Combined treatment of energy-saturated materials in external fields

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Abstract. The paper analyses the effect lead and iron ions have on slow and explosive decomposition in crystals of silver azide initiated by a contact electric field, local physical impact and UV-radiation. The reaction of decomposition registered immediately in the process of impact was examined according to gas release. This method provides accuracy of $10^{-12}$ mole. A stop-watch was used to determine time-to-explosion. The outcomes of experiments show that introduction of lead and iron ions into crystals of silver azide deteriorates strength of samples under local physical impact; furthermore, gas release caused by this type of impact stimulates fracture of samples. Experimental data indicate that crystals of silver azide with introduced lead and iron ions tend to decompose more intensively in a contact electric field. As for UV-radiation, it also has a significant decomposing effect on samples with introduced impurity substances, however, no explosion is registered, i.e. a maximal amount of gas is emitted at a certain period of time; afterwards gas release becomes less intensive and stops in approximately 20 minutes after the treatment starts. Any external impact generates misbalanced charge carriers (holes). Holes are localized on cation vacancies associated with generation of reactive centres. The number of reactive centres grows due to the increased concentration of impurity defects and might become critical. Data of experiments suggest that crystals of silver azide with introduced impurities are less stable and chemically inactive in external fields.

1. Introduction
A chemical reaction in crystals of silver azide has been successfully initiated by electric and magnetic fields, different types of radiation, simulating, this way, real and extreme conditions of storage and usage of such high-sensitive materials as azides of heavy metals [1–7]. External energy action initiates in crystals of silver azide the process of decomposition are accompanied by generation of nonequilibrium electron and hole and localized in reactionary regions which formed by regional dislocations in surface region of a crystal on a depth no more than $5 \times 10^{-6}$ m [1, 2].
The objects of the present study are used in small-sized means of initiation. They are used in the production of explosives, industrial cumulative charges, detonating cords, perforating systems, electric detonators used in the oil and gas industry for perforation and injection of wells, as well as in field Geophysics, as sensors of electromagnetic fields.

Authors of this paper have an increased interest to the issue under consideration due to recent developments in the field of physical and chemical processes taking place in azides of heavy metals in external fields. Also, interest in the study of the influence of various types of energy effects on the chemical reaction in other objects does not diminish [4, 8–13]. So, there is an urgent need to address to decomposing ability and stability of silver azide crystals with various concentrations of defects.

This paper attempts to analyse the effect of introduced impurity substances on reactivity of samples, to validate or disprove a model describing decomposition of silver azide crystals based on concentration of impurity and dislocation structure [1]. Analysing data of previous experiments, we found out that dislocation pattern on the surface of crystals is similar to that of intensive gas release, and the reaction of decomposition is initiated in reaction zones formed by fixed dislocations. Prior the reaction of decomposition dimensional change of crystals is registered [1, 2].

The aim of this paper is to explore the influence of introduced iron and lead ions on decomposition rate and stability of crystals of silver azide in external fields, in particular, in conditions of contact electric field, UV-radiation, and local physical impact. Subjects of research relate to high explosives that underlines special importance of clarification of the mechanism of processes solid phase decompositions of heavy metals azides for development of methods of management of their a reactive capacity.

Possibility of modelling of the defective structure of energy-saturated materials will allow controlling their reactivity by directional change of concentration of precisely those defects, on which are most sensitive reactions occurring in these materials after influence of the different factors during storage and transportation.

2. Research Method

We used whisker crystals of silver azide (AgN\textsubscript{3}) grown according to procedure described in [14], average dimensions - 10×0.1×0.03 mm\textsuperscript{3} with a background impurity Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Al\textsuperscript{3+}, Bi\textsuperscript{3+}, Pb\textsuperscript{2+}, Ca\textsuperscript{2+}, Si\textsuperscript{4+}, Ti\textsuperscript{2+}, Mg\textsuperscript{2+} and raised concentration of lead and iron impurity (1 wt.%), as well as with controlled density of edge dislocations for the purpose of research.

The quantitative and qualitative composition of impurity was analysed with the help of atomic emission spectroscopy (atomic emission spectrometer with inductively coupled plasma iCAP 6500). Samples were prepared in plane geometry, which enables registration of a gaseous product emitting in the process of decomposition and control topography of its spreading throughout the sample, as well as check density of dislocations in etching pits [15, 16].

The analysis of reactivity of the crystals carried out various methods (volumetric methods of the analysis, electrometric measurements (Figure 1), researches of explosive sensitivity, etc.).

A contact electric field of 300 kV/m created by power supply sources of direct current initiated slow and explosive decomposition. It is known [1, 2] that the first stage of decomposition of silver azide is the injection of holes through a specially selected contact, while the injection level determines the rate of slow decomposition. Since in our conditions the slow decomposition passes into an explosion, it should be assumed that the delay time of the explosion should depend in a certain way on the level of injection and contact material. As electric contacts we used gallium (contacts put on the most developed side (010)), with a gap between electrodes 1 mm (Figure 2). This is a mode of mono-polar injection of holes [17, 18], which (holes), being in the reaction area, facilitate the chemical reaction [1]. The beginning of injection is associated with the appearance of a super linear section on the volt-ampere curve [17]. Flashing or sound indicated explosion of a sample.
Figure 1. The scheme for electrometric measurements: 1 is the crystal, 2 is the substrate, 3 are the contacts, 4 is the shop of resistance, 5 is the voltmete electrometric, 6 is a potentiometer self-recording, 7 is the switch, 8 is the power supply.

