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Simulation of the Reactivity of Energy Materials in the Technosphere

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Abstract. methods are proposed for regulating the reactivity of energetic materials that circulate in the technosphere and are not rarely the cause of fires and explosions, both during storage and during transportation. As man-made factors that influence the stability of these materials magnetic and temperature fields and mechanical effects were used. The magnetic field (in the range from 0.01 T to 0.3 T) was used to intensify chemical processes, both at the stage of crystal growth (by the example of silver azide) and together with mechanical action (from 10^5 Pa to 10^7 Pa) in the finished crystals. The action of the magnetic field and mechanical stress leads to the stimulation of microplasticity and macroplasticity processes, which are accompanied by a slow decomposition of the samples and subsequent destruction. It was established experimentally that a slight change in storage temperature, as compared to room temperature, accelerates the aging process of samples (range of positive temperatures up to + 30°C), or leads to loss of plasticity (range of negative temperatures down to –20°C) resulting in loss of performance and in loss of useful properties of energy materials.

1. Introduction

Controlling of physical and chemical properties of materials via processing them with different physical fields which affect the defect structure has long been a question of great interest. For instance, in energy-related materials it is associated with possible intensification of chemical processes which change their reactive capacity and stability [1, 2].

This work reports the results of research concerned with the combined effect of mechanical stresses and a magnetic field on processes relevant for the change in the defect structure of energy-related materials. As an object of research a typical energy-related material – silver azide was selected, since it is a model object in chemistry of solids. Silver azide is defective according to Frencel and has mainly non-stationary interstitial cations of silver (Ag^+) [3]. The surface of silver azide crystals has a positive charge, and a near-surface region include negatively-charged cation vacancies (V_k^-). The qualitative and quantitative composition of impurities is also known: Cu^{2+}, Fe^{3+}, Al^{3+}, Bi^{3+}, Pb^{2+}, Ca^{2+}, Si^{4+}, Ti^{2+}, Mg^{2+}, mole percentage concentration $3{\cdot}10^{-5}{\div}10^{-4}$ [1].

Under mechanical stresses, in case of whiskers, it is micro-indention, the density of edge dislocations increases. Taking into consideration that lines of edge dislocations in silver azide crystals are partially charged (10^{-16} C), have a magnetic moment of $5{\cdot}10^{-21}$ $A{\cdot}m^2$, and influence the plasticity, it might be suggested that a magnetic field has an effect on the processes initiated by mechanical action [2]. Furthermore, edge dislocations are also centers initiating reactions of decomposition, therefore, action of a magnetic field might change both the character of plastic flow of crystals and their reactive capacity. This work aims at research into the influence of a magnetic field (in the range from 0.1 T to 0.3 T) on deformation of mechanically stressed silver azide whiskers. Moreover, studies were done and regularities were found out how temperature of specimens storing (from -20^{0}C to 30^{0}C) affects their deformation out of the elasticity limits.

Magnetic treatment changes some physical properties of systems (electrical conductivity, density, surface tension, dielectric permeability, magnetic susceptibility, and viscosity) [4]. The magnetic field has certain advantages as compared to other physical ways of impact, including low power, selectivity and simplicity of implementation and safety of application [5, 6].

The magnetic field (in the range from 0.01 T to 0.09 T) was used to intensify chemical processes at the stage of crystal growth. It is known that in the process of crystallization of silver azide from aqueous solutions of sodium azide and silver nitrate, a number of forces act of the magnetic field side (the magnetic component of the Lorentz force, the internal friction force, torque, gravity) that change the behavior of the system. The effectiveness of these forces is possible if they act on particles or aggregates that have a charge, a constant or induced magnetic moment [7]. Therefore, it can be assumed that by adding an admixture with certain magnetic properties, it is possible to control the crystallization process in a magnetic field. Thus, the study of the effect of an impurity with various magnetic properties on the crystallization of silver azide in a magnetic field is of both scientific and practical interest. As an additional impurity, ions of diamagnetic lead and ferromagnetic iron were used.

