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QUANTITATIVE STUDIES ON RADIATION INDUCED DISLOCATIONS
AND THE DECOMPOSITION KINETICS OF AMMONIUM PERCHLORATE*

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ABSTRACT

Ammonium perchlorate crystals exposed to gamma rays or x-ray irradiation exhibit etch pit movement and greatly increased etch pit concentrations. Few dislocations are induced below 10^5 rad, between 10^5 and 10^6 rad the concentration increases linearly, and above 10^6 rad the concentration is too large to determine accurately. These results suggest an explanation for the increased thermal decomposition rate and shortened induction period exhibited by crystals exposed to radiation prior to decomposition. Namely, since dislocations become decomposition nuclei, the accelerated decomposition rates result from the additional dislocations, i.e. nuclei, introduced during irradiation. Apparently trapped gaseous decomposition products, e.g. in voids, exert sufficient stress to generate dislocations by well known mechanisms.

INTRODUCTION

A recent note described observations indicating that dislocations are both generated and displaced when ammonium perchlorate single crystals are exposed to radiation (1). That note, and this paper, are part of a series of publications describing the thermal, radiolytic, and chemical decomposition of ammonium perchlorate and its relation to the defect and dislocation structure of the crystal lattice. The initial investigation in the series demonstrated that exposure to radiation prior to thermal decomposition shortened the induction period and markedly increased the acceleratory period decomposition rate (2,3).

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Fig. 1. Electron microscope picture of a typical etch pit formed on the 210 (m) face of an ammonium perchlorate crystal by etching with n-butanol for 5 seconds.

In terms of the Avrami-Erofeyev kinetics (4), the radiation induced effects can be attributed to an increase in the nucleation rate, the number of decomposition nuclei, or to a combination of these possibilities (5). Subsequent work established that the first stage of both chemical etching and thermal decomposition occurred where dislocations emerged from the crystal surface (6,7). Recently it was shown that the initial radiolytic decomposition occurs at dislocations and along slip systems (9). Thus, apparently all of the decomposition processes are intimately related to the dislocation related properties. Additional evidence for this point of view is described below. More specifically, this paper will present quantitative data on radiation induced etch pit displacement and generation and indicate how this information leads to an additional understanding of decomposition processes in both irradiated and unirradiated ammonium perchlorate single crystals.

EXPERIMENTAL

All measurements were made on single crystals grown by carefully cooling a seeded, well stirred, saturated aqueous solution between 35 and 30°C. Crystals approximately 3 X 3 X 1 cm were obtained which were readily cleaved along the 210 (m) and 001 (c) faces. Water-clear segments, free of all visible imperfections, approximately 4 X 4 X 1 mm were used for etch pit counting and movement studies. Well defined rectangular etch pits approximately 8 X 2 μ m, e.g. Fig. 1, were obtained by etching the m face with dry n-butanol at room temperature.

To demonstrate radiation induced etch pit generation and displacement the following procedure was used. First, pristine crystals were cleaved into roughly equal thickness halves along the 210 plane. Second, one half was exposed to the desired radiation, in air and in the dark. Third, both surfaces exposed by cleaving were etched as soon as possible after irradiation. Finally, photographs of corresponding areas of both cleavage faces were obtained with a high

magnification metallograph. To ensure that suitable statistics were obtained, etch pit counts were made on at least four, non-overlapping, corresponding areas approximately 0.6×0.75 mm on each pair. The corresponding areas on separate halves, e.g. Fig. 2, were readily and accurately ascertained from the cleavage steps. Occasionally both negative, i.e. transparent, and positive prints of corresponding areas were prepared. By superimposing such prints one could easily determine which pits appeared in both surfaces and/or had moved.

