Microscopic Observation of X-ray and γ-ray Induced Decomposition of Ammonium Perchlorate Crystals*

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The x-ray and γ-ray induced decomposition of ammonium perchlorate was studied by optical, transmission, and scanning electron microscopy. This material is a commonly used oxidizer in solid propellents which could be employed in deep-space probes, and where they will be subjected to a variety of radiations for as long as ten years. In some respects the radiation-induced damage closely resembles the effects produced by thermal decomposition, but in other respects the results differ markedly. Similar radiation and thermal effects include the following: (a) irregular or ill-defined circular etch pits are formed in both cases; (b) approximately the same size pits are produced; (c) the pit density is similar, namely ca 2-40 x $10^6/cm^2$; (d) the c face is considerably more reactive than the m face; and (e) most importantly, many of the etch pits are aligned in crystallographic directions which are the same for thermal or radiolytic decomposition. Thus, dislocations play an important role in the radiolytic decomposition process.

Radiolytic decomposition produces at least three effects not previously observed with ammonium perchlorate: (a) after 10^8 rad. γ-ray irradiated crystals effervesce during solution in water; (b) the initial x-ray and γ-ray induced decomposition sites occur throughout the volume where energy is deposited. Once formed they continue to grow. In contrast, the initial thermal pits appear at the surface and grow. New pits are formed as the reaction zone proceeds inward; (c) x-ray irradiation produces highly strained crystals. The layer adjacent to the irradiated surface becomes extensively cracked and large crystals have pronounced convex curvature.

Inasmuch as the principal decomposition is restricted to certain crystallographic sites, highly mobile energy transfer mechanisms must play an important role in the radiolytic decomposition of ammonium perchlorate. Most likely, the transfer agents are electrons, holes, excitons, or possibly protons.

Pseudo-stable solids, a group of materials that includes explosives and propellents, almost always decompose when heated (ref.1,2). Also many pseudo-stable materials decompose when exposed to radiation. The decomposition occurs at "etch-pit-like" sites in certain areas of the surface and along lines associated with twins or slip systems(ref,3). The "classical" theoretical treatments on decomposition(ref.1,2) assume that the process starts at unspecified sites on both the surface and interior of the crystals. Recent measurements show that the initial decomposition actually occurs on the surface where dislocations emerge (ref 3-8). In particular, the decomposition of ammonium perchlorate originates at isolated sites and in lines along well-defined crystallographic directions associated with slip systems. As the decomposition proceeds the reaction zone, or interface, spreads across the crystal surface and then proceeds into the interior. (refs. 7,8).

The thermal decomposition kinetics of ammonium perchlorate can be greatly modified by exposing the crystals to irradiation prior to heating (refs. 9-11). The data obtained with irradiated material, analyzed by applying Avrami-Erofeev kinetics (e.g., see ref. 2), indicates that the concentration of decomposition nuclei and/or the growth rate of individual nuclei is greatly increased. Also, this material can be decomposed by exposure to radiation. However, radiolysis effects are not obvious until the crystals are exposed to at least 10^6 rad.

The investigations described above suggest that the radiation-induced decomposition of

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ammonium perchlorate should be susceptible to investigation by transmission and scanning electron microscope techniques. Most importantly, they suggest that such a study would reveal facets of the decomposition process which would be useful for evaluating the performance of propellents containing ammonium perchlorate after exposure to relatively small total doses imparted at low dose rates. Such irradiation conditions apply to propellents used in satellites which remain in orbit for long periods, and deep-space probes which are exposed to a variety of radiations from Van Allen belts, cosmic rays, solar activity, and in particular from on-board radioactivity containing power sources.

The results described below show that numerous features of the radiation-induced decomposition are revealed by electron microscope techniques. In most respects the processes observed are similar to those produced by thermal decomposition. However, in some respects the radiation-induced decomposition is quite different.

EXPERIMENTAL

Large, approximately 5 x 3 x 3 cm., single crystals of ammonium perchlorate were grown on seeds suspended in a slowly cooled and well-stirred aqueous solution (ref. 7). The crystals were large rectangular parallelepipeds with well-defined {210}, or m, and {001}, or c, faces. They are readily cleaved on the {210} and {001} planes. Measurements were made on the original external surfaces of smaller crystals, approximately 5 x 3 x 3 mm, or interior surfaces exposed by cleaving after irradiation. Handling was minimized to reduce mechanical damage and all samples were kept in desiccators as much as possible.

All transmission-electron microscope (always abbreviated TEM) studies were made with an R.C.A. Model EMU-3D electron microscope operated at 100 kV. Graphite replicas were prepared for all specimens and shadowed at 80° from the normal with germanium oxide. Scanning electron microscope (always abbreviated SEM) studies were made with a Materials Analysis Company, Model 700 instrument operated at 5 kV. Usually the sample surfaces were uniformly coated with a layer, approximately 1000Å thick, of gold-palladium alloy deposited with a device utilizing two filaments and a rotating sample mount.

Gamma-ray irradiations were made in a Co^{60} source at a dose rate of 0.66 x 10^6 rad/hour. During irradiation the samples were at room temperature, i.e., always less than 30°C, in air and in the dark. X-ray irradiations were made with a tungsten target, beryllium window, tube operated at 50 kV and 20 mA. Without additional filtering the dose rate was 2.45 x 10^6 rad/hour at the sample surface. When a 1 mm aluminum filter was used the dose rate was 8.0 x 10^4 rad/hour. When exposed to x rays the samples were in air and in darkness.

The process of obtaining information from transmission-electron microscope (TEM), scanning-electron microscope (SEM), and optical microscope (OM) pictures such as those in this article can be greatly facilitated by using one or more of the following "tricks".

