------|------|---------|---------|---------|------|
| Standard deviation (S)                                      | 17.2 | 3.4     | 1       | 8.8     | 0.57 |

The standard deviation of the time to reach maximum luminescence with crystals grown in the electric field is less than that with crystals grown by the conventional method (0.57 ÷ 3 depending on the electric field intensity for the samples grown by crystallization versus 17.2 for the samples grown by the conventional method).

When initiating the explosive decomposition by a contact electric field it is experimentally proved that explosive sensitivity of samples grown in the electric field decreases.
Explosion delay time is 6000s in average for the samples obtained in the electric field compared with 360s for the samples grown by conventional methods.

Figure 6 shows experimental results of processing energy-related materials by non-contact electric field of different configurations on the example of silver azide whiskers in order to control explosive materials sensitivity. Electric field intensity varies from $10^{-3}\text{V/m}$ to $10^4\text{V/m}$. To make the figure distinct decimal logarithm of field intensity was plotted along the horizontal axis. The straight line in Figure 6 represents explosive sensitivity of the silver azide samples in the absence of non-contact electric field.

![Graph showing dependence of explosive sensitivity on electric field intensity]

Fig. 6. Dependence of explosive sensitivity of silver azide on the intensity of non-contact controlling: 1, 3 - cross electric field (intensity vector coinciding with the crystallographic directions [010] and [100], respectively); 2 - longitudinal electric field (intensity vector coinciding with the crystallographic direction [001]).

When non-contact electric field intensity goes down sensitive of explosive samples decreases sharply. Thus, when the non-contact electric field intensity is less than $10^{-2}\text{V/m}$ explosion, the explosion delay time is more than $6\times10^3$. Note that regardless of the mutual configuration of the electric fields, curves almost coincide passing through the extremum especially at the sites with field intensity less than $10^{-3}\text{V/m}$. The arrow in Figure 6 shows that the time before explosion is more than 4hours (after experiments stopped).

**Conclusions**

Thus, with the help of the applied technology of obtaining and processing energy-related materials in a weak electromagnetic field with the specified intensity range we can control their explosive sensitivity changing defective and dispersed structure of these materials. It makes possible to use the experimental results for a targeted control of hazardous materials stability. It should be noted that the time before samples explosion is directly dependent on the intensity of the non-contact constant electric and magnetic fields in the crystallization and on the amount of RR in the sample.

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References

[1] Walker, B.F. Energetic Materials. Physics and chemistry of inorganic azides. / Ed. by H. D. Fair, B.F. Walker. - New York: Plenum Press, 1977. - Vol. 1. - 503 p.

[2] Saprykin A.A. Influence of mechanical activation of copper powder on physicomechanical changes in selective laser sintering products. / A.A. Saprykin, E.A. Ibragimov, E.V. Babakova, V.I. Yakovlev. // AIP Conf. Proc. 1683: 020199, 2015.

[3] Gordienco, A. B. Electronic Structure of Metal Azides / A. B. Gordienco, Yu. N. Zhuravlev, A. S. Poplavnoy // Phys. stat. sol. (b), 1996. - V. 197. - № 2. - P. 707-719.

[4] Gora, T. Elektronisk struktura of the azide ion and metal azid / T. Gora, D. S. Downs, P. J. Kemmey, et al. // Energetic materials. - New York: Plenum Press, 1997. - V. 1. - P. 193-250.

[5] Aduev, B.P. Explosive decomposition of heavy-metal azides. / B.P. Aduev, É.D. Aluker, G.M. Belokurov, Yu.A. Zakharov, et al. // Journal of Experimental and Theoretical Physics. - 1999. - T. 89. - № 5. - C. 906-915.

[6] Rodzevich, A.P. On a mechanizm of an electric field influence on physicotecnical specifications of materials / A.P. Rodzevich, E.G. Gazenaur, V.I. Krasheninin // Applied Mechanics and Materials. - 2013. - Vol. 379. - p. 154-160.

[7] Rodzevich, A.P. The Technology of Production and Treatment of Materials in the Electric Field / A.P. Rodzevich, E.G. Gazenaur, G.M. Belokurov. // Applied Mechanics and Materials. - 2014. - Vol. 682. - pp. 206-209.

[8] Rodzevich, A.P. Features of Physical and Chemical Properties of Inorganic Salts, Grown in the Electric Field / A.P. Rodzevich, E.G. Gazenaur, A.S. Walnukova, L.V. Kuzmina. // The 7th International Forum on Strategic Technology IFOST2012, 2012. pp. 296-299.

[9] Sangwal K. Etching of crystals: Theory, experiment, and application. In S. Amelinckx and J. Nihoul, Eds., Defects in Solids. North-Holland: Amsterdam, 1987. 497 p.

[10] Zakharov, V. Yu. The control of solid phase decomposition of silver azide by noncontact electric field / V. Yu. Zakharov, V. I. Krasheninin, L. V. Kuz’mina, et al. // Solid State Ionics. - 1997. - V. 101-103. - P. 161-164.

[11] Kriger, V.G. The effect of crystal size on initiation of decomposition of heavy metal azides by pulse radiation. / V.G. Kriger, A.V. Kalenskii. // Russian Journal of Physical Chemistry. - 1996. - T. 15. - № 3. - C. 351-358.

[12] Aluker, E.D. Early Stages of Explosive Decomposition of Energetic Materials, in Focus on Combustion Research, ed. by Sung Z. / E.D. Aluker, B.P. Aduev, Y.A. Zakharov, A.Y. Mitrofanov, A.G. Krechetov // Focus on Combustion Research. / Aluker E.D -New York: Novapublishers, 2006. P. 55.