Fig. 2. A demonstration of radiation-induced etch pit, i.e. dislocation, motion in ammonium perchlorate. Shown are the two surfaces formed by cleaving a 210 (m) plane. Side (a) was not irradiated, but side (b) was exposed to a 10^4 rad gamma-ray dose immediately prior to simultaneously etching both sides. A set of dislocations which was displaced by the irradiation is labeled "M" and "S" identifies a set which remained stationary. The movement of the displaced set is considerably greater than ordinarily occurring when the crystals are cleaved but not irradiated.

ETCH PIT MEASUREMENTS

Etch Pit Properties

A typical ammonium perchlorate m face etch pit is shown in Fig. 1. The longest sides are parallel to the 001 direction and are steeply sloped. The other sides are considerably less steep and contain at least 40 clearly defined steps. A Normarski interferometer picture of a typical pit taken with 600 nm light, is shown in Fig. 3. From 50 pits it was determined that the average pit depth is 1500 ± 25 μ m and that each step was approximately 37 μ m thick. Since these pits occur

on a cleavage face, the steps are parallel to cleavage planes. From an examination of the crystal structure, it is apparent that each step usually corresponds to 4 layers of possible cleavage planes.

Fig. 3. Interference microscope picture, taken with 600 nm light, of a typical etch pit on the 210 (m) face of ammonium perchlorate.

Radiation Induced Etch Pit Generation

To obtain quantitative data on etch pit generation and motion it obviously is necessary to make measurements on pairs of etched but unirradiated crystals, e.g. Fig. 4. In general, after cleaving the number of etch pits on corresponding surfaces does not differ by a statistically significant amount. However, cleaving does introduce some etch pit motion and this is described in a separate section.

Fig. 4. A demonstration of radiation-induced etch pit, i.e. dislocation, generation in ammonium perchlorate. Shown are the two surfaces formed by cleaving along a 210 (m) plane. Side (a) was not irradiated, but side (b) was exposed to a 2.5×10^5 rad gamma-ray dose immediately prior to simultaneously etching both sides.

When crystals are exposed to gamma-ray doses of 10^5 rad or greater the etch pit count clearly increases. This is demonstrated in Fig. 2 which shows a crystal face exposed to 2.5×10^5 rad and the opposite (unirradiated) face. Doses below 10^5 rad do not introduce statistically significant numbers of additional etch pits. On crystals exposed to more than 10^6 rad the pit concentration is too large to measure with reasonable accuracy; the pits overlap extensively and some areas have decomposed to the extent that individual pits cannot be discerned. Etch pit counts made on crystals exposed to doses below 10^6 rad are plotted in Fig. 5. It appears that the pit concentration increases linearly in this region. The significance of this conclusion is discussed below.

Radiation Induced Etch Pit Motion

Pairs of ammonium perchlorate crystals which have been cleaved and etched but not irradiated exhibit relatively small etch pit motion. Similar effects are well known in alkali halides and are attributed to the release of strains present prior to cleaving and/or strains introduced during cleaving. In contrast, when ammonium perchlorate is irradiated prior to etching appreciable etch-pit motion is observed. This is exemplified by Fig. 2 which shows etch-pit motion in a crystal subjected to a dose of 10^4 rad. A typical set of dislocations which has remained stationary is labeled "S" and the letter "M" identifies pits in one of the sets which have moved. Usually, in both irradiated and unirradiated crystals, only a small fraction of the pits are observed to move. Often the displaced pits appear to move in groups.

Fig. 5. Radiation induced etch pit formation in ammonium perchlorate. The pairs of points, at various doses, were obtained from the two surfaces formed by cleaving. One side was irradiated, and the other side was not, prior to etching.

Fig. 6. Radiation induced etch pit movement in ammonium perchlorate. Only pits which moved have been included.

Almost all of the movement is along the [001] direction but occasionally movement is observed in the [125] and [243] directions. All three directions are appropriate for dislocation motion; in accord with previous work (7,8).

