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ION BOMBARDMENT OF MATERIALS CONTAINING ALKALI METALS OR ALKALINE EARTHS

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SUMMARY

Experiments show that argon ion bombardment of many substances results in the chemical sensitisation of the irradiated surface. As a consequence, subsequent exposure to atmospheric water vapour causes evolution of hydrogen, and in certain cases leads to severe surface corrosion.

The effect occurs on targets containing elements from the first and second column of the periodic table, and therefore includes some widely used electro-optical materials.

A mechanism is proposed to explain the observed phenomena, and the possibility of ion polishing sensitive materials is discussed.

Approved for public release

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1. INTRODUCTION

The ultimate aim of the present investigation is to increase the reliability and service life of laser systems by rendering their optical components less sensitive to damage in high intensity laser beams. Many electro-optical materials in common use for the construction of such components are mechanically soft, and as a consequence it is virtually impossible to prevent submicron sized particles of polishing agents from becoming embedded in optical surfaces prepared from these materials. At the sites of the embedded impurities laser damage can develop either through selective absorption of radiation by the impurity particles, or through avalanche breakdown at points of localised electric field intensification.

We propose to eliminate these undesirable effects by removing the embedded foreign material by means of ion polishing, to which the optical surface is subjected in a final finishing operation. To this end the effect of argon ion bombardment on a range of materials of interest has been studied, and the irradiation effects discovered in the course of this work are discussed in the present report.

2. EXPERIMENTAL DETAILS

The ion irradiation experiments were carried out in an apparatus evacuated to a pressure of about 5×10^{-6} Torr by means of a liquid nitrogen trapped oil diffusion pump.

Argon ions, produced in a hot cathode plasma ion source, were focussed into a spot of about 2 mm diameter at the target, which could be flooded with very low energy thermionic electrons to ensure surface charge neutralisation during the bombardment. Means were also provided for light microscopic examination of the target surface without breaking the vacuum.

A value of 1.5 keV was selected for the ion energy, and with a typical total current of 7 μA the beam was scanned over a distance of several millimeters both horizontally and vertically, resulting in an ion current density of about 1.2×10^{14} ions/cm^2/s over most of the bombarded area. Because of the radial current distribution within the beam, the bombardment intensity dropped off towards the boundary of the scanned area, and a very low level of irradiation was in fact incident on the entire remainder of the target surface.

The change in current density was also reflected in the profile of the erosion crater produced during the bombardment, and shown schematically in figure 1. Using potassium dihydrogen phosphate (K.D.P.) as the target material, the erosion crater reached a depth of about 0.5 μm in 3 h, corresponding to an ion ersosion rate of roughly 0.5 Å/s.

The weakly irradiated region surrounding the crater was covered by a thin polymer film, formed under ion bombardment from hydrocarbon molecules in the residual atmosphere of the apparatus. As discussed in more detail elsewhere (ref.1), the rate of formation of such contaminant films varies with the concentration of hydrocarbons present, and is thus dependent on vacuum procedures, but in the present experiments the growth rate was typically of the order of 0.05 Å/s. As will become apparent later, the difference in post-bombardment behaviour of the target material, depending on whether or not it was covered by the polymer film, proved valuable in interpreting the observed irradiation effects.

No attempt was made to ensure a very high pre-bombardment surface finish of the targets, which were dry polished with aluminium oxide powder of grain sizes down to 0.3 μm. The appearance of a typical K.D.P. sample prepared in this manner is shown in figure 2.

3. EXPERIMENTAL OBSERVATIONS ON K.D.P.

The initial experiments were carried out on K.D.P., which as a rule was bombarded for standard periods of either $1\frac{1}{2}$ or 3 h. Except for the depth of the erosion crater, the effect of the irradiation was identical in both cases. Microscopic examination of the specimen under vacuum revealed that the surface appearance in the crater was essentially that of the unbombarded material in figure 2., but that the scratch lines had in general become attenuated, with some of the more superficial ones having been almost obliterated in the erosion process. The polymer film, clearly discernible through its contrasting colour, had an extremely smooth texture, and its boundary near the crater edge was very sharply defined.

The surface appearance remained unaltered indefinitely as long as the vacuum was maintained in the apparatus, but drastic changes were observed following admission of the atmosphere. These changes were particularly rapid and dramatic on the target portion covered by the polymer film. Here, as soon as air entered the system, microscopically small gas bubbles began to form, a process which invariably began near the film boundary at the erosion crater, before spreading to the remainder of the film covered area.

An example of this phenomenon is shown in the series of photographs of figure 3. where figure 3a represents conditions approximately one minute after admission of atmospheric air. On the left side of the figure the outer rim of the erosion crater is seen as a dark zone, whilst on the right the undisturbed polymer film appears as a lighter background. Bubbles have appeared in a band of about 100 μm width along the boundary, and in this zone gas evolution is on occasion so violent that the top of a bubble is partly torn off, as illustrated in the example of figure 4.

Following figure 3a the photographs of figures 3b to 3e, taken at approximately equal intervals of time, depict the further development during the succeeding 30 min. It is seen that in this time practically the entire surface is covered by new bubbles, which in general tend to be smaller as one recedes from the film boundary. At the same time some of the already existing bubbles have coalesced into larger units, with gas flowing between them through narrow communicating channels under the polymer film.

The process of coalescence continues for some time, and figure 3f, taken after approximately one day, shows the essentially stable final configuration. With most of the gas now concentrated in relatively few large bubbles, the film is once again lying flat on the K.D.P. sample, permitting its surface features to be clearly seen. Thus, by comparing figures 3a and 3f it becomes apparent that the band of diagonal bubbles formed very soon after admission of air, is associated with a system of roughly parallel scratch lines on the surface. A similar association between bubble formation and signs of obvious surface damage is frequently found. Figure 5 shows an example of this on an area far removed from the crater edge, where therefore the bubbles are very small. Here a clustering of bubbles is noticed along portion of an approximately parabolic scratch line, but the picture also shows that the existence of visible surface damage is neither necessary nor sufficient for gas bubbles to form. Moreover, where an association between bubble concentration and a scratch mark does exist, the bubbles are not necessarily most numerous where the surface damage along the scratch line is most severe. This suggests that only certain types of damage are conducive to gas evolution.

A number of experiments were conducted to determine which atmospheric constituents take part in the chemical reaction responsible for the observed gas evolution. These observations established unequivocally that only water vapour is involved.

In summary we can say that after exposure to atmospheric moisture gas is evolved from the ion irradiated surface. It is fortunate that this process can take place under the contaminant film, which serves to contain the gas in visually observable bubbles; otherwise the presence of a gaseous reaction product might easily have escaped detection. The gas appears to be formed not uniformly over the entire surface, but rather at certain preferential sites, and since there is a degree of correlation between these sites and directly observable surface damage, it is reasonable to postulate that the sites are the locations of certain specific types of crystallographic singularity, which render them catalytically active. Other observations to be discussed further below, tend to confirm this view.

Turning our attention from the weakly irradiated area under the contamination film to the region of the erosion crater, we are now concerned with a surface subjected to a bombardment intensity higher by several orders of magnitude, where in consequence no polymer layer could develop.(ref.1). Because of this, gas evolution was unobservable here and surface changes following contact with the atmosphere were not apparent immediately, but only after a period of typically two minutes, with the appearance of a pattern of small spots. In the resolution limited optical micrograph of figure 6 these spots appear as roughly circular, with diameters of the order of 1 μm. Their number per unit area is comparable to that of the discrete centres at which gas evolution is observed under the contaminant film and, as in figures 3 and 5, there is some correlation with surface scratches. This suggests that the spots in the crater area and the centres of gas evolution under the film are in fact different manifestations of the same underlying effect of ion irradiation.

The spot pattern of figure 6 underwent gradual change with time, first noticeable by the spots becoming larger, and in particular more elongated, until finally the entire crater area was involved in what clearly was a type of corrosion reaction. Figure 7 shows the surface appearance at this stage, characterised by a very rough overall texture and by strongly enhanced scratch marks.

