JOURNAL OF SOLID STATE CHEMISTRY **26**, 215–221 (1978)

Photothermochemical Process in Ammonium Perchlorate Crystals: II

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Received January 20, 1978

The influence of phase transition (PT) on the process of thermal development of a latent image arising after X-ray and uv irradiation of ammonium perchlorate (AP) crystals has been studied. Despite the production of a large number of new dislocations accompanying PT, it essentially does not influence the thermal development: The developed image does not smear at PT, remaining as clear as before it. By comparing mirror-symmetric surfaces of cleavage planes of AP crystals, it has been shown that at doses of X-ray and uv irradiation sufficient for obtaining an image, no production of new dislocations was observed in AP crystals. It is suggested that latent image arises due to formation during irradiation of chlorine oxidic products of radiolysis: ClO_3, ClO_2, and ClO as well as the corresponding ions ClO^-, ClO_2^-, and ClO_3^-, i.e., initiators of AP low-temperature decomposition.

Introduction

In our previous work (*1*) it was already mentioned that no discussion can be found in the literature concerning the mechanism of preliminary uv irradiation influence on ammonium perchlorate (AP) thermolysis. As to the mechanism of influence of preliminary radiolysis on AP low-temperature decomposition (LTD), two alternative approaches are discussed. According to one of them (*2, 3*) the main factor determing the preliminary radiolysis influence on LTD is a chemical one—formation and accumulation of chlorine oxidic products of radiolysis: ions of ClO^-, ClO_2^-, and ClO_3^- being, according to (*4*), the initiators of nucleation during LTD of AP. Another explanation of the effect suggested by Herley *et al.* (*5–7*) is more "physical": In the process of radiolysis dislocations are produced and accumulated in AP crystals which serve, according to (*8–13*), as LTD centers. However, in (*2–7*) only qualitative correlations were used to prove the validity of these mechanisms, the considered problem being disputable even for the influence of preliminary radiolysis, which has been studied rather thoroughly. It concerns photolysis all the more. In this work an attempt has been made to analyze the dislocation mechanism of irradiation influence on AP thermolysis using as an example uv and in part X-ray irradiation. In accordance with our previous work (*1*) we assume the mechanism of influence of X-ray and hard light irradiation to be identical.

Experimental

Optically transparent AP single crystals were grown out of aqueous solutions by using slow cooling. For irradiation, an uv lamp PRK-2 and a Mars-2 X-ray radiation source with a copper cathode at the accelerating voltage (18 kV) were used. Irradiation was always performed at room temperature. Investigation of the latent image development was carried out by using a MIN-8 optical

0022–4596/78/0263–0215$02.00/0
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microscope with polarized light. The furnace temperature during AP LTD was maintained with an accuracy of ±0.5°C. Crystal etching was done using *n*-butyl alcohol according to the techniques described in (*14*). Etching pits were observed by an "Interfaco" interference microscope (Karl Zeiss Jena).

Results

As was shown in (*1*), during uv irradiation of a transparent AP monocrystal through a stencil the hidden image is memorized in it. It can be made visible (on the upper and lower surfaces) if a crystal is carefully heated at the temperatures corresponding to LTD. According to the mechanism presented in (*4*) this effect can be explained by formation and accumulation of chlorine oxidic products of AP photolysis; however, the dislocation mechanism cannot be a priori rejected, because in principle it can also contribute to the process of thermal development of latent photoimage. In this connection, a study of the influence of newly induced dislocations on the latent image obtained during uv irradiation seems extremely interesting.

An increase in the dislocation concentration can be achieved by crystal deformation, for example, by applying external mechanical load (*15*). More convenient, experimentally, is generation of new dislocations by a phase transition (PT) from the orthorhombic to cubic modification which takes place in AP crystals in the temperature interval 238 to 240°C (*16–18*). The data of (*11*) as well as direct observations show that during PT very high tensions can arise in AP crystals, sometimes leading to crystal cracking. However, cracking can be avoided if PT is performed carefully enough.

Figure 1 shows a microphotograph of an AP crystal undergoing PT. The picture was taken in polarized light with crossed polaroids.

