Processing of energy materials in electromagnetic field

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Abstract. This paper presents the research results of complex impact of mechanical stress and electromagnetic field on the defect structure of energy materials. As the object of research quite a typical energy material – silver azide was chosen, being a model in chemistry of solids. According to the experiments co-effect of magnetic field and mechanical stress in silver azide crystals furthers multiplication, stopper breakaway, shift of dislocations, and generation of superlattice dislocations – micro-cracks. A method of mechanical and electric strengthening has been developed and involves changing the density of dislocations in whiskers.

Introduction

The control over physical and mechanical properties of materials by different methods of treatment effecting on their defect structure has been a burning issue so far.

For semiconducting and energy materials this urgency is caused by probable intensifying chemical processes, as well as by improvement of some functional properties, for instance, stability and reactivity.

This paper provides the research results of complex influence of mechanical stress and electromagnetic field on the defect structure of energy materials.

As the object of research quite a typical energy material – silver azide was chosen, being a model in chemistry of solids.

The defect structure of silver azide has been well studied. Silver azide is defect according to Frankel with mainly labial interstitial cations of silver (Ag^+). The surface of silver azide crystals is positively charged, and the surficial zone is enriched by negatively charged cation vacancies (V_k^-). The information on qualitative and quantitative composition of impurities of positive metal ions is available: Cu^{2+}, Fe^{3+}, Al^{3+}, Bi^{3+}, Pb^{2+}, Ca^{2+}, Si^{4+}, Ti^{2+}, Mg^{2+} with concentration $3\cdot10^{-5}\div10^{-4}$ mole percent; edge dislocations have electric charge ($\sim10^{-16}$ C) and magnetic moment (5×10^{-21} $A\cdot m^2$) [1-3].

A decomposition reaction in an anion sub-lattice of silver azide is thought to occur when localizing of two holes on a cation vacancy. The concentration of anion and cation vacancies is determined by impurity concentration in silver azide and is to depend on doubly-charged cations concentration.

Therefore, intensifying mechanical influence is expected while electromagnetic field is effecting on the defect structure, which is of considerable importance for physical and chemical properties of silver azide. The defects are particularly important for forming reaction zones in crystals [3].

Experimental methods

The objects of research are silver azide whiskers (AgN_3), grown according to well-known methods by F.I. Ivanov, the average dimensions are $10\times0.1\times0.03$ mm^3 [4].

For sample preparation optically transparent and perfectly facetted crystals were selected as shown in Fig. 1.

To carry out experiments the samples were prepared in planar geometry which makes it possible to indicate a gaseous product, emitting during decomposition, and record topography of its distribution: both faces of crystals were БФ–6 – glued on mica plate preliminary defatted with alcohol.

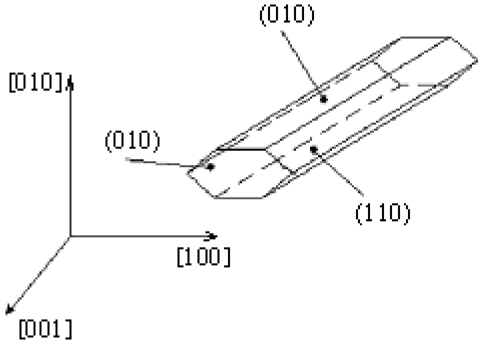
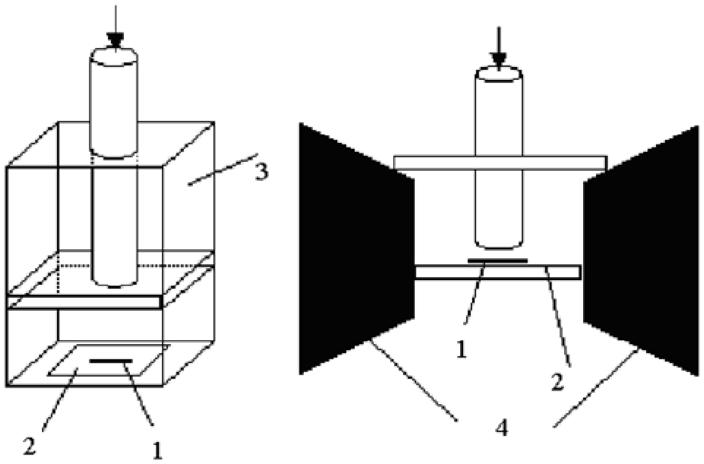


Figure 1. Indices of crystal faces and directions in silver azide whisker.