1. To determine if any of the details on the pictures are aligned, or more specifically, if they lie along relatively straight lines, view the pictures at about 70° from the normal and rotate them slowly about the normal.

2. The appearance of many features on certain pictures will change drastically when they are viewed at 20° or 30° from the normal and rotated from 90° to 180°. Often a 180° rotation will cause a feature which originally appears to protrude to subsequently appear as an indentation.

3. To determine if an artifact is above or below the surface of a TEM picture look for specks of dirt. Usually, they appear as black dots which cast pointed unshadowed areas indicating the direction of the impinging shadowing material. Thus, one can determine if a more or less vertical surface has accumulated, or is sheltered from, shadowing material.

RESULTS

In a real sense, the major results are in the pictures and captions contained in Plates 1 thru 5. In order to demonstrate how the radiation-induced effects depend on dose the principal observations will be described, in the order they appear as the dose increases; first for gamma-ray irradiated samples and then for crystals exposed to x rays.

Gamma-ray Irradiated Crystals

1. Unirradiated Crystals: The crystals are water clear and free of inclusions and gross surface defects. Crystals etched with butanol contain approx. 2.7 ± 2.2 x 10^5 pits/cm^2.

2. 10^3 to 10^5 rad: Crystals were examined after irradiations of 10^3, 10^4, and 10^5 rad. by OM, TEM and SEM. They remain water clear and radiation-related effects could not be detected on either the m or c faces. Plate 1(a) was obtained from a crystal exposed to 10^3 rad. but is typical of unirradiated samples and those exposed to 10^4 and 10^5 rad.

3. 10^6 rad: Crystals slightly opaque, i.e., milky. Surface effects were not detected by SEM. However, TEM reveals small, very flat pits on only the m face, Plate 1(b). Plate 1(c) shows a cluster of larger pits which resemble circular craters and are similar to the pits formed during the early stages of thermal decomposition (ref. 7). The pits do not appear to be aligned, i.e., they do not lie in straight lines.

4. 5.0 x 10^6 rad: The crystals are nearly opaque and appear milky white. Pits could not be detected by OM or SEM. However, circular pits and decoration of growth steps and/or cleavage steps with tiny pits are clearly visible in TEM pictures of only the m face.

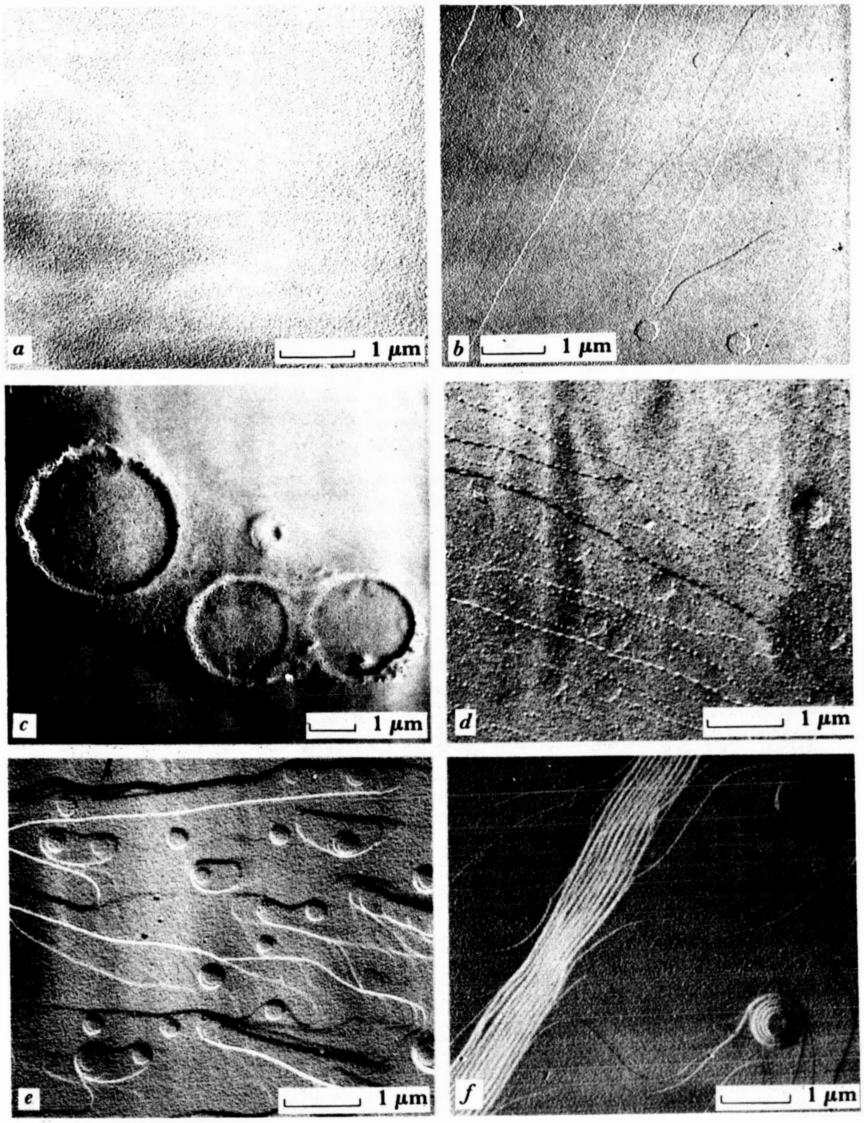

Plate 1

Plate 1. Transmission electron microscope pictures of the m face of ammonium perchlorate crystals after Co^{60} gamma-ray irradiation.

a) 10^3 rad.
b) 10^6 rad.
c) 10^6 rad. A much larger pit similar to the pits in (b).
d) 5.0×10^6 rad. Cleavage step and growth planes "decorated" during radiolytic decomposition. Similar "decoration" is produced by chemical etching.
e) 10^7 rad. At this dose the pits join or overlap to form runnels, similar to chemical etching.
f) 5.0×10^7 rad. An advanced stage of radiation-induced pitting.

