METALLURGICAL AND MATERIALS ENGINEERING

University of Pittsburgh
Pittsburgh, Pennsylvania 15261

(NASA-CR-165029) INVESTIGATION INTO THE ROLE OF NaCl DEPOSITED ON OXIDE AND METAL SUBSTRATES IN THE INITIATION OF HOT CORROSION Semiannual Report, 1 Apr. - 1 Oct. 1981 (Pittsburg Univ., Pa.) 24 p

N82-13217

Unclas
G3/26 08515

INVESTIGATION INTO THE ROLE OF NaCl DEPOSITED ON OXIDE AND METAL SUBSTRATES IN THE INITIATION OF HOT CORROSION

by

N. Birks

THIRD SEMI ANNUAL REPORT

ON

GRANT NO. NAG 3 - 44

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
CLEVELAND, OHIO

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PA 15261

PERIOD COVERED APRIL 1, 1981 - OCT. 1, 1981

INTRODUCTION

The purpose of this research program is to study morphological aspects of the conversion to Na_2SO_4 of NaCl deposits over the temperature range 500-700°C, in air with added SO_2 and H_2O.

The NaCl is deposited on a substrate (initially Al_2O_3 disks are used) at temperature in air containing SO_2 dried to about 1 ppm H_2O. Other components such as H_2O and CO_2 to represent the products of fuel combustion may be added as required.

Progress of the reaction is observed by withdrawing samples at various times and examining them under the scanning electron microscope using EDAX to assess the extent of chloride to sulfate conversion.

In the previous two reports on this project the construction and use of the apparatus was described together with the results of the initial experiments using Al_2O_3 substrate discs at 500 and 600°C.

These initial results show that the conversion to Na_2SO_4 proceeds directly on the sodium chloride surface as well as on the surrounding substrate due to evaporation of NaCl from the solid particle. The mechanism of this reaction could involve reaction in the vapor to produce Na_2SO_4 which then deposits, alternatively Na_2SO_4 could form directly on the substrate surface due to direct reaction there between the vapors NaCl, SO_2 and O_2.

These mechanisms are shown in Figure 1.

The present report concerns further experiments carried out to check the reproductability of results obtained so far, to increase the temperature range investigated to 650 and 700°C allowing the effects of liquid phase formation to be observed.

EXPERIMENTAL TECHNIQUE

This has been described in the previous two reports and consists, briefly, of depositing a sample of ground and sized, dry, sodium chloride on the surface of a substrate which is held at temperature in the hot zone of the furnace. The furnace atmosphere is air with a predetermined SO_2 content, the gases are thoroughly dried to exclude moisture using P_2O_5 or $MgClO_4$. After a predetermined time the substrate sample is withdrawn and transferred to a dessicator and subsequently examined using SEM-EDAX.

RESULTS

As in experiments reported perviously, the NaCl was ground in a dry box using an agate pestle and mortar and screened between 170/200 mesh to give approximately 100μm particles. The main content of this report concerns reactions occuring at 650 and 700°C, at these temperatures samples were exposed for 10, 30, 60, 120 and 240 minutes as found to be satisfactory in previous experiments.

Several experiments were run at 500 and 600°C to compare with identical experiments run previously. The results generally confirmed those obtained previously giving identical trends in morphological development. The absence of rate data during this part of the program prevented a strict comparison on the basis of reaction kinetics. The confirmation of the reproductability of the results allowed experiments to be extended to the higher temperatures of 650 and 700°C. Several preliminary runs with 1% H_2O in the atmosphere were also made. These results are reported in detail below.

According to the $NaCl$-Na_2SO_4 phase diagram by Fedorov and Bol'shakov[1] shown in Figure 2. There is a eutectic at about 625°C and 65 mol. % Na_2SO_4, liquid phase formation is therefore to be expected in this series of experiments.

Results at 650°C   Air + 0.99% SO_2

(a) 10 minutes

The specimen particle corners are rounded and coated in a sulfate scale as shown in Figure 3. Although the substrate is also covered by a deposit of sodium sulfate with perhaps a trace of sodium chloride. There is a region immediately surrounding the particle that shows no evidence of deposition at all. This area is referred to subsequently as the "halo" zone.