2. Experimental technique

The object of research is silver azide whiskers (AgN_3); mean sizes of them are: length 10 mm; width 0.1 mm; thickness 0.03 mm. Silver azide whiskers are formed by the method of slow evaporation of the solvent from a solution containing a weakly concentrated aqueous solution of ammonia and silver azide (obtained by exchange reaction with rapid stirring of 0.2 N potassium azide solution and 0.2 N silver nitrate solution). In most cases, they are optically transparent crystals with a perfect faceting, as one can see in Figure 1.

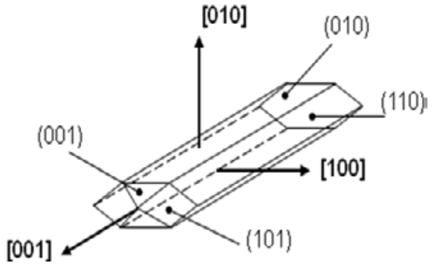

Figure 1. Crystallographic faces and directions in a silver azide whisker.

Observations of crystal growth during crystallization showed that silver azide whiskers grow from the top along the [001].

Specimens for carrying out experiments were prepared in planar geometry which makes it possible to register a gaseous product emitting in the process of decomposition and observe topography of its dissemination: using glue BF-6 which is chemically inert to silver azide, both ends of crystals were attached to a mica substrate defatted preliminary with ethyl alcohol.

Method of etching pits was used to study the dislocation structure [8, 9]. Contrast etching pits resulted from etching crystals of silver azide in 10% water solution of sodium thiosulfate. The density of dislocations was calculated as a ratio of a number of etching pits to the crystal surface area. Microscope of the type Biolam providing magnification of 120 was used to select specimens and measure their dimensions.

A magnetic field was created using an electromagnet (EM-1) with adjustable intensity up to 1 T. Magnetic induction was measured using a simple magnetometer (sensitivity 10^{-5} T).

The reactivity (in this case – degradability) of silver azide crystals under consideration was analyzed in terms of Hill's procedure [10]: specially processed silver azide crystals were dissolved in water 0.1 N sodium thiosulfate ($Na_2S_2O_3$) solution. The process of dissolution was observed by microscope in the transmitted red light. Here the diameter and spatial coordinates of emitting gaseous nitrogen were measured. The amount of emitted gas was calculated according to measured diameters of molecular nitrogen bubbles on condition of 15 parallel tests.

To obtain a qualitative picture of the process of formation of crystallization centers and their growth in a magnetic field, the micro crystallization method was used. The method was as follows: a drop of a 0.2 N solution of double-recrystallized potassium azide was placed on a glass slide and the same amount of silver salt solution was added, or the azide was obtained by rapidly mixing two drops of these solutions. To study the effect of impurities on the crystallization of silver azide in a magnetic field, ions of diamagnetic lead and ferromagnetic iron were used. By crystallization solution a solution of ferric chloride or a solution of lead nitrate was added (in an amount of 1 wt. % of silver azide content). Silver azide crystallization was monitored by microscope Biolam with magnification 120, built-in between poles of permanent magnets.

Qualitative and quantitative analysis of the content of impurities in silver azide was performed on an emission spectrometer with inductively coupled plasma iCAP 6500 DUO on an analytical line of 228.616 nm in the radial mode of observation of plasma.

Microindentation (tungsten indenter producing local pressure in the range from 10^5 Pa to 10^7 Pa) was used as a source of mechanical stress. Bending deformation of a specimen placed between the poles of an electromagnet was performed via putting a dielectric rod with a cone-shaped base. The local pressure in both cases was measured in the range from 10^5 Pa to 10^7 Pa.

At least 10 samples were examined for each point of experimental curves. The data of experiments were processed in Microsoft Excel.