Typically the transition from the spot pattern of figure 6 to the overall corrosion of figure 7 took place in laboratory air over a period of several hours, with the first signs of spot elongation becoming noticeable after about 30 minutes. The transition time was however variable; it appeared to depend somewhat on sample preparation as well as on atmospheric conditions, so that in some instances the state of overall corrosion was attained within a few minutes.

Additional insight into the nature of the irradiation effect can be gained by adopting a bombardment duration not of several hours, as above, but of only 4 seconds. It is found that after such a short irradiation the surface corrosion does not proceed beyond the "spot" stage of figure 6. Under these circumstances the stability of the surface permits the sample to be prepared for examination under the scanning electron microscope, and the resulting electron micrographs of figure 8 show the surface appearance in regions of different bombardment intensity. Thus figure 8a represents conditions at the bombardment centre, where the intensity is highest, whilst figure 8c illustrates the surface at the very edge of the crater, near the contaminant film, with figure 8b corresponding to an intermediate ion current density. Altogether the three photographs span an intensity range of about one order of magnitude.

It is seen that what appeared under the light microscope as roughly circular "spots", are in reality rod shaped corrosion regions. The earlier observation that subsequent growth of the "spots" is initially in the nature of an elongation, seems to imply that in the early stages the corrosion reaction tends to propagate from a small original site preferentially along the "rod" axis.

Examination of figure 8 also shows that the orientation of the rod axes is not random, but that there is alignment along a few preferred directions. To investigate any connection with the crystallographic axes of the material, two samples of different crystallographic orientation were prepared. In the first of these the (001) plane was irradiated with ions incident along the c-axis, whilst in the second case the (110) plane was bombarded at normal incidence. The orientation of the resulting rod structures was determined in each case. As the histograms of figure 9 indicate, there is a clear preponderance of alignment along the axes of the unit cell, and within the accuracy of the experiment, alignment along the a-axis occurs with approximately the same frequency as along the c-axis.

Finally it is evident from figure 8 that both the size and the number of rods per unit area are dependent on the bombardment intensity. Near the crater centre small rods are seen in large numbers, whilst in the region of low ion current density only a few rods are present, but these are of much larger dimensions. Figure 10 shows the relation between the total bombardment dose and the number density of the rods. Approximately 1 x 10^{13} ions/cm^2 represent a threshold dose below which no rods are detected, but beyond this value the rod density increases with dose in a highly non-linear fashion to a saturation value of about 9 x 10^5/cm^2, which is reached at an irradiation dose of 7 x 10^{13} ions/cm^2. Continuing the bombardment beyond this stage does not lead to the appearance of further rods. The saturation value of 9 x 10^5 therefore represents the number density of locations on the surface* with crystallographic properties such that ion irradiation can lead to the development of a site where the corrosion reaction can be initiated catalytically, and from where it will propagate preferentially along the a or c axis.

Although the present investigation is primarily concerned with the effects of ion bombardment, it is nevertheless of interest to know whether the phenomena we have described can also be induced by other types of irradiation, using either electrons or photons. In examining this question, no attempt was made to deal with the problem in any detail beyond establishing whether or not the effect does exist.

To this end the target was in the first instance bombarded for about 3 hours with electrons from the thermionic filament normally used to provide the slow electrons for surface charge neutralisation. The total emission current during the irradiation was 3 mA, but the current density at the target was not accessible to direct measurement. Likewise the effective electron energy was uncertain because of surface charging, but its upper limit was given by the applied accelerating potential V_a.

Since electron bombardment does not produce sputtering, it causes the entire target surface to be covered by a contaminant film. Figure 11 shows the gas bubbles produced under this film by electrons with V_a = 1000 eV., thus establishing firmly that electron irradiation can lead to the evolution of gas. The effect was however not detected when V_a was reduced to 200 eV, possibly because of a rapid decrease in the effective crossection for the process with particle energy.

In the case of photon irradiation the polymerisation crossection is too low for significant development of a contaminant film. Therefore, to permit the evolution of gas to be detected, the K.D.P. target was covered with a nitrocellulose film of a few hundred Å thickness. The specimen was then placed 7.5 cm from the target spot of an X-ray tube, operated at a beam current of 16 mA and with an anode voltage of 40 kV. At the specimen surface the photon flux of Cu K_α radiation was estimated to be about 6 x 10^{11} photons/cm^2/sec, which after 3 h produced the gas bubbles shown in figure 12.

In separate experiments irradiation of similar nitrocellulose films on Cu and Vycor glass substrates failed to produce any evidence of gas evolution. This was therefore not due to any spurious response of the nitrocellulose to radiation, and it follows that the gas observed in the first experiment originated from the K.D.P., thus confirming that the effect can also be induced by photon irradiation.

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* The saturation value is found to vary slightly from sample to sample.

4. THE MECHANISM OF THE IRRADIATION EFFECT

Any model for the phenomena we have described must account for the following salient features:

(a) A corrosion reaction involving water vapour spreads from radiation induced catalytic centres over the entire surface.

(b) A gaseous reaction product is formed at an early stage.

(c) Whilst the surface must be initially "conditioned" by irradiation, subsequent exposure to water vapour will trigger off the reaction, and maintain it over a long period of time without any further particle or photon bombardment.

The reaction mechanism we are proposing does account for these features, but it is intended to describe in no more than broad outline what is clearly a complex phenomenon. Thus the appearance of a gaseous product in a reaction involving potassium dihydrogen phosphate and water vapour immediately suggests a process in which potassium hydroxide is formed with simultaneous evolution of hydrogen. This reaction does however require metallic potassium rather than the K^+ cation available in K.D.P. We therefore postulate that under irradiation a cation is removed from its normal position on the surface of the crystal, a process which we represent by

$$K^+(H_2PO_4)^- + \text{radiation} \longrightarrow K^+ + (H_2PO_4)^- \qquad (1)$$

In the case of ion bombardment the large mass of the incident particle ensures that the displacement of the cation can proceed by simple momentum transfer on impact, but when dealing with electron of photon irradiation a multiple ionisation process of the Varley type (ref.2,3,4) or its equivalent (ref.5) must be invoked.

Once displaced from its position at a lattice point, surface mobility permits the cation to travel to an active site, where we postulate electron transfer according to

$$K^+ + e^- \longrightarrow K, \qquad (2)$$

which provides metallic potassium, so that in the presence of water vapour the reaction can proceed as

$$K + H_2O \longrightarrow KOH + H\uparrow, \qquad (3)$$

yielding the required gaseous product.

The anion in equation (1) is also available for reaction with a water vapour molecule according to

$$(H_2PO_4)^- + H_2O \longrightarrow H_3PO_4 + OH^-, \qquad (4)$$

which completes what we term the primary reaction sequence, consisting of steps (1) to (4).

This sequence depends critically on the initial displacement of the K^+ cation. If for example we consider the case of irradiation by ion bombardment, the sequence can be regarded as the immediate consequence of the impact of a single ion, and it could not be initiated if the surface were not being irradiated. But once step (4) has been completed, and has led to the formation of a hydroxyl radical, a secondary reaction sequence can begin and be cyclically repeated indefinitely without any further irradiation. This sequence, in which the hydroxyl plays a part analogous to its role in the leaching of alkali glasses (ref.6), relies on the existence of suitable catalytic sites, where the OH^- ion can dissociate the K.D.P. according to

$$KH_2PO_4 + OH^- \longrightarrow KOH + (H_2PO_4)^- \qquad (5)$$

This is followed by a reaction of the anion with a further water molecule (as in step 4), yielding a further hydroxyl ion, and thus permitting the reaction sequence to be sustained and the surface corrosion to proceed.

This simple reaction scheme leaves out of consideration a number of other possible reactions, such as for instance the part played by atmospheric CO_2, which doubtless leads to the formation of carbonates at some stage, although no direct evidence for this has so far been observed. The scheme does however adequately account for the chemical aspects of a number of the salient points listed at the beginning of this Section.