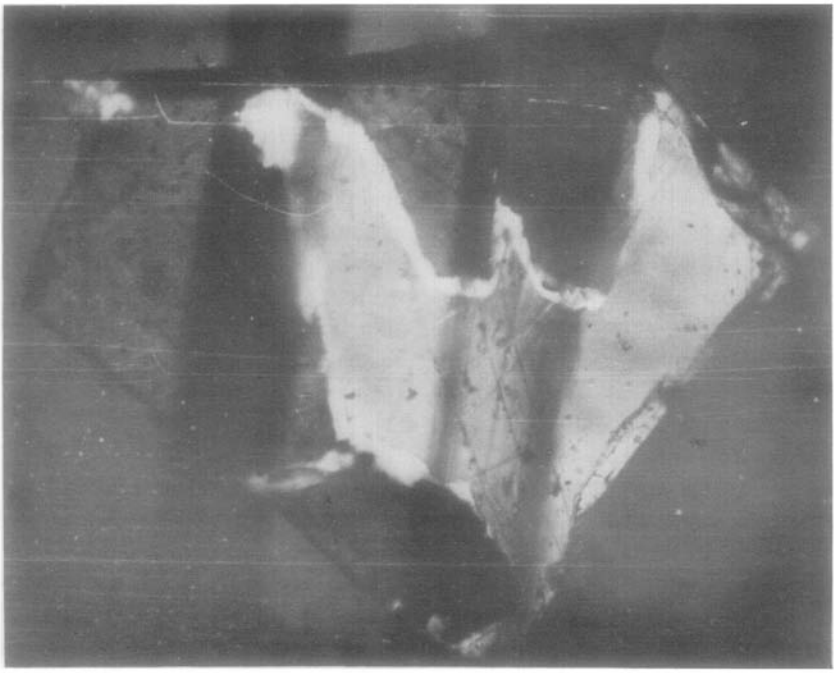

FIG. 1. Microphotograph of PT on an AP crystal in polarized light with crossed polaroids. The light region is the rhombic phase; dark is cubic. The bright edges on the phase boundary are the fields of mechanical tensions in the regions of rhombic phase. ×50.

As only a rhombic phase turns a polarization plane, it can be readily seen in the picture. A produced cubic (isotropic) phase looks dark under these conditions. As seen from the photograph a new crystalline modification appears via formation and growth of nuclei of a new phase. (Do not confuse with LTD nuclei!) A light rim near the phase boundary in the region of rhombic modification is due to the additional turn of the polarization plane owing to mechanical tensions connected with the inconsistency of crystal lattices of two contacting phases. At 238 to 239°C PT can last up to an hour. By appropriately controlling the furnace temperature one can fix any phase relation in a crystal for a long time, e.g., that shown in Fig. 1. On the contrary, PT can be quickly completed, the crystal remaining transparent, i.e., noncracked and not covered with LTD nuclei. Then thermal development of an image in the cubic phase can be observed. Figure 2 presents a stencil photograph and its image developed on the rhombic face, i.e., the face (001) of the rhombic modification, while in Fig. 3 a photograph is shown for the image obtained on that same face by thermal development of AP in the cubic modification. It can easily be seen that PT insignificantly influences the clearness of the obtained image. It can be noted that instead of the expected images of squares the rhombic images are developed in the AP crystals of cubic modification, although in both cases the stencil has square cells. The values of the angles in the rhombi vary for different crystals and depend on the perfection of the crystal in cubic modification, which in turn is partially determined by the perfection of the crystal in rhombic modification and the smoothness of the PT. It is noteworthy that the image obtained on the (110) face, i.e., a square face of AP, presents squares both for rhombic and cubic modifications.