(b) 30 minutes.

The specimen particle continues to display rounded corners and is somewhat smaller than at 10 minutes due to evaporation of NaCl. The main features of interest however are on the surrounding substrate surface as shown in Figure 4. As at 10 minutes a halo zone has developed around the original NaCl particle and SEM-EDAX now shows this to be covered by a deposit of Na_2SO_4 only. Outside this zone the general area of the substrate is covered with a dendritic scale which has evidently been liquid at temperature, has solidified when the specimen cooled and also shows evidence of long straight cracks having developed in this area only. SEM-EDAX showed that definite response to Cl, S and Na was evident, rather surprisingly a strong response to aluminum also appeared, either by penetration of the x-rays through the surface layer or due to the presence of Al in the surface layer due to reaction. This will be investigated layer due to reaction. This will be investigated later when the deposits are removed from the sample for analysis. Apart from the possible presence of aluminum the dendritic part of the substrate surface cover appears to be the Na_2SO_4 - NaCl liquid solution which, at 650°C, may range from 55-70 mol.%, Na_2SO_4 according to Figure 2.

(c) 60 Minutes

Details of the reaction morphology confirm those reported above for 30 minutes.

(d) 240 Minutes

After 4 hours the sodium chloride particles have completely vaporized, leaving the halo region of dense apparantly non-porous cover which SEM-EDAX results indicate to be Na_2SO_4 only. In the center of this region is a looser Na_2SO_4 deposit which was formed directly on the NaCl particle and now remains after the majority of the NaCl has vaporized. Outside the halo region, in the general substrate surface, the dendritic deposit appears to be more porous, also the SEM EDAX indicates little or no chlorine from this area but a large Al response. The Al response from this general area is much larger, compared with the surfur response, than in the halo region. Again, this may indicate dissolution of Al in the Na_2SO_4 - NaCl liquid or may reflect simply the more porous nature of the scale in the general area. This will be checked out in later solubility tests. These features are seen in Figure 5.

An interesting feature found on samples exposed for 4 hrs. can be seen in Figure 5. That is the growth on the liquid or dendritic regions of solid nodules apparently of Na_2SO_4. These are too small to be identified beyond doubt.

Following the above series of experiments at 650°C using a dry atmosphere, it was decided to examine the effect of adding moisture to the atmosphere. The results are described below.

Results at 500°C Air + 0.2% SO_2 + 1.0% H_2O.

(a) 10 minutes

The particles remain angular and formation of sulfate is indicated by EDAX response on both salt particle and substrate. A new feature is the development of whiskers, apparantly of SiO_2, on the substrate.

(b) 30 minutes and 60 minutes

Both conditious show denser growth of sulfate on both particle and substrate.

(c) 240 minutes

The sulfate growth on the particle is dense with the appearance of individual sulfate growths being well sintered together, or having been molten. This impression is confirmed by the presence of dendrite-like spangles on the surface - this sample will be examined further. The above details are shown in Figure 6.

The presence of water vapor has introduced new factors involving the development of silica needles, resulting from the presence of the silica reaction tube. This feature is without doubt, simply an artifact, whose presence however indicates that the water vapor may introduce extra vapor species to the system that could account for the more compact or consolidated scale shown in Figure 6.

Results at 600°C   Air + 0.2% SO_2 + 1.0% H_2O

(a) 10 minutes

Coverage of the NaCl article appears to be well advanced and uniform indicating that the reaction has started rapidly. The start of halo formation can be seen in Figure 7.

(b) 30 minutes

The salt particle has rounded contours with a very compact scale once again, with the appearznce of being well sintered or having been liquid EDAX analysis does not show any chlorine response which is surprising in view of the appearance of the scale but confirms the possibility of enhanced surface diffusion or gas phase participation introduced by the presence of moisture.

Figure 8 shows these features and also indicates the beginning of halo formation. The sulfur content being high within the halo region and falling off further from the particle.