5. 10^7 rad: Crystals are completely opaque and resemble white plastic. Radiation-induced decomposition is apparent on both faces, using OM or SEM. However, the TEM pictures show the most detail. Marked pitting and the formation of holes and channels occurs on the m face, Plate 1(e), which resembles the later stages of etching using ethanol.(ref. 8). At this dose decomposition features are also found on the c face. Most likely the lowest dose producing initial c face deterioration lies between 10^6 and 10^7 rad., but the dose was not precisely determined. The c-face pits are best studied by SEM and are quite dense; in some areas they appear random and do not appear to be aligned, Plate 2(a). In other areas the pits are aligned, Plate 2(b), especially along the [210] direction. These aligned pits extend across the surface for varying distances up to 1000 microns. In addition to the small pits described above, some parts of the surface, especially the m face, contain large bubbles and cavities, an example is Plate 2(c).

6. 2.5×10^7 rad: Both faces are extensively pitted. The SEM picture Plate 2(d), shows c-face pits whose concentration is approx. $2.3 \times 10^7/cm^2$. Some regions of the pits resemble those formed by thermal decomposition, in air, at 226°C, Plate 2(e). In addition, the alignment of pits originally observed at lower doses persists at this (and higher) dose rates, Plate 2(f). This should be expected since many of the pits induced by this dose must have been initiated at lower doses and have increased in size.

7. 5.0×10^7 rad: Extensive decomposition is observed on both faces. SEM pictures of the c face, Plate 3(a), show that there are approx. 4.2×10^7 pits/cm^2. Also, there are areas where the pits are aligned in distinct directions. Occasionally the pitted areas "meander" through the crystal; presumably these are grain boundaries, Plate 3(b). Note that the pits in the grain boundaries vary considerably in size both along and across the boundary zone. A TEM picture showing the interior of the c-face pit(s) is Plate 1(f). This shows the circular-layer-like structure, extending to the pit bottom, originally observed on chemically-etched crystals (ref. 8). This is perhaps the most striking observation indicating that the radiation-induced reactions closely parallel the solution chemical reactions. In particular, this similarity suggests that both reactions are ultimately related to the crystal surface-structure, i.e., the topography. At this dose small block-like particles break away from the crystal along fracture lines associated with and/or parallel to well-demarked lines of pits. One example, Plate 3(c), shows rows of pits parallel to the fracture surfaces. As suggested above, many of the details in this picture and especially the block-like character may become much more apparent if this picture is rotated 90° or 180°.

The m-face results, for this dose, are somewhat similar. Pitting occurs both randomly and aligned. The size of the pits vary considerably, some regions contain large holes and other regions contain "decorated" terraces or steps. For example, Plate 3(d) shows decorated steps with pits aligned along the [1$\bar{2}$0] direction. The aligned pits often lie along nearly parallel lines as shown in Plate 3(d). All of the observed alignments appear to lie along crystallographic planes. However, because these directions are close together, it is difficult to establish this beyond question. Occasionally mirror image pit arrangements are observed, Plate 3(d). One would expect to observe this particular arrangement if the pits are associated with dislocations produced by the "Frank-Read" mechanism. Often when crystals fracture along aligned rows of pits it is apparent that the pits, which are observed on the surface, occur at the end of hollow chimney-like tubes which extend into the solid, Plate 3(e). Often these tubes are quite evenly spaced. Plate 3(f) shows pit formation along the [120] direction and large bubbles formed in the interior. These are similar to the large pits shown in Plate 1(c).

X-ray-Irradiated Crystals

The search for x-ray induced radiation damage and/or decomposition in ammonium perchlorate utilized both hard (or filtered) and soft (or unfiltered) x rays. Doses as large as 3.5×10^6 rad, of 50 kV tungsten x rays filtered by 1 mm Al, did not produce any radiation-induced damage when the crystals were examined by OM, TEM, or SEM. However, unfiltered x rays from the same tube produced numerous effects which are described below. Inasmuch as the incident x-ray beam is attenuated as it penetrates into the crystal, one can employ a somewhat novel technique to study x-ray induced decomposition vs. dose. Namely, the crystals can be irradiated and cleaved normal to the c face and microscope studies made on both the irradiated and cleaved face.

1.6×10^7 rad: Both the m and c surfaces appear smoky and translucent and have developed cracks which could outline grain boundaries, Plate 4(a). Individual artifacts, e.g., etch pits, were not observed.

3.3×10^7 rad: A milky-white well-defined thin layer of product is formed on the m face. On the c face pits are found in isolated areas, Plate 4(b), and in some areas they are aligned. There are roughly 5×10^6 pits/cm^2 and they vary in size.

5.6×10^7 rad: On the c face the pit density at this dose is $3.5 \times 10^7/cm^2$, Plate 4(c). The pits are circular and fairly uniform in size. Most importantly, this is the lowest dose producing pits on the m face, Plate 4(d). There are approx. 2.1×10^7 circular and uniformly sized m-face pits/cm^2. In some areas on both faces the pits are aligned.