3. Results and Discussion

According to the results of observations, the dependences of the time of formation of the crystal structures of silver azide of minimum sizes visible in an optical microscope (which is not less than 3 microns) on the induction of a magnetic field were constructed (see Figure 2).

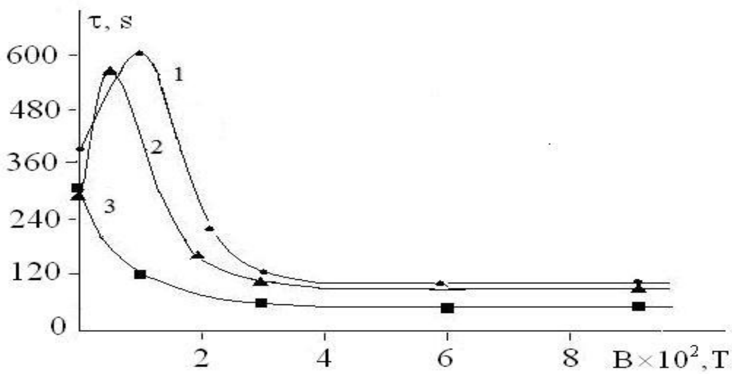

Figure 2. Dependence of the time of formation of microcrystal of silver azide (1 - with background impurity, 2 - with additionally introduced impurity of lead ions, 3 - with additionally introduced impurity of iron ions) on the induction of a magnetic field.

It can be seen from the graph in Figure 2 that a magnetic field of up to 0.01 T slows down the appearance of microcrystal compared to crystallization without applying a field (this point corresponds to 300 s), then the crystallization process is accelerated, and after 0.03 T does not depend on magnetic induction fields. These results concern the crystallization of silver azide with a background impurity (see curve 1 of Figure 2) and with an additionally added impurity of diamagnetic lead ions (see curve 2 of Figure 2). Note that the additionally introduced lead impurity has little effect on the crystallization process (see curve 2 of Figure 2), while the admixture of ferromagnetic iron accelerates the formation of crystalline structures (see curve 3 of Figure 2). Thus, the admixture of ferromagnetic iron, which has a large magnetic moment, is easily oriented along the magnetic induction lines, and coagulation can occur as a result of magnetic interaction, after which crystallization centers appear for substances dissolved in the liquid.

Figure 3 shows the dependence of the size of the crystal structures of silver azide, visible in a microscope, on the time of crystallization in a magnetic field of 0.09 T.

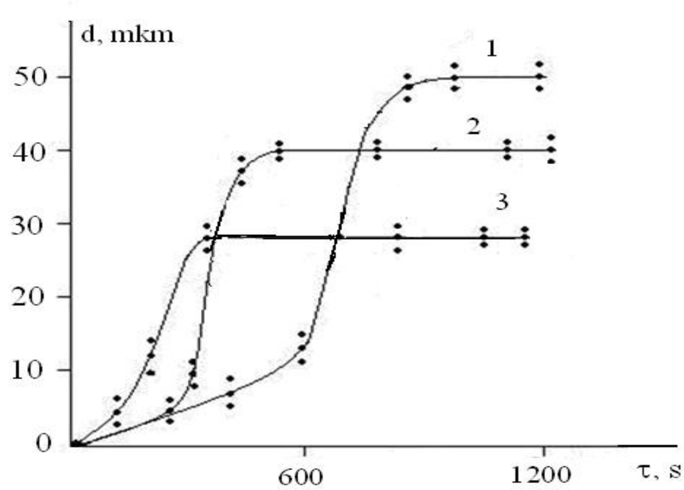

Figure 3. The dependence of the size of the crystal structures of silver azide (1 - with a background impurity; 2 – with an admixture of lead; 3 - with an admixture of iron) on of the time of crystallization in a magnetic field 0.09 T.

From figure 3 it can be seen that the smallest crystals of silver azide in a magnetic field are obtained with the introduction of an impurity. It should be noted that the addition of an admixture of iron ions to a greater extent influences the size of the crystals.