(c) 60 minutes

The halo area is well defined showing a heavy deposit of sulfur rich, apparantly Na_2SO_4, scale. The overall appearance is similar to that seen at 650°C in the absence of moisture after 4 hours with evidence of considerable NaCl vaporization. The features are shown in Figure 9.

(d) 240 minutes

Features simply confirm those described for 30 minutes.

Results at 700°C Air + 0.2% SO_2 + 1% H_2O

(a) 10 minutes

Very rounded edges, heavy deposits around the particle sites and the absence of large particles are evidence of rapid vaporization as shown in Figure 10. The halo around the original particle sites is rich in sulfur with no chlorine response, however both sulfur and chlorine are formed outside the halo region. The surface of the surviving salt particles is covered in a fairly dense layer that appears to have been liquid, see Figure 11c. Further growth of nodular appearance has occurred on top of this dense layer and probably represents the reaction of NaCl in the liquid to form Na_2SO_4.

(b) 30-60 minutes

Both conditions show very little evidence of the original salt except where a bulkier sulfate deposit is seen, as in Figure 11. The whole area is covered with secondary growth nodules of Na_2SO_4 formed from the Na_2SO_4 - NaCl liquid that forms in the early stages.

(c) 240 minutes

Very similar appearance to 30/60 minutes with no remaining trace of NaCl to be detected.

DISCUSSION

The points requiring discussion are (1) the formation and role in the reaction of the liquid mixed salt phase (2) The increasing role of NaCl vaporization at the higher temperatures (3) the role of moisture in the gas.

650°C Air + 0.99% SO_2

During the early stages of the reaction (10 minutes), the halo zone develops with no evidence of deposition, presumably due to the increased NaCl evaporation, at this stage. This feature is shown in Figure 3, together with the outlying areas of the substrate which is covered with a deposit of Na_2SO_4. These conclusions are suported by the EDAX responses for the two areas indicating absence of Na, S and Cl in the halo region but presence of Ni and S only in outlying regions.

As the reaction progresses the deposition continues showing, after 30 minutes, the presence Na_2SO_4 in the halo area and the development of a liquid Na_2SO_4 - NaCl solution in the outlying region. This latter feature results from the strong NaCl evaporation producing a partial pressure of NaCl in the gas phase high enough for some to survive reaction on the gas phase and to deposit subsequently on the substrate causing the eutectic liquid to form. The resulting microstructures are shown in Figure 4 together with EDAX readings supporting the above mechanism. Should the original salt particle become coated with Na_2SO_4 - NaCl liquid at this stage the rate of evaporation of NaCl will fall. Thus allowing Na_2SO_4 to deposit in the halo region as observed.

After four hours the salt particles have evidently completely evaporated thus providing no further source of NaCl in the gas phase to sustain the liquid formed in outlying substrate regions. Consequently the NaCl in the liquid deposit begins to react with the SO_2 and O_2 in the gas phase to form Na_2SO_4. Thus eliminating NaCl from the liquid deposit which consequently converts to solid Na_2SO_4 only. The intermediate stage in this process is shown in Figure 5 where chlorine is seen, from EDAX results, to be in low concentrations or absent from both areas.

It is not clear how much significance should be attached to the high Al readings shown by EDAX for these areas. This could be due to penetration of the characteristic X-rays through the deposits alternatively especially where the liquid phase is formed. There is the possibility of reaction to form sodium aluminate in which case the EDAX response from the outlying areas could indicate the incorporation of Al into the liquid deposit. This will be investigated further when the specimens are sectioned and the deposit is removed.

<u>500°C Air + 0.2% SO_2 + 1.0% H_2O</u>

The development of silicon-rich needles referred to earlier is regarded mainly as an artifact due to the presence of silica in the apparatus. It does however suggest that the presence of moisture in the atmosphere may introduce extra vapor species into the system. This is also suggested, at this temperature by the more compact, sintered, appearance of the coating formed on the NaCl crystals, an additional feature introduced under these conditions are the spangles that appear on the surface of the deposit shown in Figure 6. So far these have not been identified and this aspect required further study. The EDAX results from the coating formed on the NaCl crystal shows a low response for Al. This must also be born in mind when considering the formation of additional vapor species in the presence of moisture in the atmosphere, the Al response may also be connected with the presence of the spangles.