Thus the initial gas evolution, which in the target region covered by a contaminant film manifests itself through the formation of bubbles, is clearly the outcome of the primary reaction sequence. Its effects are on an atomic scale in the sense that one collision act produces only one hydrogen atom*. As a result there is no damage on a macroscale, which could degrade the surface from an optical point of view. This can be seen by referring back to figure (4), showing an exploded bubble. It is apparent that the substrate surface exposed by the explosion, which in this respect is representative of a large number of similar examples, does not exhibit any signs of corrosion.

The reason for this is that the irradiation has to play the dual role of displacing the K^+ cation as a first step in the primary reaction, and secondly to activate the catalytic sites necessary for the various other reactions to proceed. The target area in question had clearly been irradiated sufficiently to cause a substantial evolution of hydrogen, which also implies that active sites were available to catalyse the first reaction sequence. It will be remembered that the existence of these sites is deduced from the observation that hydrogen is not evolved everywhere on the uniformly irradiated surface, but that it appears only in a number of selected locations. On the experimental evidence one can however not exclude the possibility that the active sites involved here are simply naturally occuring crystallographic singularities, which need no further activation by irradiation. If this is the case, then, as far as the first reaction sequence is concerned, the bombardment is merely necessary to separate the K^+ cation from the K.D.P. molecule.

The position is different with respect to the secondary corrosion reaction. Here the experiments indicate that irradiation is indeed required to make the sites effective in promoting the reaction, and from the observation that the total number of sites activated increases non-linearly with the ion dose (see figure 10) we may infer that some sites are more difficult to activate than others. In particular, on the film covered target region of figure 4 the bombardment intensity, whilst adequate for initiating the primary sequence, appears to have

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* It must be borne in mind that one impinging ion can, through a collision sequence, produce a number of collision acts, each of which can cause a hydrogen atom to be evolved.

been insufficient for producing secondary reaction sites.

Turning now to the nature of the activation process, since the number of surface atoms in the K.D.P. lattice is of the order of $10^{15}/cm^2$, and since according to the experimental results only 7×10^{13} ions/cm^2 are required to activate all available sites, less than 10% of the atoms will on average have been hit by an impinging ion during activation. Collision cascades will ensure that the number of atoms indirectly affected is larger than this fraction, but nevertheless the bombardment is evidently too weak to cause changes in the large scale surface topography(ref.7). In constrast to the secondary reaction itself, its effect can only be on an atomic scale, resulting in the displacement of individual atoms from their normal position and in the creation of dangling bonds, which could help to catalyse the reaction.

Over a range of low dosage levels the experimental relationship between the number of sites S activated per cm^2 and the corresponding ion dose D can be roughly represented by a square law expression

$$S \approx cD^2 \tag{6}$$

where c is a constant.

Hydroxyl ions generated in the first reaction sequence will migrate to the centres activated according to equation (6) and initiate there the corrosion process. It is reasonable to expect the number n of OH^- radicals produced per cm^2 to be directly proportional to D at least to the first order, so that

$$n = c'D \tag{7}$$

from which follows that

$$\frac{n}{S} \propto \frac{1}{D} \tag{8}$$

According to equation (8) $\frac{n}{S}$ is large for small D, which implies that at low dosage levels the number of hydroxyl ions available at each activated site is larger than at a high doage, when more potential sites have been made effective. This explains the experimental finding (see figure 8) that in the weakly irradiated target region the relatively few rods formed are substantially larger than those in the intensely bombarded area where the rod density is much higher, but where the rod dimensions are significantly smaller.

The fact that the rods are preferentially aligned in the directions of the a and c axes (see figure 9) suggests that many of the active sites may be located at crystallographic ledges of the type indicated in figure 13 which represents schematically the arrangement of unit cells in the K.D.P. lattice. Dangling bonds will exist at such ledges; these could promote the corrosion reaction and, once it is initiated, could assist its preferential propagation along the ledge.

As was remarked earlier, alignment of the rods along the two principal axes occurs with approximately the same frequency. Since on the axis of the K.D.P. unit cell phosphorous atoms only are arranged, whilst in the c direction phosphorous and potassium atoms alternate (see inset figure 13), it appears that the direction in which the reaction tends to propagate depends to a larger extent on the geometrical than on the chemical aspects of the surface topography.

The saturation density of active sites ($9 \times 10^5/cm^2$) agrees roughly with reasonable values of dislocation densities, but it is very much smaller than the number of atoms/cm^2 located on the principal axes. The possibility therefore exists that the active sites arise at the intersection of dislocations with atomic ledges.

Other types of surface singularity can however evidently also be effective. Thus whilst the a and c axes are preferred directions, they are so not to the exclusion of all others. Not only does experiment reveal a background of apparently random rod orientation (figure 9), but an association has also been established between the creation of catalytic centres and certain types of mechanical surface damage. A detailed understanding of the nature of the active sites therefore requires further investigation.

5. EXPERIMENTS ON OTHER TARGET MATERIALS

The type of chemical reaction discussed in the previous Section is clearly not specific to K.D.P. In particular the first sequence, leading to the evolution of hydrogen and to the formation of hydroxyl radicals, is likely to follow the irradiation of a range of substances, which contain cations from the first or second column of the periodic table. The rate at which the reaction proceeds, and in particular whether it will lead to the secondary corrosion sequence, will however depend on the thermodynamic properties of the initial substance and the final products, on the surface mobility of the reactants, and presumably also on the crystallographic properties of the material, since these will control the possibility of creating suitable active sites.

With these considerations in mind, a number of substances, selected largely on the basis of ready availability, were subjected to an argon ion bombardment of 3 hours duration under standard conditions. The results of the experiments are summarised in Table 1, which shows that in all samples containing significant amounts of alkali metals or alkaline earths the primary reaction sequence was induced. But only in the first group of materials listed, all of which were chemically and crystallographically similar to K.D.P., did the ensuing secondary reaction proceed to the stage where corrosion of the entire irradiated surface took place. The behaviour of the materials in the first group was in fact practically indistinguishable from that of K.D.P. The same applied to the substances in the second group as far as the primary reaction was concerned, but in common with nearly all the remaining materials examined, they showed no evidence of the corrosion reaction.

In comparison with materials in the first two groups, those in the third group showed primary reaction rates slower by several orders of magnitudes, with evidence of gas evolution becoming apparent after typically about 5 hours, an exception being magnesium fluoride, for which the appearance of bubbles was delayed by more than one day.

Likewise in the range of glasses listed in group 4, gas evolution became detectable only after several hours exposure to the atmosphere. As judged from the size and surface density of the bubbles, the effect of irradiation in these materials diminished as the percentage of alkali in the glass became less, until ultimately in the case of a glass specially formulated for low alkali content (Corning 7059) no gas evolution was noticed over a period of 2 months. On the other end of the scale the behaviour of an alkali rich glass* was interesting in that it showed evidence not only of the primary, but also of the secondary reaction. This was in the form of corrosion spots reminiscent of those previously found in the early stages of K.D.P. corrosion, but in this case the reaction did not spread beyond a very localised stage, even after prolonged bombardment and after long periods of exposure to the atmosphere. Also, since a non-crystalline material was involved, the corrosion spots had neither the simple rod shape, nor did they exhibit the preferred orientation previously observed. These and other aspects of the irradiation of glass will be more fully reported elsewhere.

Finally Table 1 includes two organic materials, sugar and urea, selected because they contain neither alkali metals nor alkaline earths. As expected from our picture of the irradiation effect, not even the primary reaction was induced in these substances.

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* The exact composition of this soft glass, in the form of microscope slides of chinese manufacture, is not known.

6. CONCLUSION

Our experiments have shown that the irradiation effects described in the present work can occur in a wide range of substances, but it has also been found, that these effects will lead to very severe surface degradation only in a relatively small, though from a practical point of view important group of materials. For substances in this group surface finishing by ion polishing is not possible, unless means can be found for inhibiting the secondary reaction.