In the cases described above, a latent image was obtained by uv irradiation of AP. The same results have been obtained by replacing

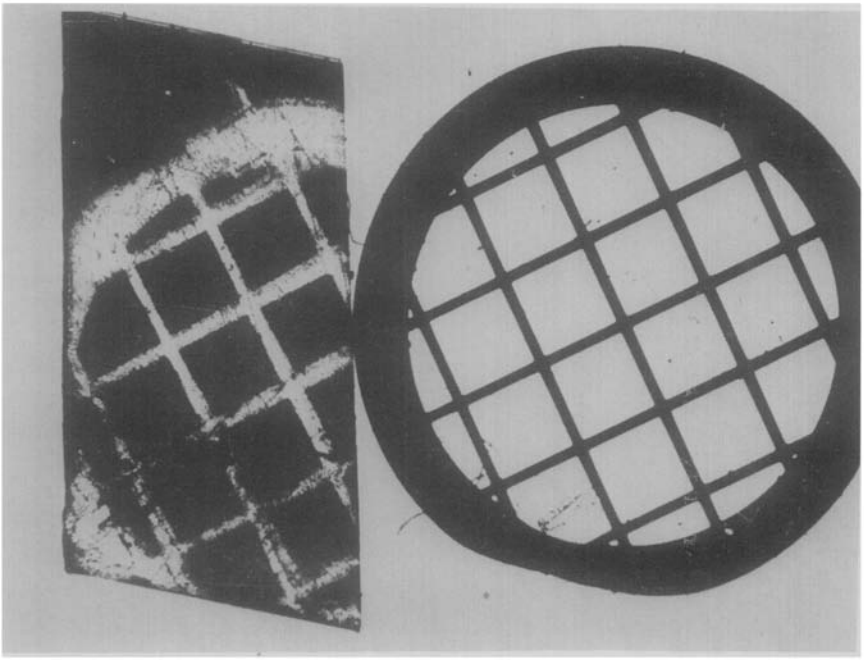

FIG. 2. Thermally developed image of a stencil on AP monocrystal. Development was performed in the rhombic phase on a face (001). At the right is a stencil picture. ×40.

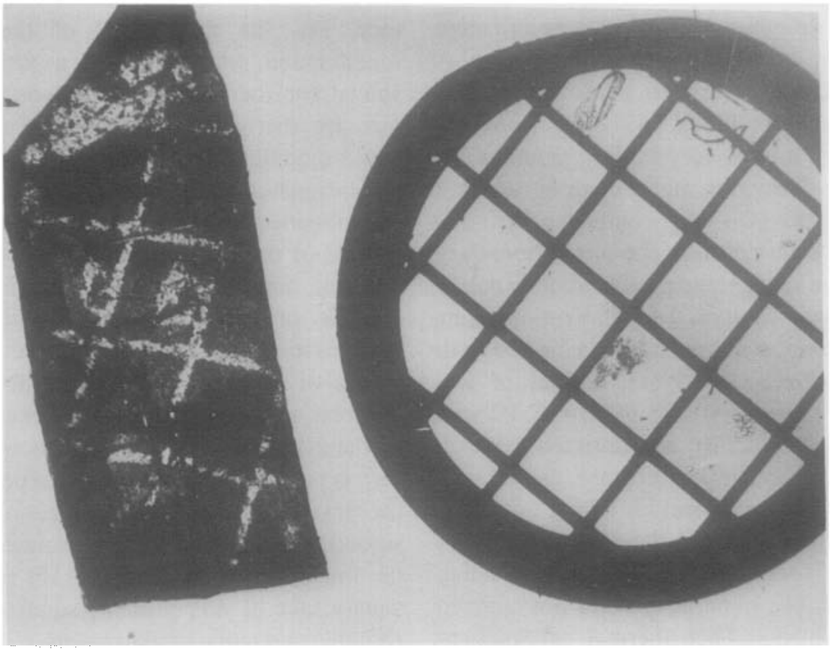

FIG. 3. Thermal development of a latent image of a stencil in AP cubic phase on a face (001) at $T = 245\,^{\circ}\mathrm{C}$. ×40.