600°C Air + 0.2% SO_2 + 1.0% H_2O

The morphologies at early stages of the reaction, after 10 minutes, Figure 7 and after 30 minutes, Figure 8 shows that the reaction starts rapidly and the salt particles have rounded contours indicative of heavy evaporation. Halo formation is evidently starting after 10 minutes and is seen to be well developed and sulfur rich after 30 minutes. The overall appearance of this zone after 60 minutes, Figure 9, is very similar to that at 650°C after 4 hrs in air + 0.99% SO_2, Figure 5. Once again the indication is that the presence of H_2O in the atmosphere speeds up the reaction somewhat, possibly through the introduction of additional vapor species. There is no proof available so far for these suggestions and it is particularly desirable to obtain some means of measuring the reaction kinetics. This will be difficult to achieve by weight gain measurements since excessive interference from NaCl evaporation will cloud the results. However, later in this investigation, sectioning of samples may provide some evidence in terms of deposit thickness. So far the samples have not been sectioned or otherwise subjected to destructive analysis until full morphological examination of the surface features has been completed. The specimens are being retained under moisture-free cover for this purpose.

700°C Air + 0.2% SO_2 + 1.0% H_2O

Under these conditions the deposit on both salt particle and substrate is clearly liquid and the salt particle has evaporated strongly such that after 10 minutes only small particles remain for examination. These features are seen in Figure 10. So much NaCl has evaporated even after 10 minutes that the original liquid Na_2SO_4 - NaCl deposit has begun to react to form Na_2SO_4 solid graphs. After 4 hrs., as seen in Figure 11, this process is virtually complete and the substrate surface is covered in solid Na_2SO_4.

GENERAL DISCUSSION

Discussion on the role of H_2O in the atmosphere is, at this stage, mainly conjecture until more information is obtained, either from the literature or from further experiments concerning the generation of complex vapor species. In contrast the effect of temperature through its strong effect on the vapor pressure of NaCl is very clear, as is the effect of formation of the Na_2SO_4 - NaCl liquid eutectic above 625°C as shown in Figure 2.

The mechanism shown in Figure 1 for temperatures up to 600°C is modified in Figure 12 to account for the above features.

Initially (Figure 12a) strong evaporation of NaCl occurs and results in the deposition of Na_2SO_4 beyond the "halo" zone. This reaction probably takes place in the gas phase with direct deposition or condensation of Na_2SO_4 initially. NaCl from the gas phase then reaches these deposits and forms the Na_2SO_4 - NaCl eutectic liquid. Na_2SO_4 formed in the gas phase similarly deposits within the 'halo' zone which is under the 'trajectory' of most of the NaCl that evaporates from the particle as it is turned by the effect of the gas flow. This will continue until the NaCl of the original particle is exhausted either due to evaporation or to direct reaction to form Na_2SO_4 on the particle surface.

When this stage is reached and there is no further supply of NaCl to the atmosphere, the NaCl in the eutectic liquid then reacts with the atmosphere to form Na_2SO_4. This results in solidification of the deposits which eventually are comprised of Na_2SO_4 entirely. (Figure 12b)

During the stage that a liquid deposit exists on the substrate surface it is conceivable that some Al_2O_3 may dissolve from the substrate. This possibility will be investigated further.

The development of the observed fractures may well depend upon the interplay between the direction of evaporation of NaCl and the direction of the gas flow. Reversing the gas flow may produce quite different results so far as deposition in concerned. Changing the gas flow velocity is also expected to affect the morphology of the deposit. These aspects will be followed up after completion of the next group of experiments involving higher moisture contents and higher temperatures.

Conclusions

The presence of H_2O in the atmosphere appears to increase the reaction rate and produce a denser deposit. This effect is difficult to evaluate.