In the majority of cases however only the primary reaction will take place, and ion polishing appears feasible, since, as was stated earlier, this reaction causes surface changes only on an atomic scale, provided the irradiation is not excessive. This will certainly be so when the reaction is initiated by ion - as distinct from electron or photon bombardment, because in the former case sputtering will set an upper limit to the dose which any layer of the target material can receive before being eroded away. This maximum dose is given by the number of ions/cm^2 required to sputter off material to a depth equal to the ionic range.

In our experiments on K.D.P. this maximum dose was equivalent to a bombardment of only 20 to 30 seconds. After this time the micro-topography of the surface, and the concentration of disintegration products on it would be expected to be indistinguishable from that on a target subjected to bombardment for several hours. The fact that in the latter case a macroscopic erosion crater was formed would appear to be of no consequence in the present context, but whilst a long bombardment produced overall surface corrosion, the propagation of the process stopped at the localised rod stage when the irradiation lasted for a few seconds only. The reasons for this are not yet known, and a more detailed understanding both of the nature of the active surface sites, and of the manner in which the reaction is propagated from these sites, will require further investigation.

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TABLE 1.

	Primary reaction	Secondary reaction
KH_2PO_4 KD_2PO_4 CsD_2AsO_4	Gas bubbles form immediately after exposure to atmosphere.	Corrosion spots appear after several minutes and ultimately cover the whole eroded region.
NaCl Li Cl Cs Cl $Sr(NO_3)_2$ BaF_2	As above.	No corrosion observed.
$LiNbO_3$ $CaWO_4$ $CaMO_4$ MgF_2	First bubbles appear typically after several hours.	No corrosion observed.
Soda glass (High alkali content)	First bubbles after several hours. Number density much lower than for K.D.P.	Only localised corrosion spots observed.
Tempax (Na_2O 3.6% K_2O 0.4%)	Very few irregularly spaced bubbles after more than 5 hours.	No corrosion observed.
Vycor (Na_2O 0.2% K_2O 0.02%)	Comparable to Tempax, but bubble density less.	No corrosion observed.
Corning 7059 (less then 0.2% alkali)	No gas evolution observed.	No corrosion observed.
$CO(NH_2)_2$ $C_{12}H_{22}O_{11}$	No gas evolution detected.	No corrosion observed.

NOTE: A process is classed as "not observed" when undetected over a period of 2 months.

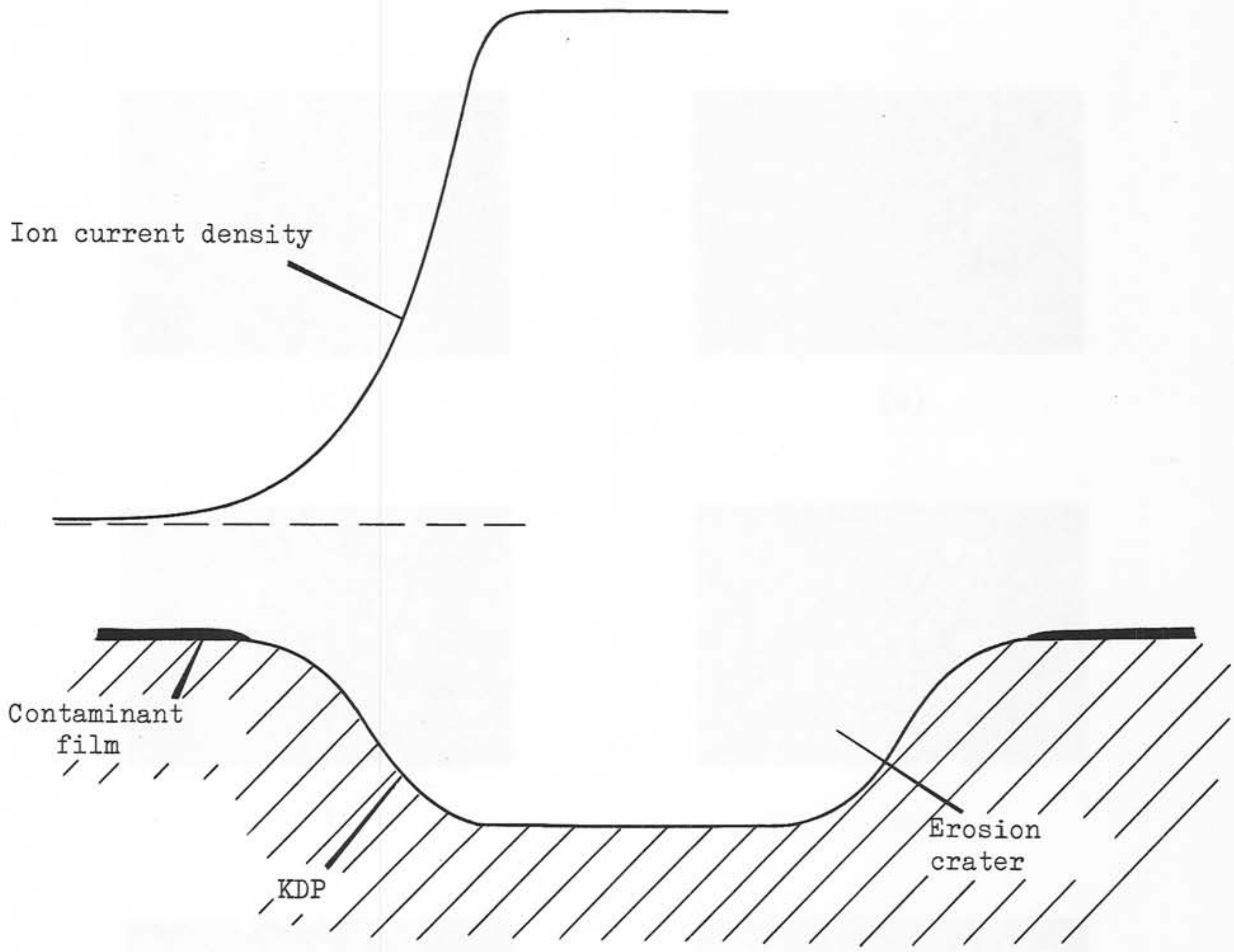


Figure 1. Ion erosion crater (schematic)