At this dose it is convenient to study the reaction at various distances from the exposed surface, using crystals cleaved parallel to the radiation beam. Place 4(e) shows both an irradiated surface and the perpendicular surface revealed by cleaving. The density of etch pits at various distances from the surface is shown in Fig. 1. Also, shown, is the x-ray intensity as a function of distance from the surface, as determined by interposing

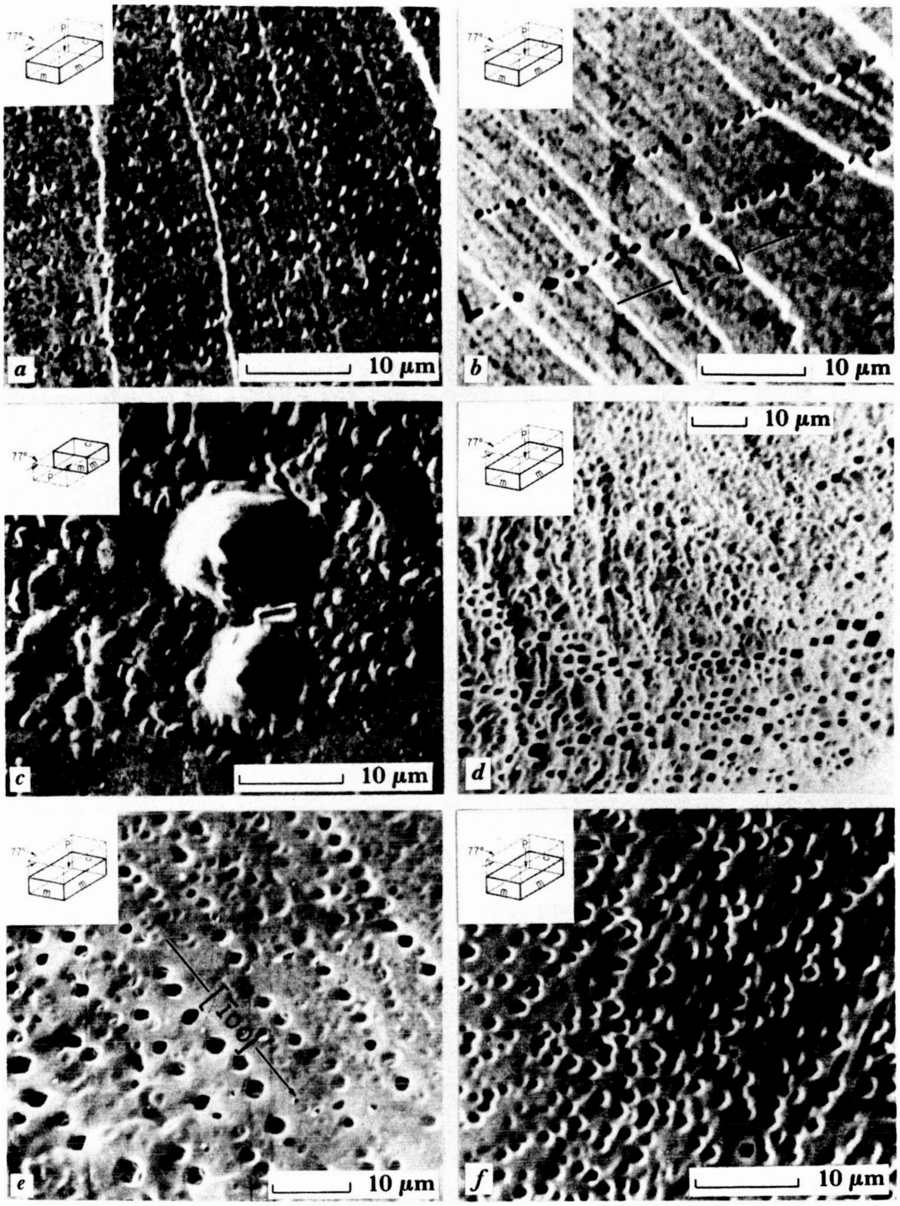

Plate 2.

Plate 2. Scanning electron microscope pictures of ammonium perchlorate surfaces after Co^{60} gamma-ray irradiation.

a) c face, 10^7 rad. Uniformly distributed circular pits.

b) c face, 10^7 rad. Marked alignment of pits in [210] direction.

c) m face, 10^7 rad. In addition to the smaller pits larger "bubbles" are formed.

d) c face, 2.5×10^7 rad. Rectangular shaped holes, resembling those found in thermal decomposition product.

e) c face, 2.5×10^7 rad. Marked alignment of the pits in the [$\bar{1}$00] direction.

f) c face, 2.5×10^7 rad. Pit density: $2.3 \times 10^6/cm^2$.