Mechanical stress in samples was developed by uniaxial compression on the axis [010] in a specially made acrylic resin cell (Fig. 2.a). Samples were stressed in magnetic and electric fields in a non-magnetic cell in the conditions of uniaxial compression generated by constant stress (Fig. 2. b).



a) b)

Figure 2. Plan of experiments: a – mechanically stressed samples; b – mechanically stressed samples in constant magnetic or electric fields: 1 – crystal; 2 – mica plate; 3 – acrylic resin cell; 4 – electromagnet poles or copper electrodes.

To provide bend deformation of a sample a dielectric bar with a conic edged base was put into an inter-electrode space.

Local pressure in both cases was changed within the range $5{\cdot}10^5$ H/m^2 - $5{\cdot}10^7$ H/m^2. Electrodes were energized by a source of direct current (Б5-44, Б 5-50). Electrodes – crystal space was minimal and didn't exceed 50 µm (external voltage decreases completely on the crystal provided that air clearance has such dimensions). Non-contact electric field intensity was 10÷40 W/m, that one of a contact electric field – 30 kW/m (gallium was used as a contact).

Magnetic field was formed by electromagnet (ЭМ-1) with adjustable intensity up to 0.3 T.

Magnetic induction was measured with a magnetic induction indicator Ш1-8 or tesla-meter (sensitivity 10^{-5} T).

A supersonic wave in samples was excited by the method of complex vibrator involving the magnetostrictive converter with the proper frequency 20 kHz. The intensity of exited waves didn't exceed ≈1.5 W/cm^2. The samples were placed on the top of the magnetostrictive converter with the plane (010).

Gaseous products of decomposition were tested volumetrically [3-5]. Over a period of time after energy deposition the sample was placed into a cell with water solution of sodium thiosulfate. Dissolution was observed by a microscope in transmitted red light, and diameter and space coordinates of bubbles of emitted gaseous product were registered.

For dissolving whiskers and further calculation of emitted gas we used a standard cell for measuring optical constants of liquids with the space between walls up to 10^{-3} m. The solvent was held in the horizontally placed cell by surface tension forces. When measuring the volume of gas bubble it was assumed that gas pressure inside the bubble was equal to air pressure.

The volume of gas emitted when crystals dissolving was attributed to face area where gas emitting was observed.

We know that reaction regions in silver azide, i.e. in crystal zone where gaseous products of dissolution emit (Fig. 3), are similar to places of dislocation rising, therefore, it is necessary to reveal them.

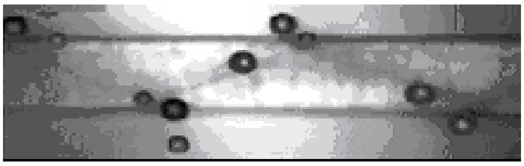


Figure 3. Dislocation structure of silver azide revealed volumetrically.

The dislocation structure was tested by the method of etching pits. Contrast etching pits were formed when etching of crystals AgN_3 in 10 % water solution of sodium thiosulfate. The crystal glued on both faces was put in solution $Na_2S_2O_3$ for 2 – 3 seconds, and then it was rinsed in distilled water or alcohol. This procedure was repeated in order to assure that the density of etching figures (pits) didn't increase, but their dimensions and depth grow slightly, then etching pits can be caused by dislocation rising.

The density of dislocations was determined as relation of the number of etching pits to the area of crystal surface.

For each point of experimental curves at least 10 samples were taken. The results of experiments were processed by computer with the software Microsoft Excel.