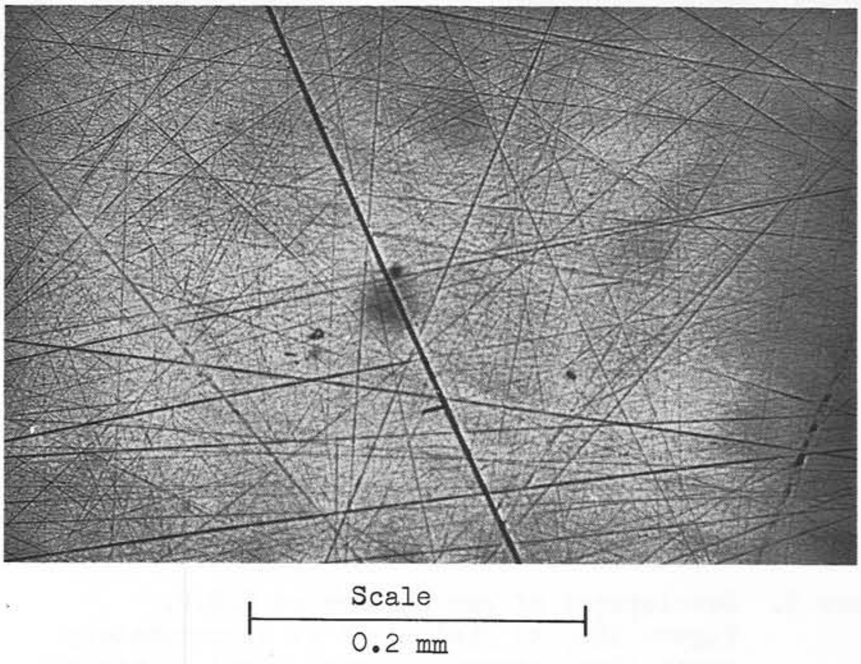
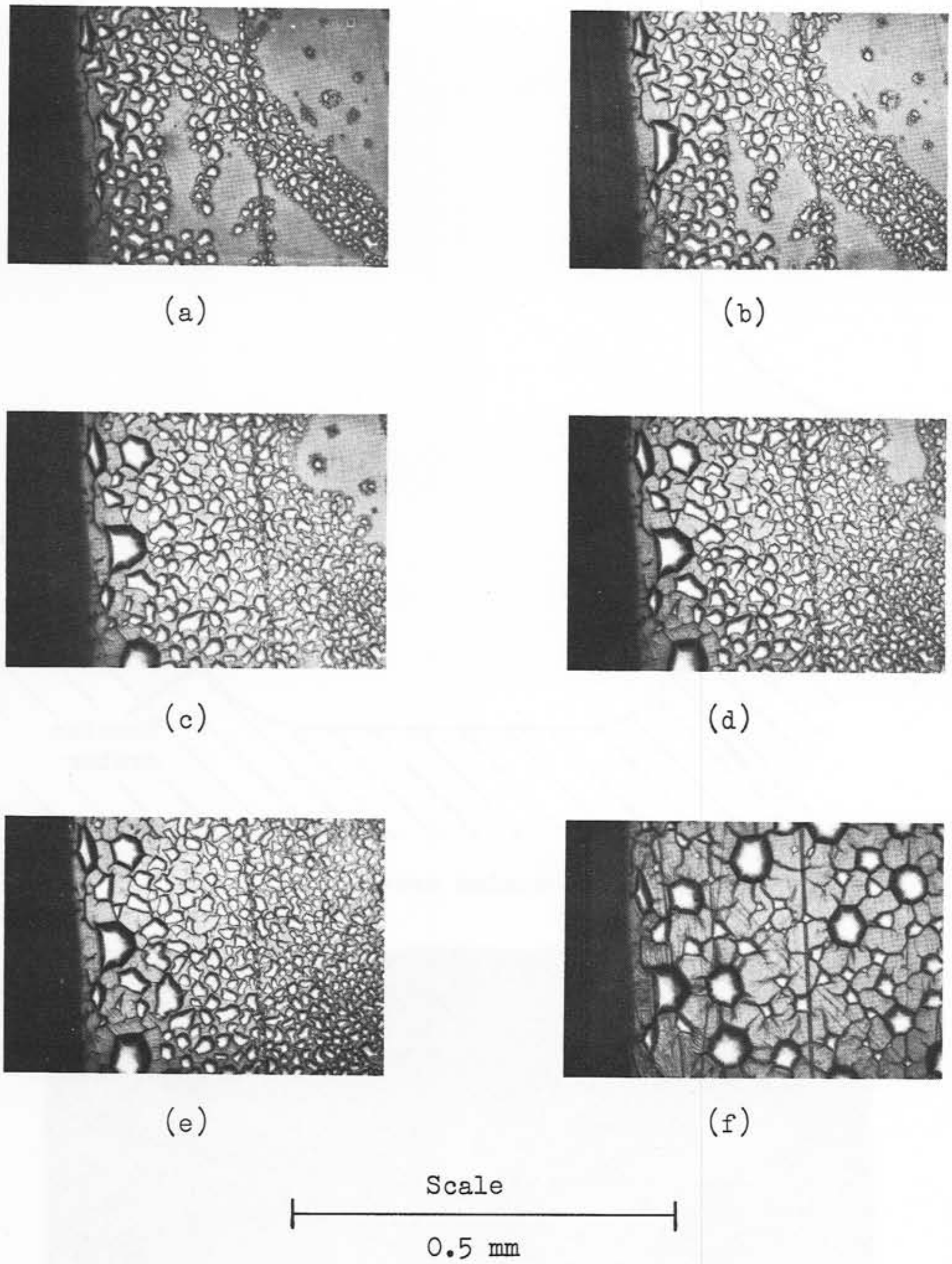


Figure 2. K.D.P. Surface before ion bombardment



(a) (b)

(c) (d)

(e) (f)

Figure 3. Development of gas bubbles on K.D.P. Figure 3(a) to 3(e) taken at approximately equal time intervals during first 30 minutes. Figure 3(f) taken after approximately one day.