Figure 2. Experimental procedure for registration of external gas release in crystals of silver azide in conditions of external impacts, where a is contact electric field; b are local physical impact, electric field, UV-radiation, 1 is glass carrier, 2 is crystal, 3 are gallium contacts, 4 is tungsten indenter (rounding radius 10 µm, local pressure 5×10^5 N/m²) with a spring of certain deflection rate, 5 are copper electric contacts, 6 is source of UV-radiation; 7 is microscope eye lens.

A structure of dislocation was examined using the method of etching pits [15] (0.1 N sodium thiosulfate solution in water was used as an etching agent). In crystal of silver azide, the transverse size of the etching pits reaches 20 microns, which allows them to be examined using conventional optical microscopy. Traces of individual edge dislocations were measured by optical microscope of the type Biolam providing magnification of 120.

Products of decomposition in anion sub-lattice emitting in reaction of slow decomposition (external gas release) were registered using Hill’s method [19]. Using the Hill method allows us to study not only the kinetics of the accumulation of products in a substance, but also the topochemical features of the decay processes on structural defects of a crystal under energy exposure. Research of kinetic the processes proceeding after power influence in crystals of silver azide, we spented by a technique of “external of gas evolution” [1] which sensitivity makes 10^{-13} mol.

Micro-indenting was used as a source of physic impact. A pressure of indenter providing longer non-failure of a sample was determined experimentally, which consists 5×10^5 N/m².

As a source of ultraviolet we used a mercury-discharge lamp DRSH – 100 (365 nm; intensity of lighting is 1.92×10^{15} quanta/cm²·s).

Measurement of time of a delay of explosion, certainly, cannot quantitatively characterize change of explosive sensitivity as is not physical parameter, and develops of many parameters defined by kinetic of process [4]. In our case, under time of a delay of explosion we understand time of power influence for the sample at whom with reliability of 100 % it is possible to fix the fact of explosion of the sample defined on flash. Complexities are connected with labour input of experiment and the analysis of the received data as the measured size of time of a delay of explosion as have shown experiments, depends on the biography of the sample. Therefore, it is offered to accept for the account as reference - time of a delay of explosion at intensity of a contact electric field 300 kV/m. This intensity of a field corresponds at probability of 50 % to times of a delay of explosion of the order of 6 minutes (see Figure 3). Note that the external gas release after the action of the contact electric field occurs locally in 4–5 reaction regions, which spatially coincide with the locations of dislocations on
the developed crystal surface (010), as shown in the Figure 4. Visual observations showed that during the action of the contact electric field, the number of gas evolution sites and, consequently, the number of reaction zones gradually increases.

Figure 3. Photographs of external gas evolution in a silver azide crystal under the action of a contact electric field

Figure 4. Photographs: a) etching pits and b) external gas emission, after processing the samples with a contact electric field of 300 kV/m

In the study of crystal decomposition, the volume of gas released for different samples may differ significantly. In this regard, it is necessary to study a large number of identical samples. About 10 samples were taken for one point of experimental curves. The data of experiments were processed in Microsoft Excel. Experiments were carried out at ambient temperature.

3. Results and Discussion
This paper reports on decomposition of silver azide crystals with introduced lead and iron impurities under local physical impact, in a contact electric field and UV-radiation.

In the process of local indenting, decomposition of crystals was registered according to gas release. Numerically, the process of decomposition based on gas release is plotted as a function of released gas volume vs. time of indenter action.
The graph (see curve 3 of Figure 5) displays that indenting of samples with background impurities within 6 seconds doesn’t cause any gas release; applying this method in a longer period of time, decomposition is registered; furthermore, fracture of a sample takes place in 8–9 seconds.

Samples with lead impurity fracture in 1.5 seconds; that is 6 times quicker than samples with a background impurity, regarding physical impact it equals to a pressure of around $10^7$ N/m$^2$ applied to samples with a background impurity.

These data suggest that alongside with dislocations of a certain density (see Figure 6) local fracture of a crystal is registered.

![Figure 5. Volume of gas release in crystal of silver azide with impurity of lead (curve 1), iron (curve 2), and a background impurity (curve 3) vs. time of local physical impact $5\times10^5$ N/m$^2$](image1)

![Figure 6. Density of dislocations ($\rho$) in crystals of silver azide with introduced impurities of lead (curve 1), iron (curve 2), and a background impurity (curve 3) vs. time of a local physical impact $5\times10^5$ N/m$^2$](image2)

A previous model describing decomposition in crystals of silver azide involved several processes: shift of dislocations, formation of reaction areas and initiation of gas release, however, results obtained are not fully in line with the model, but still not contradicting.