Results and Discussion

The effect of different types of stresses (mechanical stress, electric field) on the defect structure (dislocations and impurity) has been already tested in silver azide crystals [1,6,7].

The kinetic dependencies of accumulating dislocations have been obtained for mechanical stress ($5{\cdot}10^5$ - $5{\cdot}10^7$ N/m^2), according to them it has been stated that in 7-9 seconds of exposure the sample loses its mechanical integrity and is subject to brittle fracture.

As for the co-effect of magnetic field (0.3 T) and mechanical stress, the kinetics of accumulating dislocations regarding the time of exposure is a complex dependence, depicted in Fig. 4. In these experiments preliminary deformed samples were used, the input density of edge dislocations was $4\cdot 10^3$ cm^{-2}.

Mechanical stress influencing the crystal equaled to $5\cdot 10^5$ N/m^2 – an optimal value for reliable recording the accumulation of dislocations, provided that mechanical stress exceeds this value the sample is subject to brittle fracture.

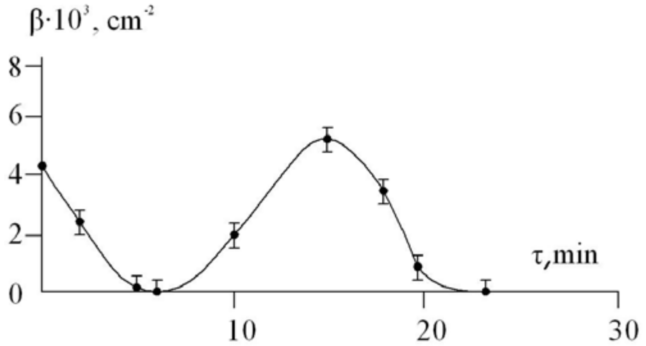


Figure 4. The dependence of dislocations density in silver azide crystals on the time of co-effect of mechanical stress ($5\cdot 10^5$ N/m^2) and magnetic field (0.3 T).

Fig. 4 demonstrates that increasing time of exposure results in a cyclically changing density of dislocations, in 30 minutes of exposure the density of dislocations falls up to 0. However, while dislocations structure in silver azide crystals changes when being influenced mechanically, in magnetic field a slow dissolution is seen: gaseous products – gas bubbles are emitting (Fig. 5, curve 2). If the period of exposure is longer the samples are subject to brittle fracture without explosion. For comparison dissolution in magnetic field (0.3 T) without strength failure is depicted in the same Figure (Fig. 5, curve 1.).

It is worth noting that mechanical stress of samples, placed between the poles of electromagnet, is attended by directed movement of edge dislocations (it is determined according to displacing etching pits).

Let us discuss the obtained results of experiments.

Brittle fracture of samples recorded over a certain period of exposure can probably comprise 2 phases – micro-crack nucleation and its propagation. The cause of micro-crack nucleation is probably development of a super-dislocation which is formed as the result of integrating dislocations near the stopper. Meanwhile, the pressure of stopped dislocations exceeds several times the pressure of their free movement. This rising pressure can improve the strength of a crystal and at the stopper place there is a crack occures being the sink for newly forming dislocations. Any accumulation of point defects can be considered as a stopper.

In magnetic field one observe the decreasing energy of dislocations – paramegnetic impurity centers interaction, it facilitates the separation of dislocation from other obstakles. In non-magnetic materials dislocations move in constant magnetic field and without external effect due to the slow relaxation of dislocation structure in the field of internal stresses.