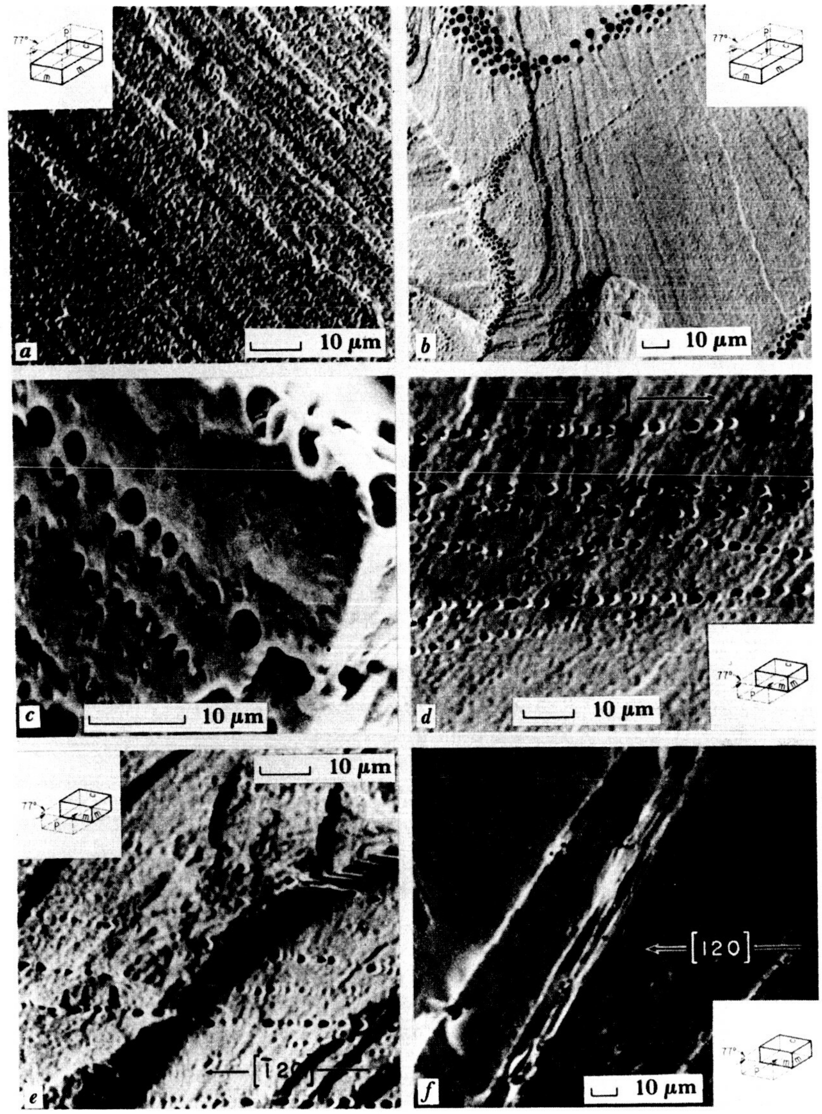

Plate 3

Plate 3. Scanning electron microscopy pictures of ammonium perchlorate surfaces after a 5.0×10^7 rad. Co^{60} gamma-ray irradiation.

a) c face. The pit density is $4.1 \times 10^7/cm^2$.

b) c face. Pitted areas "meandering" through the crystal, presumably along grain boundaries.

c) Block-like particles formed by radiation-induced pits. The crystal has fractured along intersecting pit alignments to produce the block. The block-like character may become more apparent if this picture is rotated 180°.

d) m face. Pits aligned in the $[1\bar{2}0]$ direction.

e) m face. The aligned pits occur at the ends of chimney-like tubes extending into lower layers of the solid.

f) m face. In addition to small well-aligned pits on the $[\bar{1}20]$ direction, the surface contains a larger pit similar to those shown in Plate 1(c).

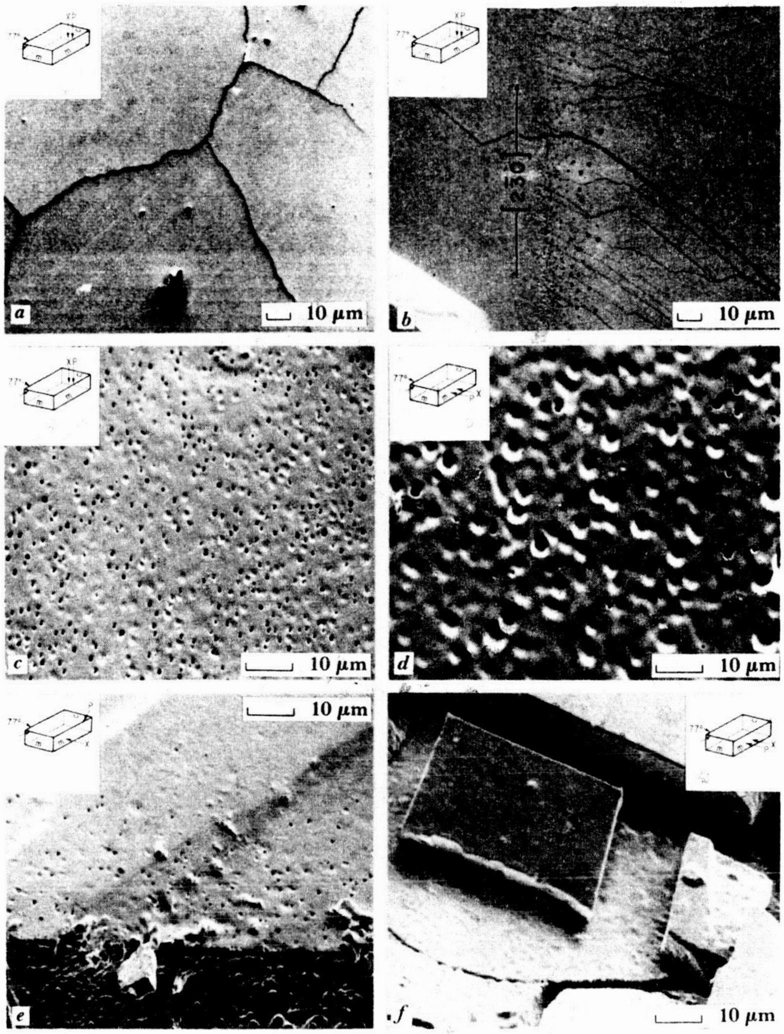

Plate 4

Plate 4. Scanning electron microscope pictures of ammonium perchlorate surfaces after 50 kV, tungsten target, and unfiltered, x-ray irradiation.

a) m face, 1.6 x 10^7 rad. Cracks form on the external surface.
b) c face, 3.2 x 10^7 rad. Initial pit formation aligned in $[\bar{2}30]$ direction.
c) c face, 5.2 x 10^7 rad. Pit density: 3.5 x $10^7/cm^2$.
d) m face, 5.2 x 10^7 rad. Shallow and deep pits, density 2.1 x $10^7/cm^2$.
e) c and m face, 5.2 x 10^7 rad. After irradiation the interior m face was exposed by cleaving. Note the pit density at various distances from the irradiated surface. This c face is the same as in (c) above.
f) m face, 7.2 x 10^7 rad. Block-like product on surface with underlying cracking and pit formation.

thin Al absorbers between the x-ray tube and a detector placed at the sample position. Thus, it would appear that the x-ray intensity decreases monotonically from the irradiated surface while, in contrast, the pit density is very low at the front surface, rises abruptly to a prominent maximum, and then decreases monotonically. This somewhat surprising result is considered in the discussion section.