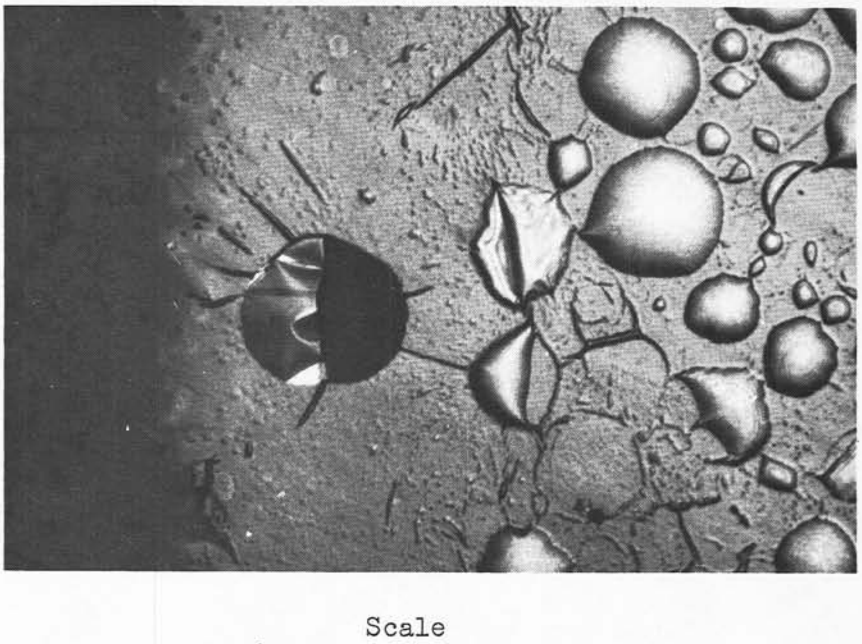


Figure 4. Exploded gas bubble

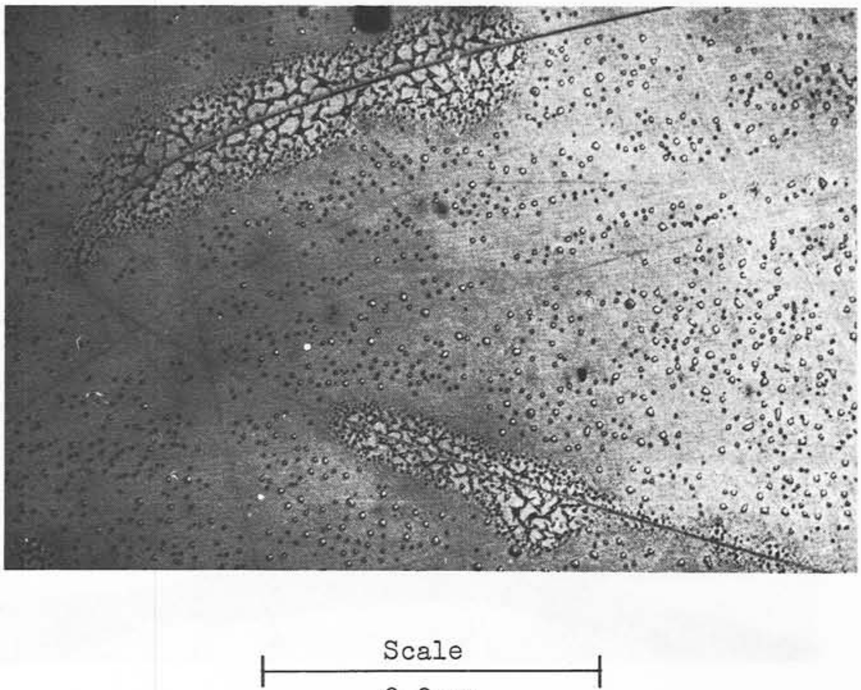
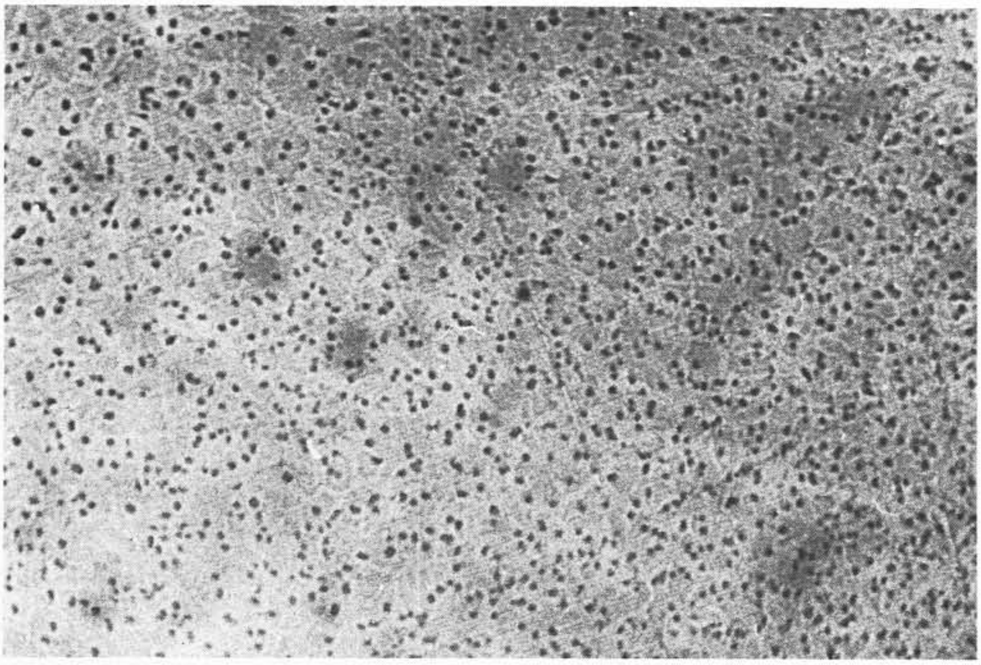


Figure 5. Gas evolution at surface scratch on K.D.P.



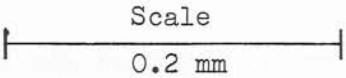
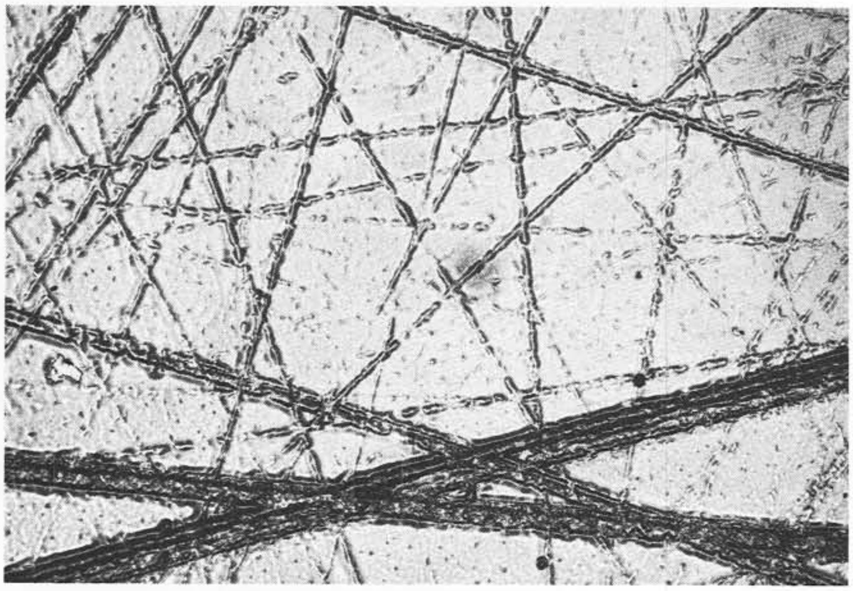


Figure 6. Corrosion spots on K.D.P.



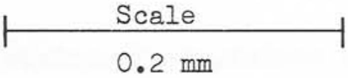


Figure 7. Overall corrosion on K.D.P.

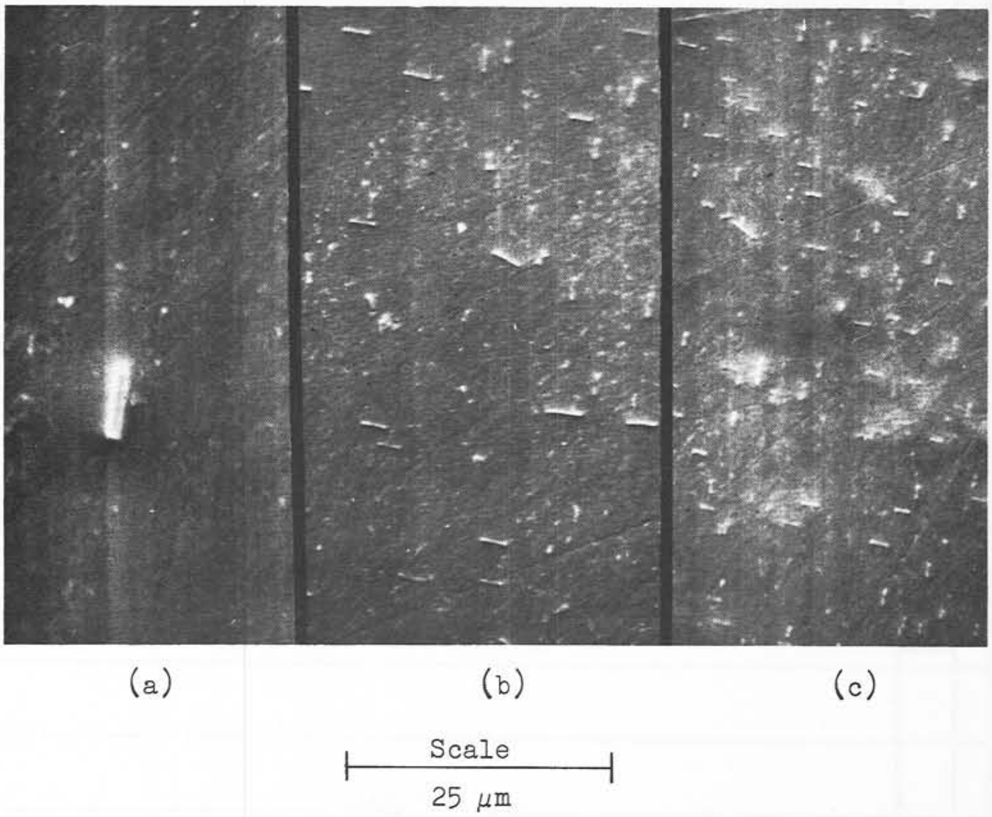


Figure 8. Rod shaped corrosion sites on K.D.P.
(a) High ion current density ($\geq 7 \times 10^{13}$ ions/cm^2)
(b) Intermediate ion current density
(c) Low ion current density ($\approx 1 \times 10^{13}$ ions/cm^2)