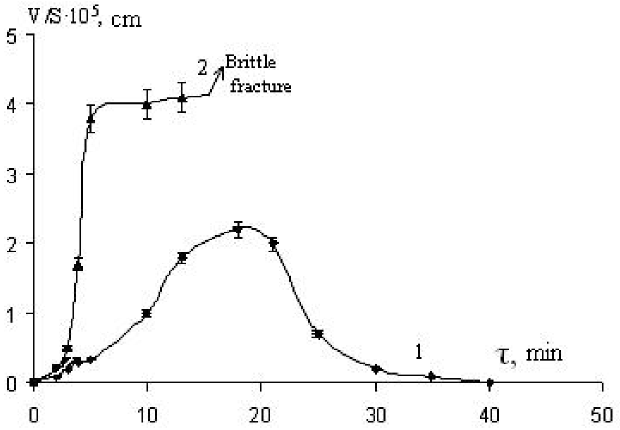


Figure 5. The dependence of retained gas in silver azide crystals on the time of exposure: 1 – magnetic field (0.3 T); 2 – co-effect of magnetic field and mechanical stress.

The external force (mechanical) influencing on the sample simultaneously with magnetic field accelerates the relaxation of dislocation structure that increases the path of dislocations when the sample is effected both by magnetic field and mechanical stress.

As we observe directed movement of negatively charged edge dislocations, possible in electric field only, an attempt was made to find a non-contact electric field, which provides no movement of dislocations recorded as changing etching pits. This external non-contact electric field, which compensates the developed by magnetic field internal one, was found, it doesn't contradict to the earlier discovered magnetoelectric effect in silver azide crystals [4].

Similar cyclic change in dislocations density is also observed when ultrasonic processing. In terms of specific character of the experiment initially dislocation-free crystals were used (Fig. 6). In this case the time of transformation of dislocation structure is far shorter, i. d. over 5 minutes of exposure 2 maximums of dislocations density are recorded, then the sample fails.

After samples are processed ultrasonically and the reaction of decomposition by a contact electric field is initiated (30 kW/m), it was recorded that in the zone of minimal dislocations the samples exploded after 3 minutes of being energized and in the zone of maximal dislocations – after 9 minutes. It demonstrates that the reaction of slow decomposition dominates principally over the critical fracture in conditions of significant concentration of dislocations in the sample.

Strengthening near-surface layer of the sample after ultrasonic processing is considered to be one of the reasons of this effect.

As the number of dislocation increases a longer effect of electric field up to sample explosion is required, whereas the samples expose earlier in conditions of decreasing density of dislocations.

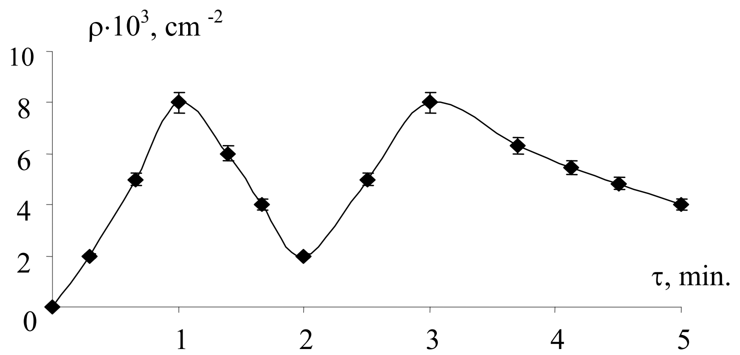


Figure 6. The dependence of dislocations density on the time of ultrasonic processing in silver azide crystals.

Various results can be probably explained by the fact that the increasing number of dislocations causes the dispersion of charge carriers on them and complicates the approach of these carriers to reaction zones. Meanwhile, slow decomposition of basic charge carriers – reagents of chemical reaction – is recorded and followed by explosion when the concentration of pits gets critical. As the number of dislocations decreases an inverse process takes place.

Conclusions

In conclusion it is to say that ultrasonic processing and mechanical stress of silver azide crystals causes generation and a wide-range change in the density of dislocations, constant magnetic field effect facilitates the separation of dislocations from accumulated defects, and electric field (internal field of polarization or the non-contact internal one) is the reason of dislocations output.

A co-effect of magnetic field and mechanical stress in silver azide crystals furthers generation, stopper breakaway, shift of dislocations, and generation of superlattice dislocations.

Therefore, a method of mechanical and electric strengthening is proposed and based on changing dislocations in whiskers.

References

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