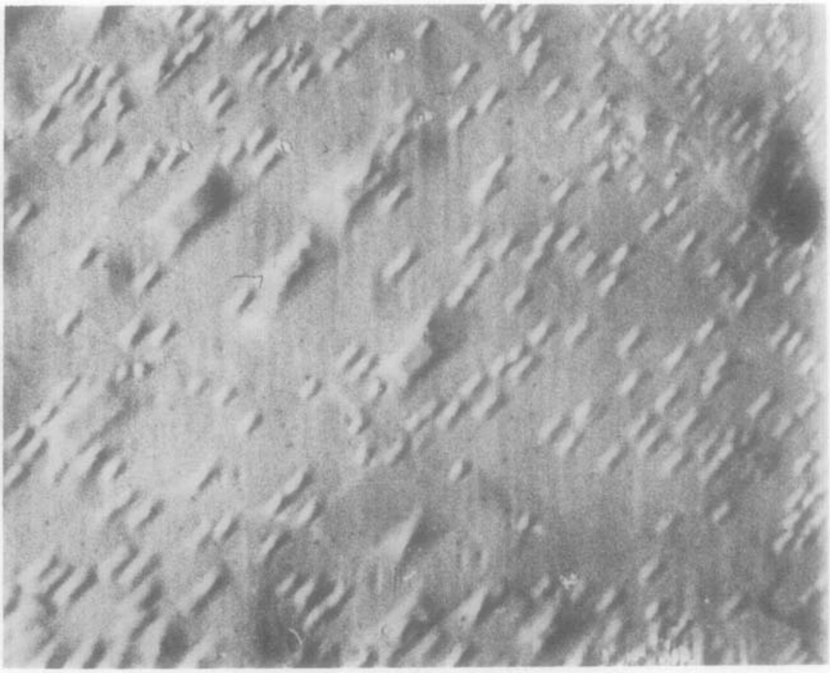

FIG. 4. New dislocations (small etching pits) produced in AP rhombic phase before a front of a growing nucleus of cubic phase. ×120.

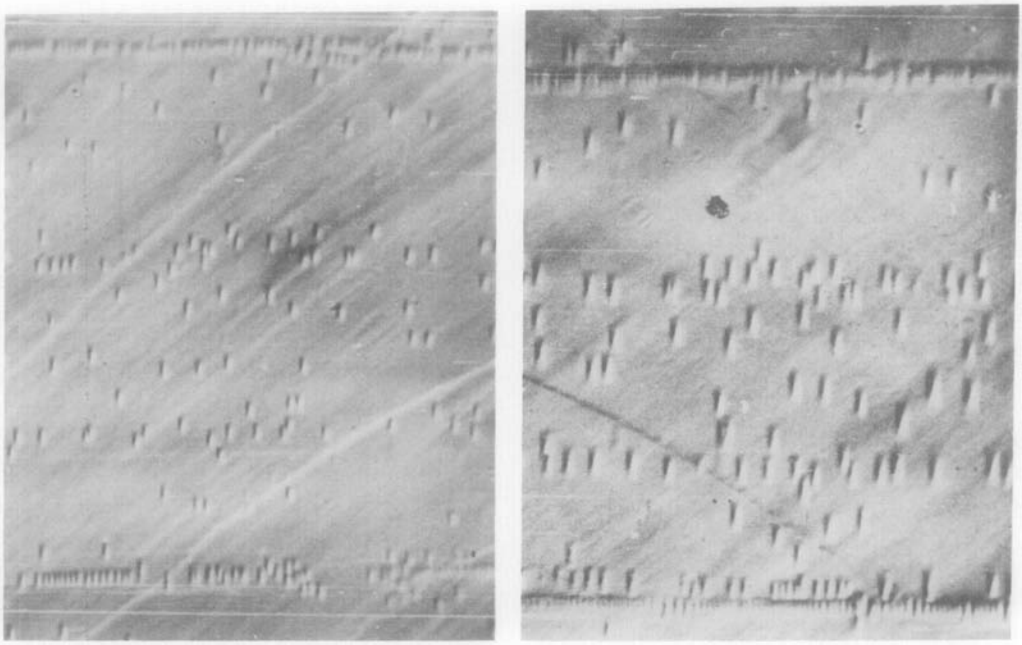

FIG. 5. Mirror-symmetric surfaces of cleavage planes of an AP crystal. The surface shown at the right was uv-irradiated for 0.5 hr before etching. × 120.

the uv irradiation with X-ray at doses from 10^2 to 10^3 rad.