Based on studies of the crystallization of silver azide in a magnetic field, we can draw the following conclusions. The influence of the magnetic field on the crystallization process is complex: the effect of increasing the number of crystallization centres and the effect of accelerating the formation of crystalline structures occurs in a narrow region of magnetic induction. These effects cannot be associated only with the orientational action relative to the force lines of particles with a charge or magnetic moment (paramagnetic impurities).

Consequently, it is necessary to take into account other possible causes, which at first glance have a debatable character, for example: the formation of water associates (clusters) that can memorize a magnetic field; the destruction of the hydration environment of ions, leading to an increase in particle mobility.

The influence of mechanical stresses on the density of dislocations in silver azide crystals was studied. Kinetic relations concerning the accumulation of dislocations under mechanical stresses (from 10^5 Pa to 10^7 Pa) were obtained; from these relations it is apparent that mechanical strength of a specimen stressed for 7-9 seconds deteriorates and it is subjected to brittle destruction. When microindentation, emission of a gaseous product from the outer surface of silver azide whiskers (including the case of a specimen being under a layer of Vaseline oil) was observed, or there were gas bubbles when crystals were dissolved in 0.1 N $Na_2S_2O_3$ after mechanical stresses. In both cases the volume of a gaseous product is determined and divided by the face area of crystal where emission of a gaseous product from the surface was seen [2].

It is established that the density of dislocations correlates with intensity of gas emission: the number of etching pits is similar to the number of gas emission centres working synchronously.

Mechanical stress of approximately 10^7 Pa causing brittle destruction was determined theoretically and experimentally. Under combined action of mechanical stresses and magnetic field the kinetics of accumulation of dislocations gets more complicated depending on the action time of mechanical stress (see Figure 4). Specimens with initial density of edge dislocations of around $4{\cdot}10^3$ cm^{-2} were used in these experiments.

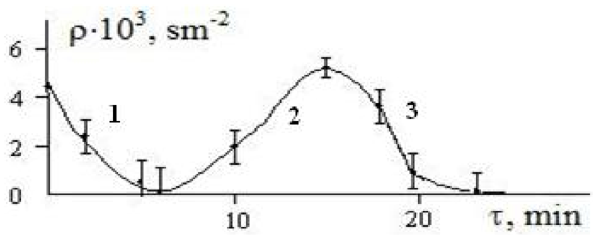

Figure 4. Dependence of the density of dislocations in silver azide whiskers on time of action mechanical stress (10^5 Pa) and magnetic field (0.3 T).

It is shown that a constant magnetic field furthers the shift of edge dislocations in silver azide crystals by microindentation.

Consider the processes occurring in crystals of silver azide during of microindentation. First, it is movement of free dislocations brought in by the indenter (see part 1 of curve Figure 4). Afterwards, accumulation of dislocations is observed («forest» of dislocations), which is possible due to slowing down by the Cottrell atmosphere consisting of impurity atoms (see part 2 of curve Figure 4). In this case, the speed of dislocation movement is limited by the migration speed of atmosphere atoms. Dislocations are stopped for a short time resulting in creation of centers where a reaction of dislocation starts and gas emission is observed. These dislocations don't move anywhere in the crystal. Further impact leads to disruption of dislocations and, accordingly, to a decrease in the density of dislocations (see part 3 of curve Figure 4).

A long mechanical stress (more 30 minutes) is associated with a maximal increase in the density of dislocations (more $5.5{\cdot}10^3$ cm^{-2}) and a maximal change in linear dimensions of a specimen – $(2.5\pm0.5){\cdot}10^{-2}$, finally, a micro-crack occurs and grows in the indenter zone, and a specimen splits into two parts; in case of a maximal stress the whole specimen is subjected to brittle destruction.

If a magnetic field is applied, dislocations brought in by the indenter, are moving almost constantly (it was demonstrated by etching pits appearing at a maximal density of dislocations).

