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REACTIVITY AND DISLOCATION STRUCTURE OF SILVER- AND LEAD-AZIDE CRYSTALS EXPOSED TO A VARIABLE MAGNETIC FIELD

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The physical-chemical processes caused by a variable magnetic field of strength 0.1 T and frequency 10 kHz in nonmagnetic silver- and lead-azide crystals are studied. The experiment shows slow decomposition accompanied with plastic deformation both under the action of the variable magnetic field and in post processes. The dependence of relative volume of gas released during post processes on the magnetic-field frequency is examined.

INTRODUCTION

Heavy-metal azides (HMA) are typical materials undergoing irreversible changes under the action of external factors of various nature to yield inert end products (molecular nitrogen and metal) and release much energy. When affected by external perturbation, the system can go to both a steady state with the constant decomposition rate in the cation and anion sublattices and to a self-accelerating regime resulting in an explosive decomposition of a sample.

Earlier, both the effect of transverse electric fields of varying strength and the effect of their combination with a magnetic field on solid-phase decomposition of HMA crystals were studied experimentally [1, 2]. Recently, it is found that the decomposition can be initiated by a constant magnetic field [3, 4]. The role of external energy action in HMA crystals consists in unbending the bands in the crystal subsurface region and, thereby, removing the barrier for the charge-carriers (holes) to go to the reaction zone. The reaction zone in the HMA crystals is made of edge dislocations and point defects [4].

These materials were chosen for the following reasons: first, they are used as model objects in solid chemistry, and second, they possess unique properties: point and linear defects as well as their surfaces are electrically charged, edge-dislocation lines have magnetic moments, and certain impurity defects are paramagnetic.

The purpose of the work is to study physical-chemical properties caused by a variable magnetic field (VMF) of magnetic induction up to 0.1 T and frequency up to 10 kHz in HMA crystals.

EXPERIMENTAL TECHNIQUE

The experiment was performed as follows. A variable magnetic field was produced in two ways.

1) A planar sample was placed in a specially manufactured cell rotated between the electromagnet poles. This allowed us to examine physical-chemical processes caused by the variable magnetic field of frequency up to 200 Hz;

2) the cell with the sample was put in a gap made in the magnetic circuit of a generator consisting of two windings. An alternating voltage of a specified frequency was applied to the finishes of the primary winding. In addition, a low active resistor was included in the primary-winding circuit. The voltage drop on the resistor was proportional to the current in the winding and was controlled using an oscilloscope connected to the resistance. This allowed us to generate a variable magnetic field of induction 0.1 T and frequency 0.2–10 kHz. The secondary winding also had an active resistor causing the strength of the variable magnetic field in the gap to be unaffected (at a specified value) in the frequency range 0.2–10 kHz.

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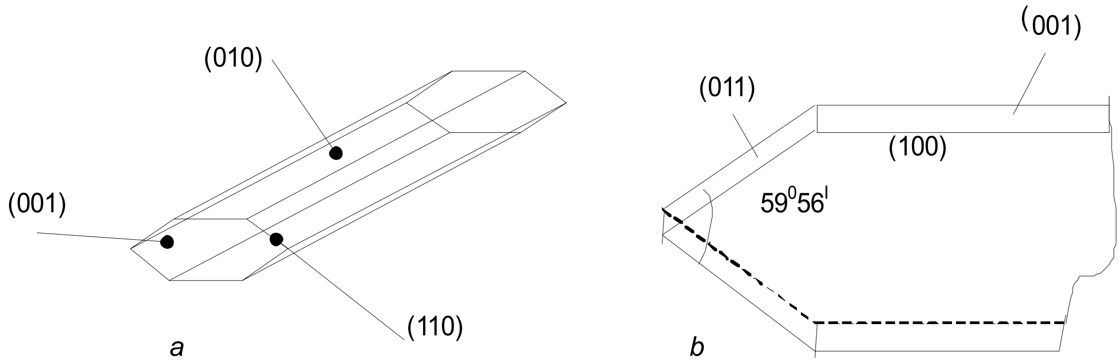

Fig. 1. Crystallographic indices of crystal faces: silver azide (*a*) and lead azide (*b*).

Use was made of planar silver- and lead-azide crystal samples of size 10×0.1×0.03 mm and 6×0.1×0.03 mm, respectively, grown using the methods described in [5]. Crystallographic indices of silver- and lead-azide crystal faces are shown in Fig. 1.

In order to examine the dislocation structure, use was made of the etch pitting technique [6]. A 10% water solution of sodium thiosulphate and ammonium acetate were used as etchants for silver- and lead azides, respectively. The samples were immersed for 2–3 s and then washed either in distilled water or alcohol.