The question arises about the character of PT influence on the dislocation structure of AP crystals. Cracking of crystals means that substantial tensions exist during PT; hence, one can expect that under these conditions a number of new dislocations may be formed. Figure 4 shows a microphotograph of the (001) face of the AP crystal after partial PT and cooling to room temperature. The etching pattern implies that besides old dislocations (large etching pits) a large number of new dislocations (small etching pits) arise in the crystal region not transformed into cubic modification.

On the other hand, it is interesting to analyze the irradiation influence on the dislocation concentration. The most direct experimental way of investigating this consists of comparing the dislocation patterns on mirror-symmetric surfaces of cleavage planes of a monocrystal, one of the surfaces of which was exposed to uv illumination. Figure 5 presents microphotographs of the single-crystal mirror planes obtained in such a manner. The right-hand part corresponds to the crystal uv-illuminated for 30 min before etching. It can easily be seen that illumination did not substantially influence the dislocation concentration. One should remember that a latent photoimage arises at uv irradiation doses an order of magnitude lower than those for a cleaved part of crystal depicted in the right-hand side of Fig. 5.

In the case of X-ray irradiation, according to (*19*), the dislocation picture can be changed by using doses of only $\sim 10^5$ rad. In this case also the latent image arises at considerably smaller (by 3 orders of magnitude) irradiation doses, when no substantial variation of the dislocation concentration occurs.

Discussion

We believe that the experimental data presented allow one to exclude the dislocation mechanism of latent image formation in AP crystals. In fact, in accordance with this mechanism it should be expected that in an irradiated AP the following relation must hold for the dislocation concentration:

$$n_0 \ll n_{\mathrm{irr}}, \tag{1}$$

where n_0 is the initial dislocation concentration and n_{irr} is the concentration of dislocations formed during irradiation. However, as seen from Fig. 5, at doses sufficient for obtaining latent images the inverse relation is valid:

$$n_0 \gg n_{\mathrm{irr}}. \tag{2}$$

On the contrary, if new dislocations with a concentration n_{ind} are induced in the crystal containing the latent image already so that

$$n_{\mathrm{ind}} \gg n_{\mathrm{irr}}, \tag{3}$$

the image would not be developed, i.e., would be disguised by new dislocations. The experimental data, as seen from Fig. 4, taking into account Eq. (2), show that after PT, Eq. (3) is held in the crystal; however, the image clearness changes slightly

One may think that the dislocation mechanism can be saved by stating that only some dislocations with chemical peculiarities are meant, rather than all of them. Two objections arise. First, such a mechanism is new, i.e., neither "physical" nor "chemical," but physical–chemical, the third mentioned in this work. Second, even in this form it seems not to be valid, taking into consideration Eq. (2) and the unusual contrast of the image (see Fig. 2) not correlating with the concentration of dislocations in AP. This allows one to eliminate the "physical" mechanism of latent image formation in irradiated AP crystals.

The considerations presented seem to be valid in a more general case—influence of preliminary radiolysis on LTD—as radiolysis, in accordance with the data mentioned, differs only quantitatively from uv irradiation.

Finally, the results presented make necessary a more critical estimation of the dislocation mechanism of nucleation during AP LTD, which is the most popular today (*8–14*). As seen from Figs. 2 through 5, a factor exists in AP which determines nucleation and is much more powerful than dislocations. As mentioned above, this factor—chlorine oxidic products of photolysis and a $\mathrm{ClO_3^-}$ ion—is among them. The role of small impurities of $\mathrm{ClO_3^-}$ ion in LTD is well known (*3, 4, 20–22*). This impurity is technological in nature and it is extremly difficult to remove it (*23*). Besides that, according to numerous data in the literature, no attempt has ever been made to protect AP from the bright daylight, sometimes containing a considerable component of the uv band. One may think that for "complete" purification from chlorine oxidic impurities ($[\mathrm{ClO_3^-}] \leqslant 10^{-5}$% mol) AP that is initially "chemically pure" must be recrystallized five times in darkness or in light which is not actinic for AP. As the majority of LTD investigators did not perform such purification, one can suppose that in all cases they deal with contaminated AP.

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