Both the number of dislocations effected and the observed displacements are greater in samples exposed to radiation in comparison with crystals subjected only to cleaving. In crystals subjected to doses of 0, 10^4 and 10^5 rad equal areas contain 736, 709 and 1003 pits respectively, of which 110, 190 and 65 moved. The last figure is unreliable inasmuch as the pit density is so high it is difficult to determine which pits have moved. Furthermore, the extent of dislocation motion is related to the dose. This is shown in Fig. 6 which includes data only for dislocations which have moved. Clearly, as the dose increases the distribution widens and the average displacement increases. The average movement is 4, 15.8 and 17.6 microns for doses of 0, 10^4 , and 10^5 rad, respectively.

APPLICATION TO THE AVRAMI-EROFYEV DECOMPOSITION KINETICS

The etch pit concentration vs. dose data, described above, can be used to obtain additional understanding about the thermal decomposition processes in both unirradiated and irradiated ammonium perchlorate. Previously it was shown that thermal decomposition data could be used to determine one constant and another relation between constants, in the Avrami-Erofeyev kinetics for thermal decomposition, which varied continuously with increasing dose (5). Namely, k_1 the nuclei formation rate, and $C^* = (\text{const})N_0k_2^3 = (\text{const.}) \times (\text{number of nuclei}) \times (\text{nuclei growth rate})^3$. Furthermore, both k_1 and C^* were determined for various doses applied prior to thermal decomposition. The data described above, especially Fig. 5, suggests that the increased thermal decomposition rate observed in pre-irradiated samples is, to

Fig. 7. The ratios $k_1/(\text{pit density})$ and $C^*/(\text{pit density})$ vs. gamma-ray dose. As explained in the text, these ratios should be independent of dose if the thermal decomposition rate is due to the introduction of dislocations, i.e. decomposition nuclei, during irradiation.

a large extent, attributable to the introduction of dislocations during irradiation which, in turn, become decomposition nuclei. In terms of the Avrami-Erofeyev kinetics this radiation effect would appear as an increase in the number of decomposition nuclei. If this conjecture is valid plots of $k_1/(\text{etch pit density})$ and/or $C^*/(\text{etch pit density})$ vs. dose should be independent of dose. Such plots, prepared from the data in (5) and Fig. 5, are shown in Fig. 7. Obviously, the plotted points show deviations from the expected constant values. However, considering the errors in the data, this analysis provides relatively strong support for the conclusion that all, or a large part, of the radiation induced acceleration of the thermal decomposition in

ammonium perchlorate can be attributed to the introduction of dislocations during irradiation.

Additional support for this conclusion follows from a comparison of the etch pit vs. dose data with one of the principal conclusions of a previous study on the shortening of the thermal decomposition induction period in crystals exposed to radiation (10). It was concluded that the induction period vs. dose data could be explained if the radiation related effect was a linear function of the dose and if the subsequent induction period thermal decomposition processes followed an exponential dependence on heating time. Furthermore, it was suggested that one of the more probable explanations for the radiation shortened induction period was a linear increase in decomposition sites during irradiation. At the very least, the data in Fig. 7 can be regarded as an independent justification for concluding that the etch pit concentration, i.e. decomposition sites, increases linearly with applied dose and that this increase in nuclei concentration accounts for all, or a large part, of the increased rate of decomposition in irradiated ammonium perchlorate.

Fig. 8. An example of radiation induced strain in ammonium perchlorate. The upper surface, a 210 (m) face, was exposed to 4.7×10^5 rad of 50 kV x rays. The x rays penetrate part way into the crystal producing decomposition, i.e. strain, only along the upper surface.