The decomposition products in the anion sublattice were analyzed by the Hill method, whose advantage is high sensitivity up to 10^{-13} mol. The principle of the method is that the HMA crystals upon the corresponding exposure were placed into a dish with a solvent (an 0.38% sodium-thiosulphate solution was used for silver azide, and ammonium acetate solution – for lead azide). The process was observed using a microscope with a micrometer scale being in transmitted red light. In so doing, the diameter and space coordinates of released gas-phase nitrogen were measured [7].

A relative volume of the released nitrogen was calculated from the ratio of the volume observed in solution of the gas V to the crystal surface area S, from which the gas release occurred.

RESULTS AND DISCUSSION

The following experiments were performed. Azide crystals were glued by both ends to a mica substrate (in so doing, as is known from [2], 4–5 dislocations are induced on the (010) face, which is supported by pre-etching), exposed to a variable magnetic field of induction 0.1 T in the frequency range 0.2–10 kHz, and then the dislocation structure was examined using the method of selective etching.

No etch pits were found on the (010) face. Thus, we can conclude that dislocations are eliminated from the (010) face under the action of a VMF. It takes about few seconds depending on the strength and frequency of the magnetic field applied.

Since it is well-known that reaction zones in silver-azide crystals spatially coincide with areas of dislocation outcrop [1], the following experiment was performed: the sample was first exposed to a high-frequency variable magnetic field, the (010) face was exposed to UV radiation, and then the sample was examined using the Hill technique – no gas release was found at the working face. It was shown in [8] that the dislocations in silver azide possess magnetic moments, therefore the magnetic field abstracts the dislocations from the stoppers, the Cottrell cloud consisting of positive metal ions Ag^{+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Bi^{3+}, Pb^{2+}, Ca^{2+} of concentration $3\cdot10^{-5}$–10^{-4} mol % being considered as such a stopper. Vortex electrical fields or intrinsic stress fields of dislocations facilitate motion of the dislocations. In lead-azide crystals, however, where there is a similar number of impurities but the dislocations have no magnetic moments, the effect was not observed.

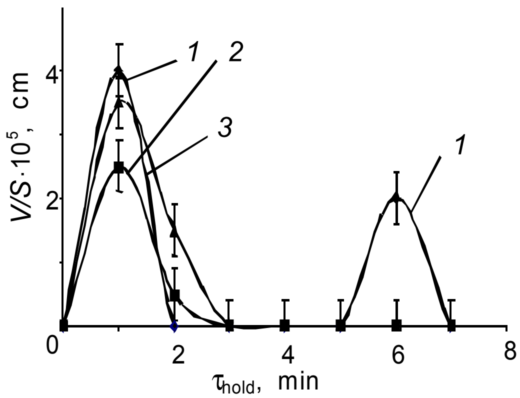

Fig. 2

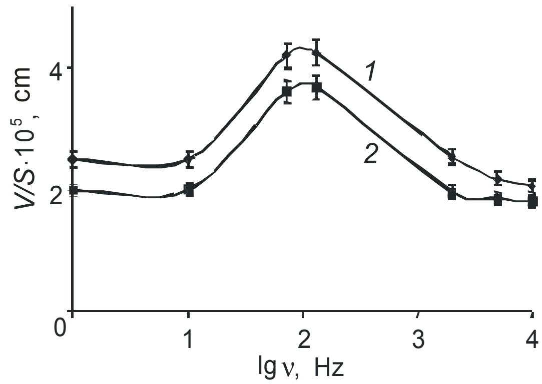

Fig. 3

Fig. 2. The quantity of released gas versus holding time in silver- and lead-azide crystals upon exposure to a VMF of varying frequency: ν = 10–200 Hz (in silver-azide crystals) (*1*), ν = 0.2–10 kHz (in silver-azide crystals) (*2*), and ν = 0.01–10 kHz (in lead-azide crystals) (*3*).

Fig. 3. The quantity of released gas versus VMF frequency: (H = 0.1 T) of the crystals: lead azide (*1*) and silver azide (*2*).

It was mentioned earlier that in silver azide, the dislocations are eliminated from the (010) face but remain on the (110) face. Hence, there are reaction zones, and a vortex electrical field facilitates the motion of holes to these regions, where multiplication of the latter occurs, that is, we believe, that slow decomposition brought about by the VMF is localized in the reaction zone. It was experimentally found that decomposition post processes occur in silver-azide crystals from the (110) face and in lead-azide ones from the (010) and (011) faces in 20 and 25 min, respectively, upon exposure to a VMF of induction 0.1 T and frequency 10–10^4 Hz. These are of decaying character (Fig. 2).