The presence of H_2O may also involve extra vapor species that affect the reaction mechanism. This requires further research into the literature and further experimentation.

As the temperature increases the higher rate of evaporation of NaCl causes more deposit to be formed on the general surface of the substrate and less on the actual particle.

At temperatures above 625°C, the formation of a liquid Na_2SO_4 - NaCl eutectic on the substrate provides a means for reaction with Al_2O_3 and its dissolution with the liquid phase. It is not established with certainty that this occurs and the possibility will be examined.

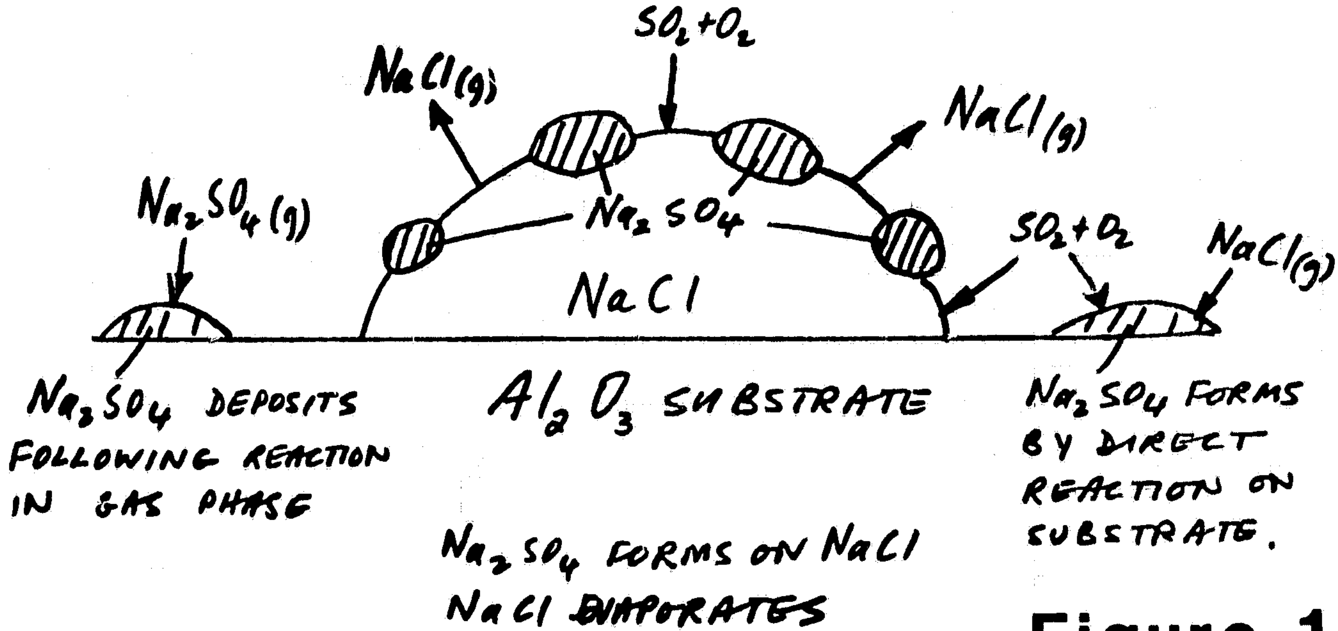


Figure 1

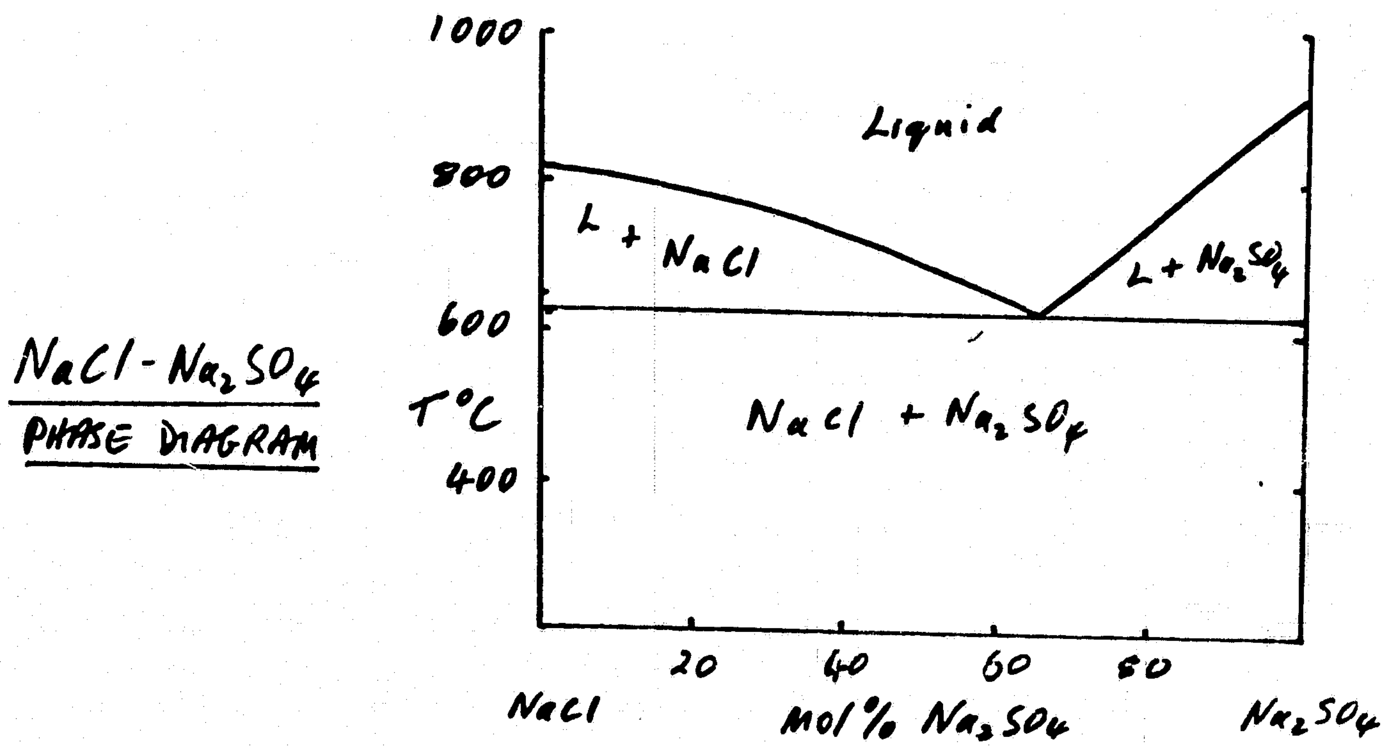
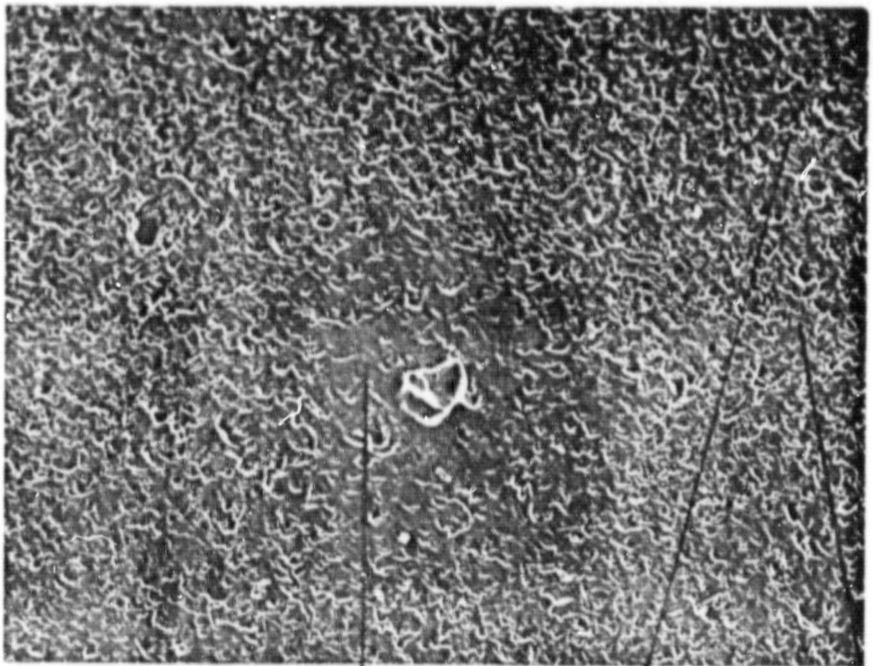
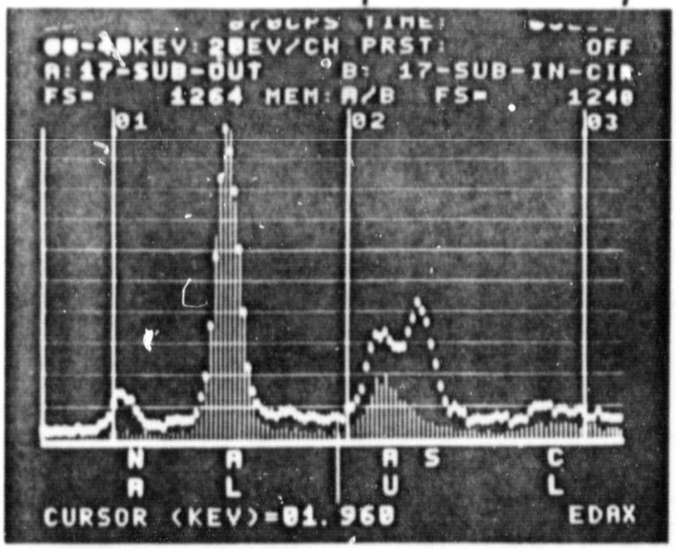