7.5×10^7 rad: This dose causes the surface to break up into blocks similar to those formed during gamma-ray irradiation, Plate 4(f). Also, reaction product occurs on the fracture surfaces below the loose blocks. Almost all of the external surface is covered with pits. Often the pits are markedly aligned, particularly along the [$\bar{1}$25], [350], and [241] directions on the m face, Plate 5(a).

Radiolytic Decomposition of Strained Crystals

Straining crystals prior to thermal decomposition or chemical etching produced effects which could be correlated to dislocations and related effects (refs. 7,8). Immediately below, it will be demonstrated that similar strain-related effects are observed with radiolytically decomposed ammonium perchlorate crystals. A really detailed presentation of the available data on the radiolysis of strained crystals would include observations at a variety of different doses. However, to be brief, only data obtained at one dose level, namely, 5.1×10^7 rad will be described in this paper. First, crystals compressed by squeezing the m faces prior to x-ray exposure develop broad bands of pits on the c face which lie along [120] directions, Plate 5(b). These directions are parallel to, or lie along the intersection of, prominent slip systems. Second, other areas on the same surface contain individual etch pits aligned along crystal directions previously associated with slip systems. For example, Plate 5(c) shows pits aligned along [120] and several other directions. Third, strained crystals fracture into blocks whose sides usually are low index crystal planes, Plate 5(d). The blocks separate from the original crystal along planes parallel to the original surface. Furthermore, the parallel fracture planes contain numerous etch pits similar to those formed on the original surface.

X-ray irradiation produces a high degree of strain on the crystal. Apart from the extensive cracking and block formation, pronounced curvature on large 10 x 6 x 0.5 mm m-face samples develops during an x-ray dose of 1.6×10^7 rad. Also, pronounced curvature occurs along the b axis of c-face crystals having similar dimensions and for the same x-ray dose.

DISCUSSION AND SUMMARY

The observation on gamma-ray and x-ray induced decomposition of ammonium perchlorate, described above, provides generalizations which can be grouped into two categories. First, there are many radiation effects which are similar to those occurring during thermal decomposition and chemical etching. Second, radiation induces some effects not observed during thermal and chemical treatment. These two categories will be described separately.

Radiation-Induced Effects Similar to Chemical and Thermal Effects

A. An induction period precedes the appearance of the initial decomposition. Specifically, when exposed to heat or radiation an initial heating period must elapse, or the sample must receive a specific dose, before decomposition is observed (ref. 11). For example, if a three-second etch produces well-defined pits a two-second etch may not produce any observable effects.

B. The initial radiation-induced effect, as well as the thermal and chemical effect, is the appearance of small etch pits which are aligned in some, but randomly distributed in other, areas of the same crystal.

C. The characteristics of the etch pits formed by all three stimuli are similar: the pits have roughly the same size; the pit density is comparable, namely, approx. $2\text{-}40 \times 10^6/cm^2$; and the aligned pits lie in the same crystal directions no matter how produced.

D. A second, or intermediate, decomposition stage is found in all three cases when the decomposition has extended over the entire external crystal surface. Concomitantly, extensive decomposition is observed on macroscopic defects such as cleavage steps, slip systems, etc.

E. The last stage of decomposition produced by etching is characterized by blocks of undissolved crystals separated by fissures. Extensive thermal and radiolytic decomposition produces similar, apparently unaffected, blocks connected at edges or corners to form a "sponge-like" or coral structure containing rectangular voids. This structure is similar to that previously reported by Kraeutle (ref. 12).

F. In all cases decomposition on the c, or (001), face is well developed before the initial etch pits appear on the m, or (210), face. However, the final appearance of both faces is similar, except for differences imposed by the crystal structure.

Radiation-Induced Effects

When ammonium perchlorate crystals are subjected to radiation effects, described below, are observed which do not appear during thermal or chemical decomposition.

A. Crystals subjected to gamma-ray doses of 10^8rad, or larger, effervesce when dissolved in water. A similar effect was observed by Heal (ref. 13) in x-ray irradiated $KClO_4$ crystals.

B. Gamma-ray induced decomposition occurs on sites which are uniformly distributed through the crystals. X-ray induced decomposition occurs on sites thoughout the volume irradiated. In contrast, thermal and chemical decomposition starts on the surface and penetrates inward.