At the frequency of VMF 10–200 Hz, gas release is observed in silver-azide crystals for up to 7 min after exposure. On increase in the frequency of VMF, one can observe a decrease in the quantity of released gas, and the duration of post processes decreases down to 2 min. It should be noted that the magnitude of induction of the magnetic field affects the quantity of released gas but slightly.

In lead-azide crystals, gas release is slightly lower than that in silver-azide crystals, and the duration of post processes amounts to 3 min after exposure to the VMF. In so doing, the quantity of released gas from the (010) and (011) faces was observed to be 1 : 1 in lead-azide crystals, which is likely to be due to the fact that the subsurface face-zone bend is of insignificant difference and, hence, the quantity of released gas is the same.

It is seen in Fig. 2, the gas-release maximum is observed in 1 min after exposure to the VMF in all the cases. Thus, it allows us to determine the optimal holding time upon exposure to study the dependence of a relative volume of released gas on the variable-field frequency (Fig. 3).

The processes occurring in the variable magnetic field up to frequency of 10 Hz are similar to those in a constant magnetic field. Thus, it can be referred to as low-variable. With further increase in the frequency of VMF up to 50 Hz, one can observe a sharp increase in gas release. This is due to the fact that the magnitude of the vortex electrical field is increased, which facilitates unbending of subsurface zones, that is, going of holes to the reaction region. However, a decrease in the volume of released gas is observed with further increase in frequency, since the induced currents (vortex currents) interact with the magnetic field. As a result, there is a force affecting the motion of a charged particle. According to the Lenz principle, the magnetic field of these currents is directed opposite the magnetization vector of the material itself,

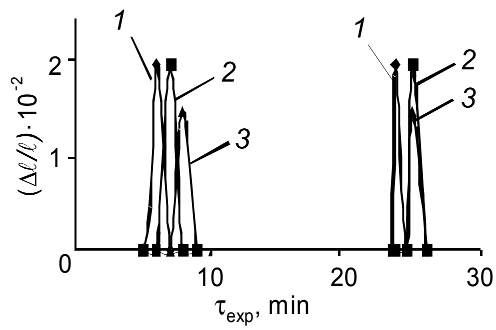

Fig. 4. Relative change in silver-azide crystal size versus exposure time in magnetic field: B = 0.1 T, ν = 0.01–0.9 kHz (*1*), B = 0.1 T, ν = 1–5 kHz (*2*), and B = 0.1 T, ν = 5–10 kHz (*3*).

a change in which produces these currents. Therefore, an electromagnetic field of high frequency in the material is forced upwards to the sample surface because of electromagnetic induction.

It should also be noted that the quantity of released gas-phase product is independent of the VMF strength.

A giant change in the linear size along the [100] axis was found experimentally in silver-azide crystals, which is $(\Delta\ell/\ell)_{100} = (2\pm0.5)\cdot10^{-2}$ for frequency 0.01–5 kHz and $(\Delta\ell/\ell)_{100} = (1.5\pm0.5)\cdot10^{-2}$ for frequency 5–10 kHz (Fig. 4).

It is worth noting that the observed deformation is reversible and can be found only during exposure in contrast to the case of a constant magnetic field, where relaxation time to the previous size is 40 hs [4].

Similar experiments were also performed using lead-azide crystals, however, no deformation of the samples under the VMF was found. Thus, we suggest that the cation sublattice directly affects deformation of the crystals under study. To support this assertion, the silver chloride and silver bromide crystals were examined. The samples showed changes in size along the [100] axis matching those in the silver-azise crystals by an order of magnitude.

The change in size comes before and further correlates with the decomposition process of silver azide in time. Moreover, as the frequency of variable magnetic field is increased, the exposure time necessary to achieve maximum changes in size also increases. Thus, there is a certain relationship between deformation and decomposition processes. We assume that the action of VMF upon initially dislocation-free crystals is accompanied by the occurrence of an internal elastic field resulting in the generation of dislocations which provide for the chemical reaction running.

CONCLUSION

Based on the experimental data obtained one can draw the following conclusions: a variable magnetic field of strength about 0.1 T and frequency up to 10 kHz significantly affects the dislocation structure in silver-azide crystals and initiates a decomposition reaction on the anion sublattice in silver- and lead-azide crystals. In so doing, reversible plastic deformation can be observed, which comes before and further correlates with the decomposition process. The results of the investigations are of practical importance, since during production, storage, transport, and usage, HMAs can get under the action of magnetic fields of technogenic origin and undergo various types of deformation which can result in changes in their performance.

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