It can be assumed that a magnetic field facilitates detaching of dislocations from a paramagnetic impurity; afterwards they moved in a particular direction, the most probable cause of which is magneto-electric effect [2].

When microindenting in a magnetic field, first, gaseous products of decomposition are emitted due to the accumulation of edge dislocations in a specimen of silver azide, and a hollow appears in the indenter place, leading to a fracture in some time (see Figure 5, curve 2). In a magnetic field without a mechanical stress there is no destruction of crystal observed, the time kept the same (see Figure 5, curve 1) [2, 3]. The amount of emitted gas was calculated as the ratio of the measured volume (V, cm^3) of the bubbles of molecular nitrogen released during the decomposition of crystals to the surface area of the crystal (S, cm^2).

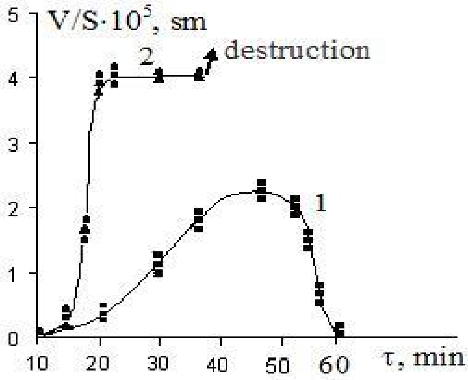

Figure 5. Dependence of the amount of emitted gas in silver azide whiskers on time of action: 1 – magnetic field (0.3 T); 2 – mechanical stress (10^5 Pa) and magnetic field (0.3 T).

As revealed in experiments, silver azide crystals subjected to preliminary mechanical stresses and kept for a long time (at least 30 days) at a temperature above 30^{0}C, blacken intensively (their surface is covered with colloid silver). When dissolving, they destruct without any additional action, and gaseous products are emitted. In this case, a slight increase in the temperature of storing in comparison with the room temperature is the reason of ageing of specimens, leading, as a consequence, to worsening of useful properties and operational characteristics of materials.

The influence of low temperatures (range of negative temperatures down to –20°C) should be noted: specimens become brittle, and additional investigations are hardly possible. That is, the effect of negative temperatures on whiskers is similar to the action of mechanical stress (leads to a decrease in their tensile strength).

4. Conclusions

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

1. The complex effect of the magnetic field on the crystallization rate and morphology of crystals was revealed in the experiments. The magnetic field of up to 0.01 T slows down the appearance of microcrystal compared to crystallization without applying a field, then the crystallization process is accelerated, and after 0.03 T does not depend on magnetic induction fields. The possibility of obtaining samples of different dispersion is shown. The efficiency of introducing ferromagnetic impurity of iron ions during the crystallization of silver azide in a magnetic field has been experimentally shown: ferromagnetic impurity of iron ions affect the rate of nucleation of crystallization centers and the growth rate of crystals (the admixture of ferromagnetic iron of accelerates formation of crystalline structures).

2. The action of the magnetic field and mechanical stress leads to the stimulation of microplasticity and macroplasticity processes, which are accompanied by a slow decomposition of the samples and subsequent destruction.

3. The action of the magnetic field and mechanical stress leads to the stimulation of microplasticity and macroplasticity processes, which are accompanied by a slow decomposition of the samples and subsequent destruction. It was established experimentally that a slight increase in storage temperature (range of positive temperatures up to + 30°C), as compared to room temperature, accelerates the aging process of samples (which leads to loss of strength and stability of energy materials) while heat treatment at negative temperatures (range of negative temperatures down to –20°C) leads to

microcracks and brittle fracture of samples, that resulting in loss of performance and in loss of useful properties of energy materials.

The results of this study allow us to simulate the conditions for obtaining, storing and transporting energy materials, allowing to regulate their level of stability and reactivity, which will significantly reduce the risk of using energy-saturated materials in various areas of the technosphere.

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