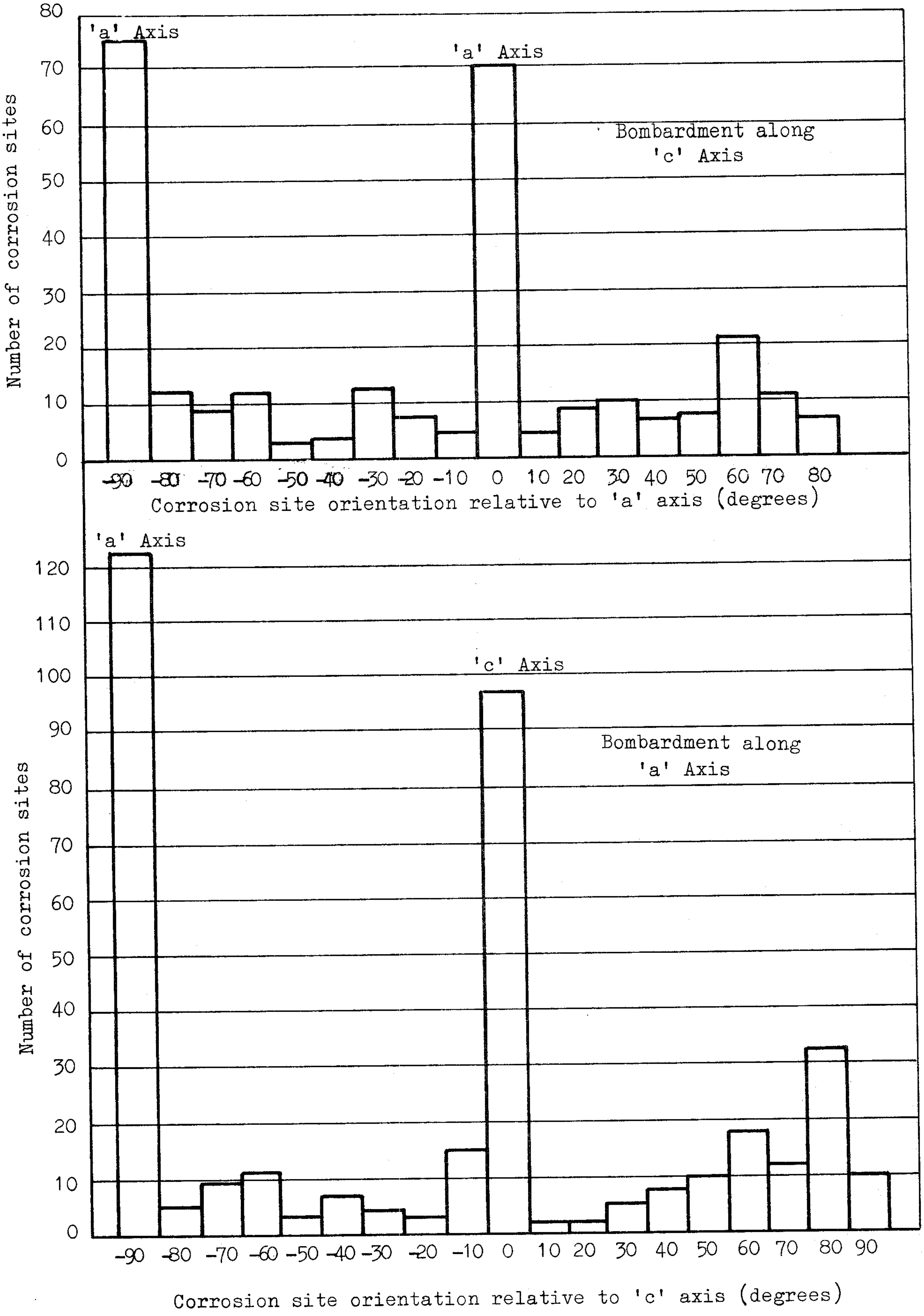


Figure 9. Orientation distribution of corrosion sites

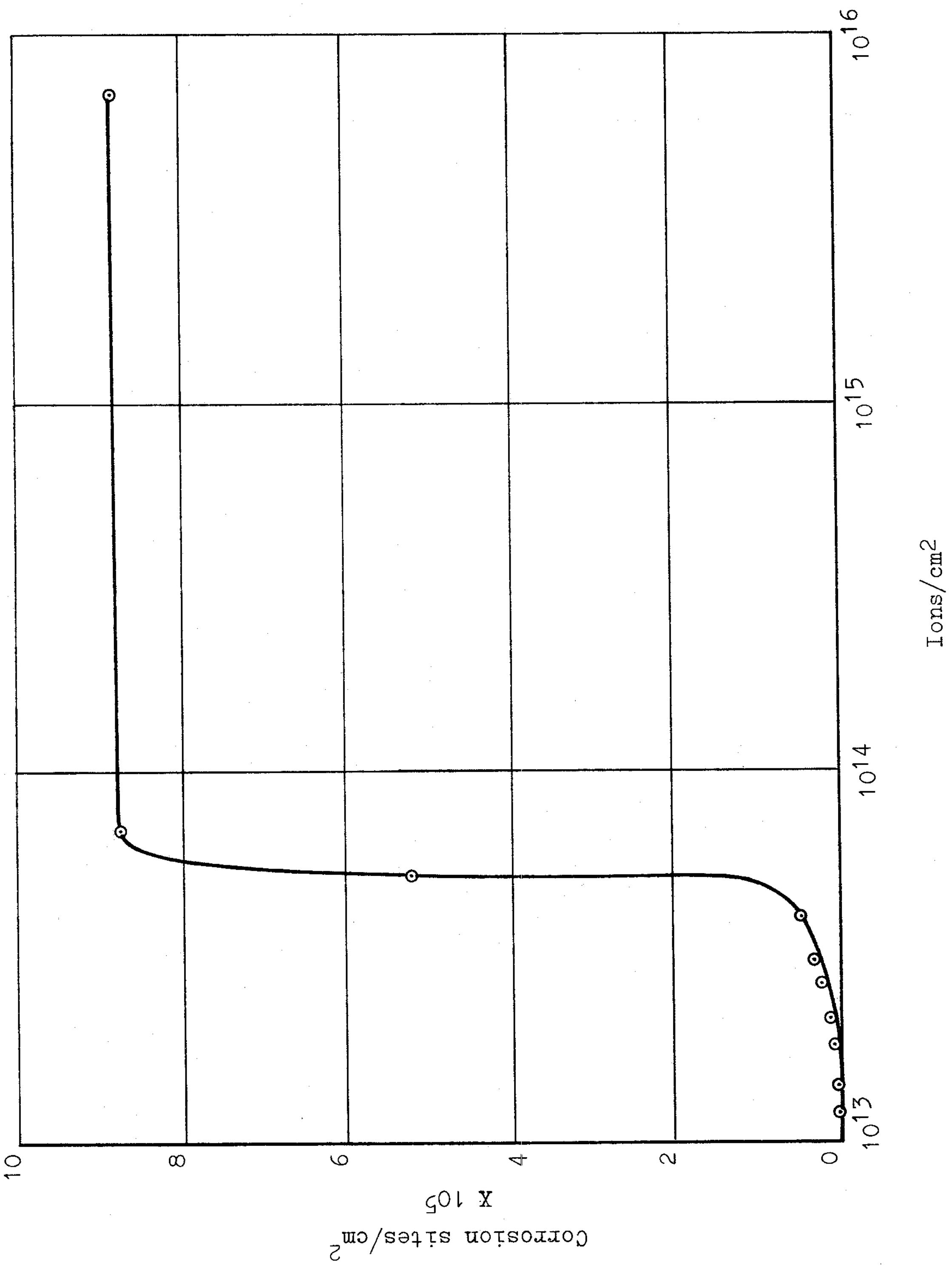


Figure 10. Number density of corrosion sites as a function of ion dose

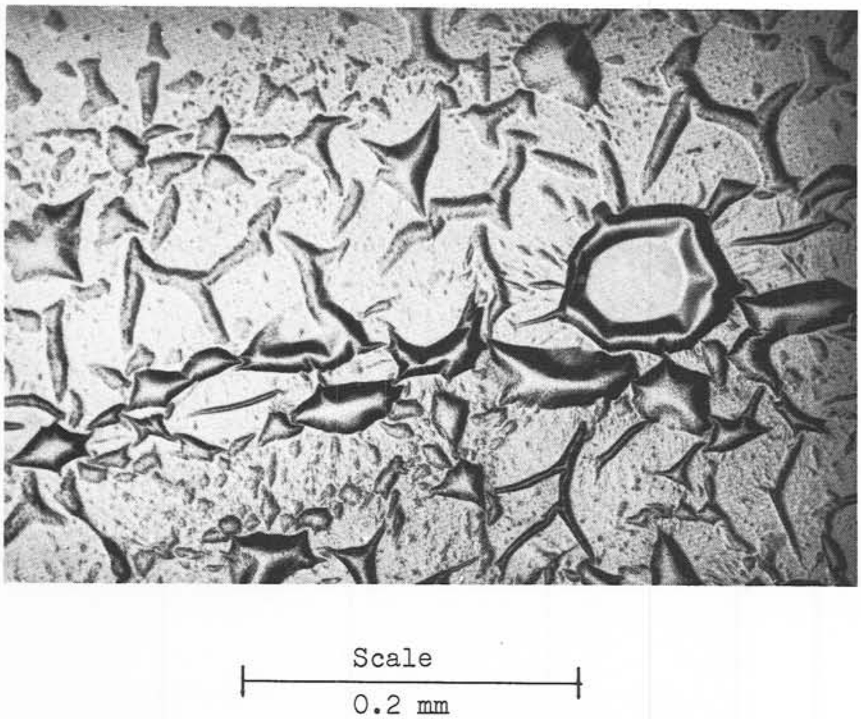


Figure 11. Gas bubbles produced on K.D.P. by electron bombardment

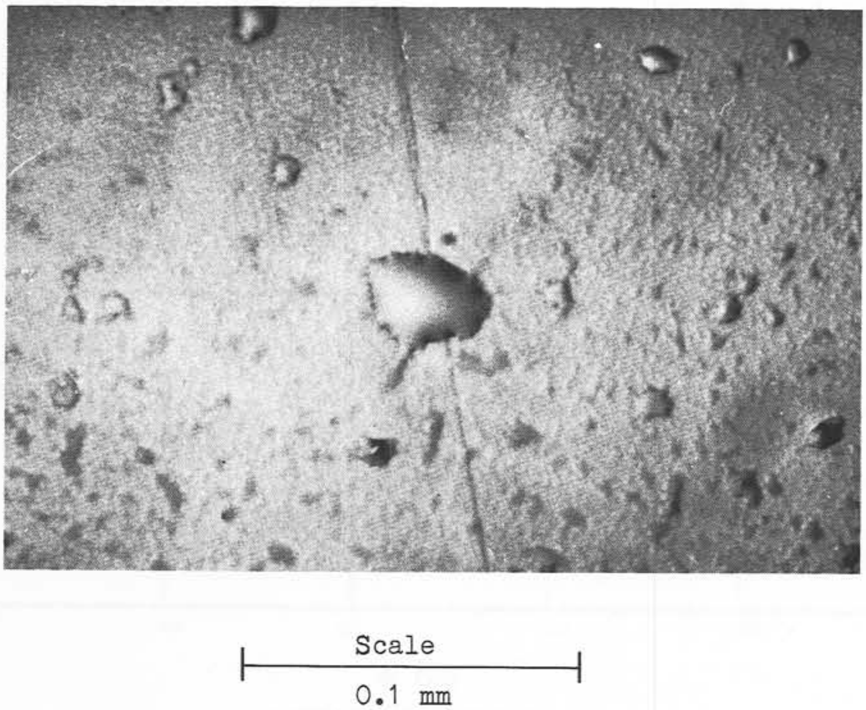


Figure 12. Gas bubbles produced on K.D.P. by CuK_{α} radiation

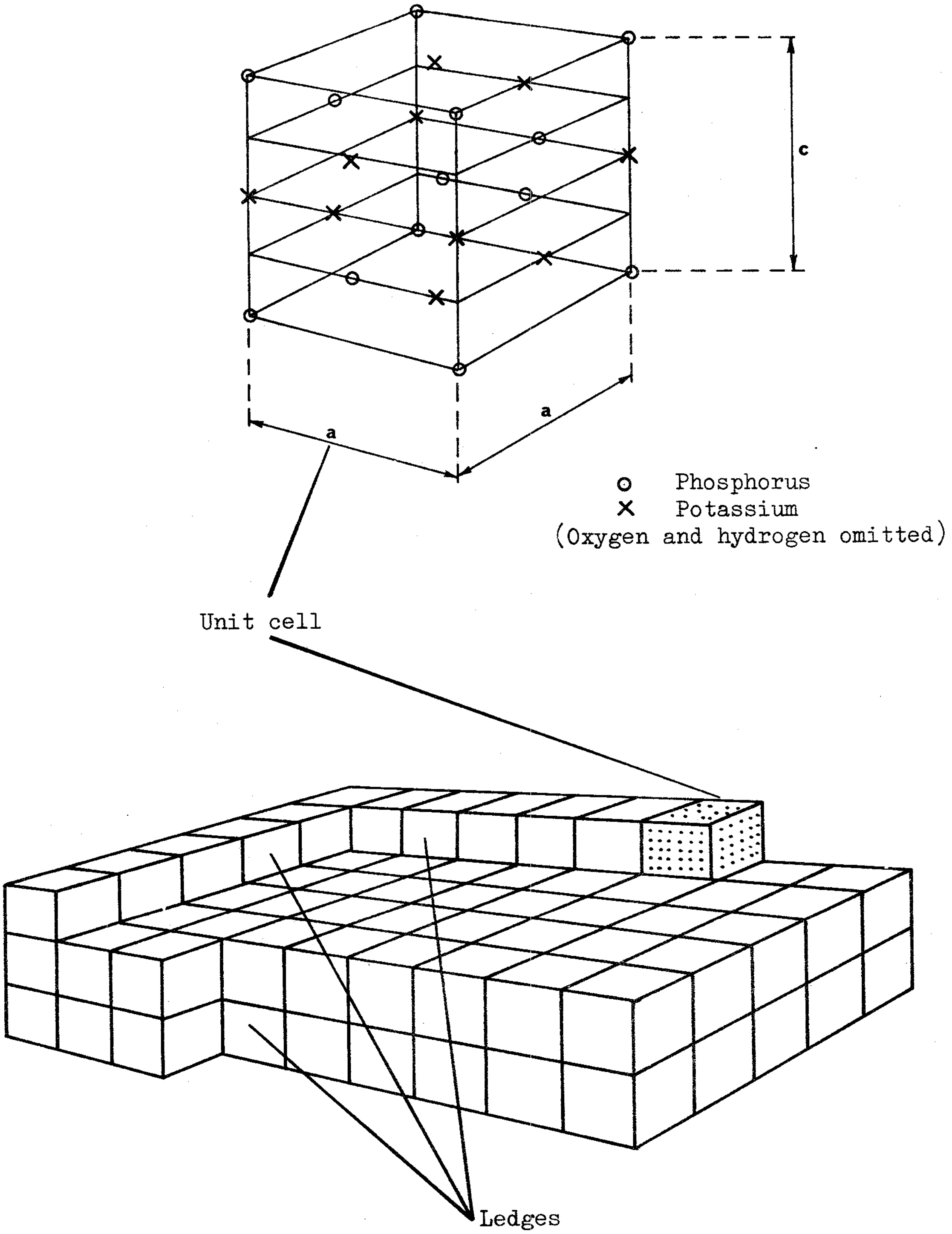


Figure 13. Ledges on K.D.P. crystal (schematic)

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Lasers	Optical equipment
Laser beams	Particle beams
Ion beams	Optical materials
Ion irradiation	Optical glass
Photosensitive glass	Argon

b. Non-Thesaurus Terms

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Experiments show that argon ion bombardment of many substances results in the chemical sensitisation of the irradiated surface. As a consequence, subsequent exposure to atmospheric water vapour causes evolution of hydrogen, and in certain cases leads to severe surface corrosion.

The effect occurs on targets containing elements from the first and second column of the periodic table, and therefore includes some widely used electro-optical materials.

A mechanism is proposed to explain the observed phenomena, and the possibility of ion polishing sensitive materials is discussed.

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