C. Radiation-induced strain causes several different effects. First, some curved surface cracks are formed. Second, appreciable surface cracking occurs along cleavage planes to create numerous regularly shaped blocks. Third, crystals irradiated on one

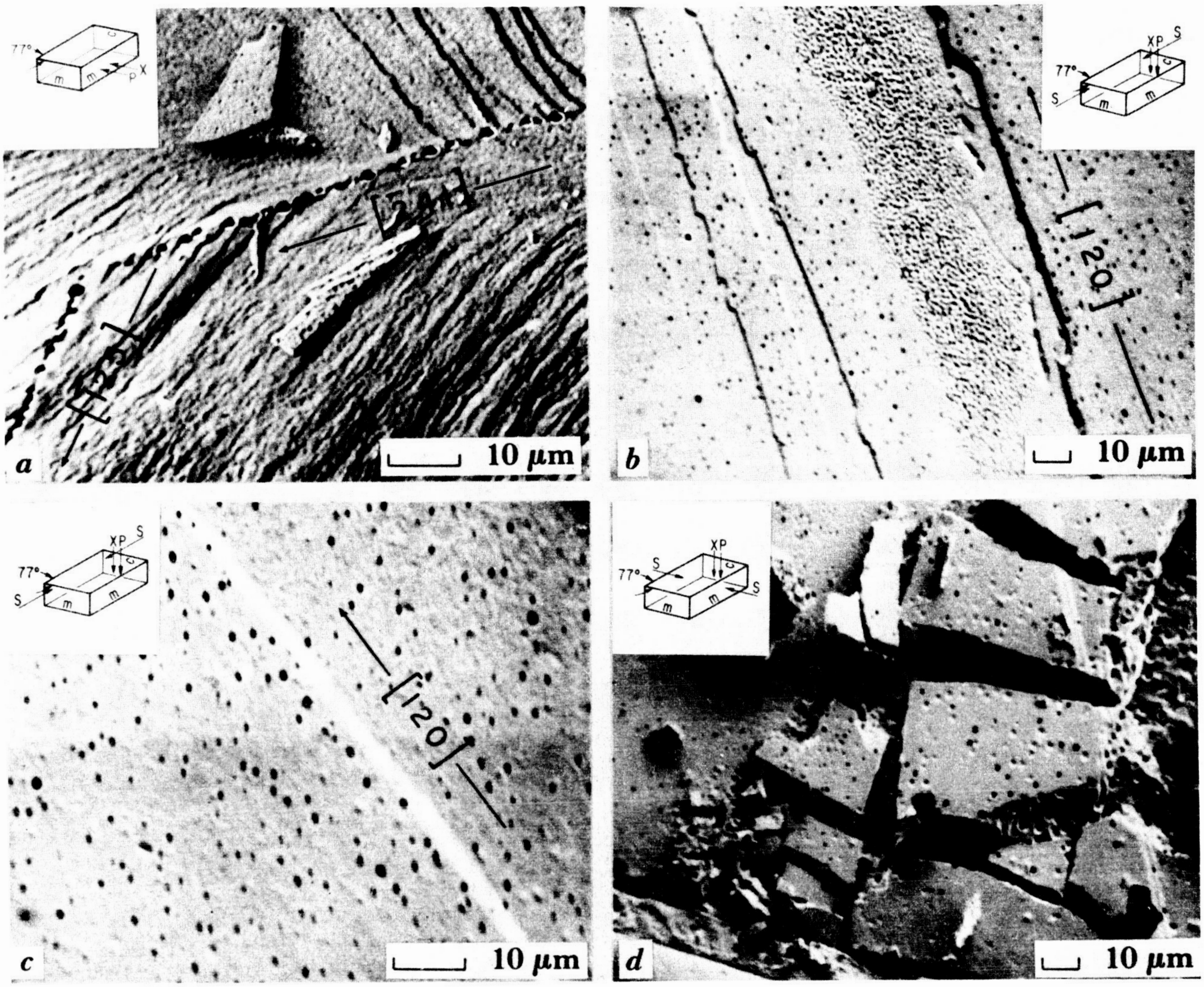

Plate 5

Plate 5. Scanning electron microscope pictures of ammonium perchlorate surface after 50 kV, tungsten target, unfiltered, x-ray irradiation.

a) m face, 7.2 x 10^7 rad. Pit alignment along the [125] and [$\bar{2}$41] directions.
b) c face, 5.1 x 10^7 rad. Region of marked activity in [120] direction. The slip planes were produced by compression on m faces.
c) c face, 5.1 x 10^7 rad. Pits aligned in [120] direction after compressing the m faces.
d) c face, 5.6 x 10^7 rad. Block-like product on strained material. Also, there is sub-surface pitting.

surface with x rays, in which case the irradiated volume is confined to a slab on the surface, develop very pronounced convex curvature.

D. One of the most interesting effects associated with radiation is the localization of the decomposition on certain sites. It has been established that the initial chemical and/or thermal decomposition sites occur where dislocations, slip systems, etc. intersect the crystal surface (ref 7). It must be concluded that the radiation-induced process on the surface also occurs at the same type of site. This particular process may be regarded as radiation-induced etching.

Decomposition in the interior of x-ray or gamma-ray irradiated crystals also occurs at sites which do not appear to be randomly distributed. Furthermore, the decomposition does not appear to be simply related to the ionization density during irradiation. This is illustrated in Fig. 1 which shows that the concentration of radiation-induced etch pits near the surface is considerably less than one would expect if the decomposition site count was proportional to the dose. A similar effect has been observed (not illustrated) on the surface of irradiated crystals which contain cleavage steps and/or similar macroscopic imperfections; namely, appreciable decomposition occurs on the steps, cracks, etc., but the area immediately around them is usually free of decomposition sites.