A MECHANISM FOR RADIATION INDUCED DISLOCATION GENERATION

Even though the available information is meager, it is possible to propose a reasonable, albeit speculative, mechanism to explain the formation of dislocations in ammonium perchlorate crystals exposed to sufficiently large doses of radiation. To begin, when ammonium perchlorate crystals are exposed to gamma-ray doses of 10^7 rad or more and then cleaved a large number of voids between 0.1 and 10 microns are observed (9). At doses of 10^6 rad or less some precursor of the voids must be present, e.g. clusters of vacancies, i.e. tiny voids too small to observe, growth of radiation induced defects such as ClO_2^- radicals, etc. Since it is now fairly well established that radiation induced decomposition on the crystal surface occurs at dislocations, it is reasonable to surmise that internal decomposition occurs along dislocations (especially small loops), dislocation intersections, pinning points, and at larger defects such as grain boundaries, etc. No matter how nucleated, once the internal decomposition has proceeded to the point where gaseous decomposition products are formed, each void will exert a distending strain on the lattice. When

the stress is sufficiently large the well known mechanism for stress induced dislocation generation, e.g. Frank-Reed sources, etc., can operate. This last stage would occur when the dose levels reach roughly 10^4 rad, the minimum dose needed to produce observable radiation induced etch pits.

Support for the ideas described in the preceding paragraph, especially the build-up of strain and/or stress during irradiation, can be demonstrated in a novel fashion. When a $10 \times 5 \times 1$ mm ammonium perchlorate crystal is irradiated, with a dose of 4.7×10^5 rad of 50 kV x rays, normal to a large side, (e.g. an m face) pronounced convex curvature is observed. An example is shown in Fig. 8. The soft 50 kV x rays do not penetrate very far into the crystal and the radiation induced decomposition and accompanying stress are largely confined to a thin layer adjacent to the irradiated surface. The stress required to produce the observed curvature is quite sufficient to produce copious dislocation, i.e. etch pit, concentrations. In fact, the strain exhibited by the crystal pictured in Fig. 8 is between 5 and 15 percent. In alkali halides such strains produce very large etch pit concentrations.

SUMMARY

When ammonium perchlorate crystals are exposed to gamma-ray radiation dislocations, i.e. etch pits on the 210 or m surface, are moved or displaced and, for doses in excess of 10^5 rad the dislocation concentration increases with dose. Some of the observed dislocations move when the crystals are cleaved. However, the average dislocation motion in irradiated crystals is appreciably greater than that introduced by cleaving.

Recently completed work has shown that thermal and radiolytic decomposition initiates at dislocations. Details of the etch pit topography have now been determined. Their average depth is $1500 \mu\text{m}$ and each contains approximately 40 terraces. The average height, on an atomic scale, of each terrace is four cleavage planes.

Earlier work had shown that the thermal decomposition induction period was shortened and the acceleratory period decomposition rate was increased by exposing the crystals to irradiation prior to decomposition. Also, these effects could be described, in terms of the Avrami-Erofeyev equation for thermal decomposition, by one constant and a separate combination of constants which increased monotonically as the decomposition dose increased. A separate theoretical study on the shortening of the thermal decomposition induction period indicated that the observed effects could be explained if the concentration of decomposition nuclei increased linearly during irradiation. The present study showed that the concentration of etch pits increases linearly in the dose range 10^5 to 10^6 rad. All of these observations suggest that all, or nearly all, of the radiation induced changes in the thermal decomposition kinetics can be explained if it is assumed that radiation introduces dislocations which function as decomposition nuclei. In terms of the kinetics this effect would appear as an increase in the number of nuclei which is consistent with the results derived from the observed pit density vs. dose plots. Furthermore,

it has been observed that heavily irradiated crystals contain numerous small voids which are presumably filled with decomposition gases that could exert appreciable stress on the lattice. Once a sufficient stress level is attained dislocations would be generated by well known stress and/or strain related mechanisms. The formation of stress levels sufficient to produce strains well in excess of 5 percent was demonstrated by irradiating one surface of an ammonium perchlorate crystal with soft x rays. This arrangement restricted the decomposition to a thin layer near the irradiated surface and, as expected, the crystal developed pronounced curvature. In conclusion, it can be stated that all, or nearly all, of the radiation induced changes in the thermal decomposition kinetics can be attributed to radiation induced dislocations which function as decomposition nuclei.

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