At the moment of action of the indenter a slight gas release is normally registered close to the indenter position. The position of indenter is easily etched; as a consequence, a quite big etching pit is formed (30 µm). In this case gas release furthers fracture of samples when indenting. Experiments conducted revealed that impurity introduced into crystals of silver azide facilitates chemical reactivity of all faces in crystals. Normally it is associated with UV-radiation in the area of self-absorption (365 nm). In this case regular gas release is registered on all faces of crystals.

Figure 7 displays outcomes of experiments on decomposition of samples with impurities under UV-radiation. Figure 7 demonstrates that the maximal gas release is registered in 6-7 minutes of impact. In 20 minutes, no gas emission is registered. The crystal is covered with a layer of colloid silver, because it decompositions in a cation sub-lattice. Indeed, in solid state chemistry, the reactants of a chemical reaction are electrons and holes. The localization of the hole on the defects is associated with the formation of an anionic radical, which is a reactive particle. Electrons, as reagents, are involved in the formation of metal nuclei, which we observe.

The gas release in samples with introduced iron exceeds that of samples with a background impurity. This is evidenced by the comparison of curves 2 and 3 in Figure 8. In a contact electric field (300 kV/m, gallium – electric contact (see Figure 2a) in the mode of mono-polar injection of holes the most intensive decomposition of samples is registered both in a gap between electrodes, and beyond the contact area of a crystal, this fact is not relevant for samples with a background impurity.

The reaction turns quicker into explosion in samples with introduced impurities. Samples for these experiments were glued to the base, so there is no dimensional change of crystals under the contact electric field, but there is deformation on the bend of a sample before explosion.
Figure 7. External gas release in crystals of silver azide with impurities: iron ions (curve 1); lead ions (curve 2); and a background impurity (curve 3) under UV-radiation.

Figure 8. External gas release caused by contact electric field in crystals of silver azide with a background impurity (curve 1); lead ions (curve 2); iron ions (curve 3).

Note that the transition time of slow decomposition to explosion in silver azide crystals with different impurity contents depends on the shelf life, as shown in Table 1. It is seen that crystals of silver azide with an additionally introduced impurity of iron are more sensitive to the action of an electric field for a long time than samples with a background impurity from Table 1. As for samples with an additional impurity of lead, their storage for more than 1 year is undesirable.

So, samples of silver azide with impurities tend to more intense fracture if exposed to a contact electric field and UV-radiation. A physical impact also deteriorates chemical instability of samples with impurities and makes them more brittle [20]. Authors [1] analyse a slow-to-explosive decomposition in crystals of silver azide with a background impurity. Previous experimental studies indicate that lines of edge dislocations in crystals of silver azide are negatively charged [2, 20].

Table 1. Decomposition of crystals with additionally added impurities depending on the storage time

| Silver azide crystals             | Storage time | The time before the explosion                                      |
|----------------------------------|--------------|-------------------------------------------------------------------|
| with a background impurity       | up to 6 months | 5 – 7 minutes                                                     |
|                                  | 1 year       | 5 – 7 minutes, but the probability of an explosion decreases       |
| with additionally introduced iron impurity | up to 6 months | 3 minutes                                                          |
|                                  | 1 year       | 2 minutes                                                          |
| with an additional impurity of lead introduced | up to 6 months | 3 minutes                                                          |
|                                  | 1 year       | crumbled into dust                                                 |

After introduction of a new dislocation (e.g. scratching), positively charged point defects form a Cottrell atmosphere within a certain (estimated) period of time [1, 2]. As a result, a porous structure – vacancy cluster or reactive zone is formed close to the surface of a crystal. Previous studies have suggested their depth approximately 5 µm [1].

Cation vacancies close to the surface tend to form agglomerations with a positively charged impurity. Therefore, it takes less time for formation of a reactive zone, provided that concentration of the impurity introduced is higher [1–3, 5].

As soon as a reactive zone is formed (an etching pit is formed), a reaction of decomposition can be initiated in it. The dislocation in a crystal is immovable, and positively charged ions of an impurity act as a stopper (in our study crystals are reinforced by introduced impurities of lead and iron).
Decomposition in the anion sub-lattice of azides of heavy metals necessitates holes in reactive zones; they are possible only under the action of electric field [1, 2, 20]. In our study we increase concentration of lead and iron impurities, consequently, samples are more reactive, as demonstrated by the gas release rate under the action of electric field. The rate of gas release in crystals with impurities is significantly higher than in samples with a background impurity.

We note that external gas release in samples with impurity of lead is registered not only in zones of localized (immovable) dislocations. For instance, Figure 7 and Figure 8, in the initial phase of curves plotting external gas release and up to saturation show some gas, and on curves plotting the density of dislocations an increase of density is registered at the same period.

4. Conclusion
The analysis of the results obtained in this work allows us to draw the following conclusions.

1. According to experiments, additionally introduced ions of lead and iron into crystals of silver azide deteriorate strength of samples, and emission of gaseous decomposition products under the physical impact, that facilitates fracture of silver azide crystals.
2. Experiments suggest that crystals of silver azide with introduced impurities of iron and lead tend to decompose more intensively in a contact electric field and in UV-radiation.
3. To sum up, crystals of silver azide with introduced impurities are less stable and chemically inert in external fields.

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