These observations suggest conclusions which, at this time, must be regarded as tentative. First, inasmuch as external decomposition occurs at the intersection of the dislocations and the surface, it is reasonable to expect that internal decomposition occurs at dislocation-related sites such as intersections, pinning points, etc. Second, internal decomposition occurs, almost certainly, at voids, inclusions, cracks, etc. Third, radiation-induced ionization events must occur uniformly throughout the regions reached by the incident x rays or gamma rays. Since the decomposition occurs only at specific sites, a mechanism must exist for the transfer of energy from the location of each ionization event to the site. The most likely processes are electronic and involves one or more of the usual carriers, i.e., electrons, holes, and/or excitons. This was originally proposed to explain the radiation-induced decomposition of KN_3 and NaN_3 (ref. 3). Fourth, once a decomposition site has become active, it would appear to retard the formation of additional sites in its immediate vicinity, and the area of influence, i.e., the interaction radius, is related to the pit size. In other words, it would seem that the charge and/or energy carriers mentioned above are much more likely to interact with nearby existing sites than to initiate new sites.

These ideas provide one, or several, possible explanations for the observed decomposition site distribution shown in Fig. 2. The external surface can be expected to be an efficient carrier collector, i.e., decomposition site. Thus, carriers produced within a fixed distance from the surface, perhaps a mean-free path, almost certainly cause decomposition at the surface and do not contribute to the formation of interior sites. Further from the surface it is much more likely that the carriers will interact at sites. Thus, the site concentration will be low at the surface, increase toward the interior, and then decrease as the x-ray beam is attenuated.

To emphasize that alternative explanations are possible, one other possibility will be mentioned. Because the samples are prepared by cleaving, the crystals may be more highly strained near the surface than in the interior. Thus, if the decomposition rate is reduced by the strain one would expect the site density to be low near the surface. Clearly, other surface related effects may be expected to reduce the decomposition site concentration near the surface. However, as mentioned above, the decomposition rate is observed to increase in the vicinity of strain produced slip systems.

In summary, the radiolytic decomposition of ammonium perchlorate is similar in many respects to thermal or chemically-induced decomposition. The decomposition processes are related to the defect and dislocation-related properties. However, the effects observed only with radiation suggest that electronic carriers, e.g., electrons, holes, excitons, and possibly protons play an important role in the decomposition process, whether or not the stimulus is chemical, thermal or radiation.

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PLATE AND FIGURE CAPTIONS

The inserts provide the following detailed information on each picture:

m - m face
c - c face
X - direction of incident x rays
S - direction of applied strain
P - the view photographed

The part of the crystal removed by cleaving, usually after irradiation, is indicated by dashed lines.

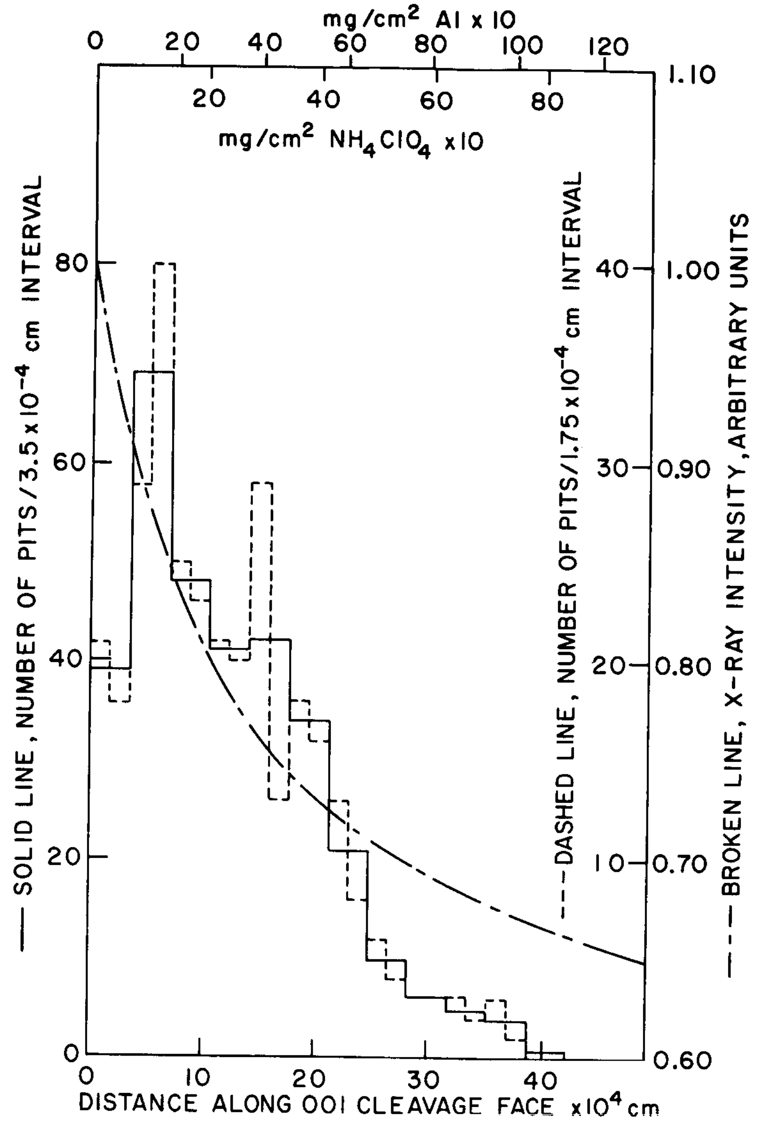

Figure 1

Fig. 1. Histographs showing the distribution of internal decomposition sites normal to the c surface of an ammonium perchlorate crystal irradiated to a total dose of 1.6 x 10^7 rad. with unfiltered x rays from a tungsten tube operated at 50 kV. Also shown is the x-ray intensity vs. penetration depth computed from x-ray attenuation measurements made with thin Al foils. The site concentration increases inward from the surface to a maximum and then decreases, i.e., near the surface it is <u>not</u> proportional to the deposited energy.