Figure 2

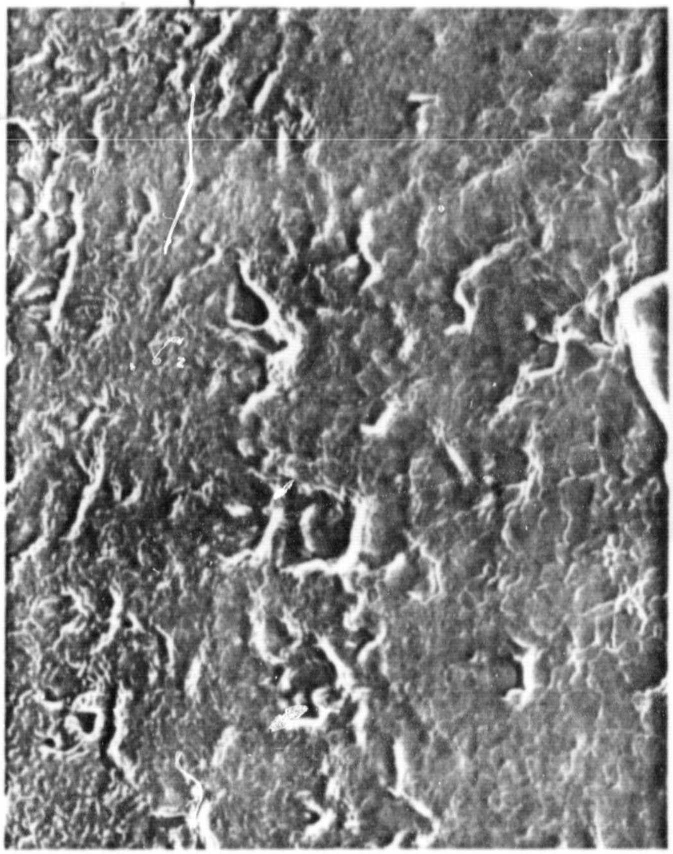


a.) X 750

b.) X 1750

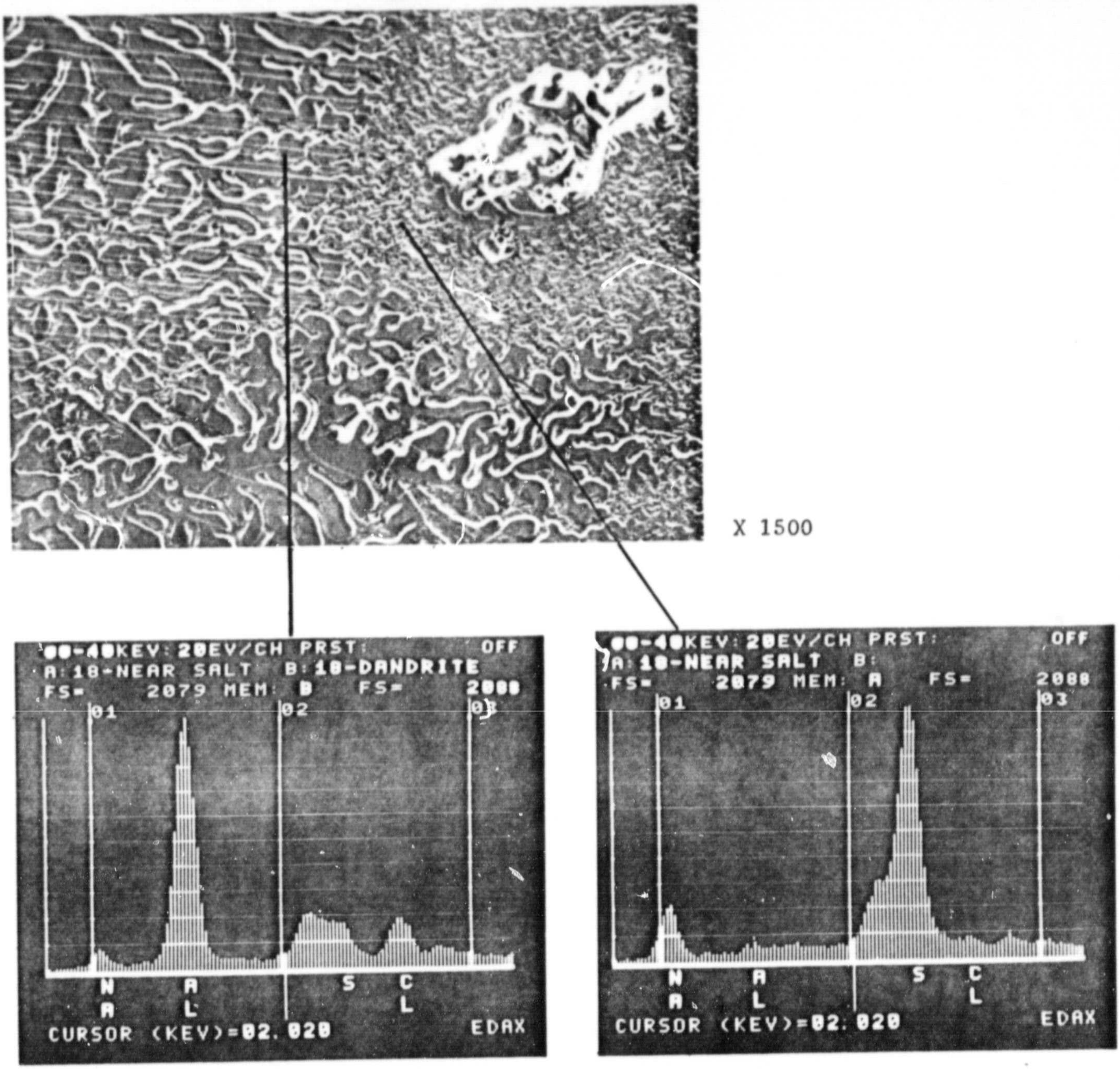


EDAX OF AL_2O_3 SUBSTRATE; COMPARES ELEMENTAL COMPONENTS OF THE INNER AND OUTER RINGS.



AL_2O_3 SUBSTRATE EXPOSED TO AIR AND 0.99% SO_2 AT 650^0 C. FOR 10 MINUTES.

Figure 3

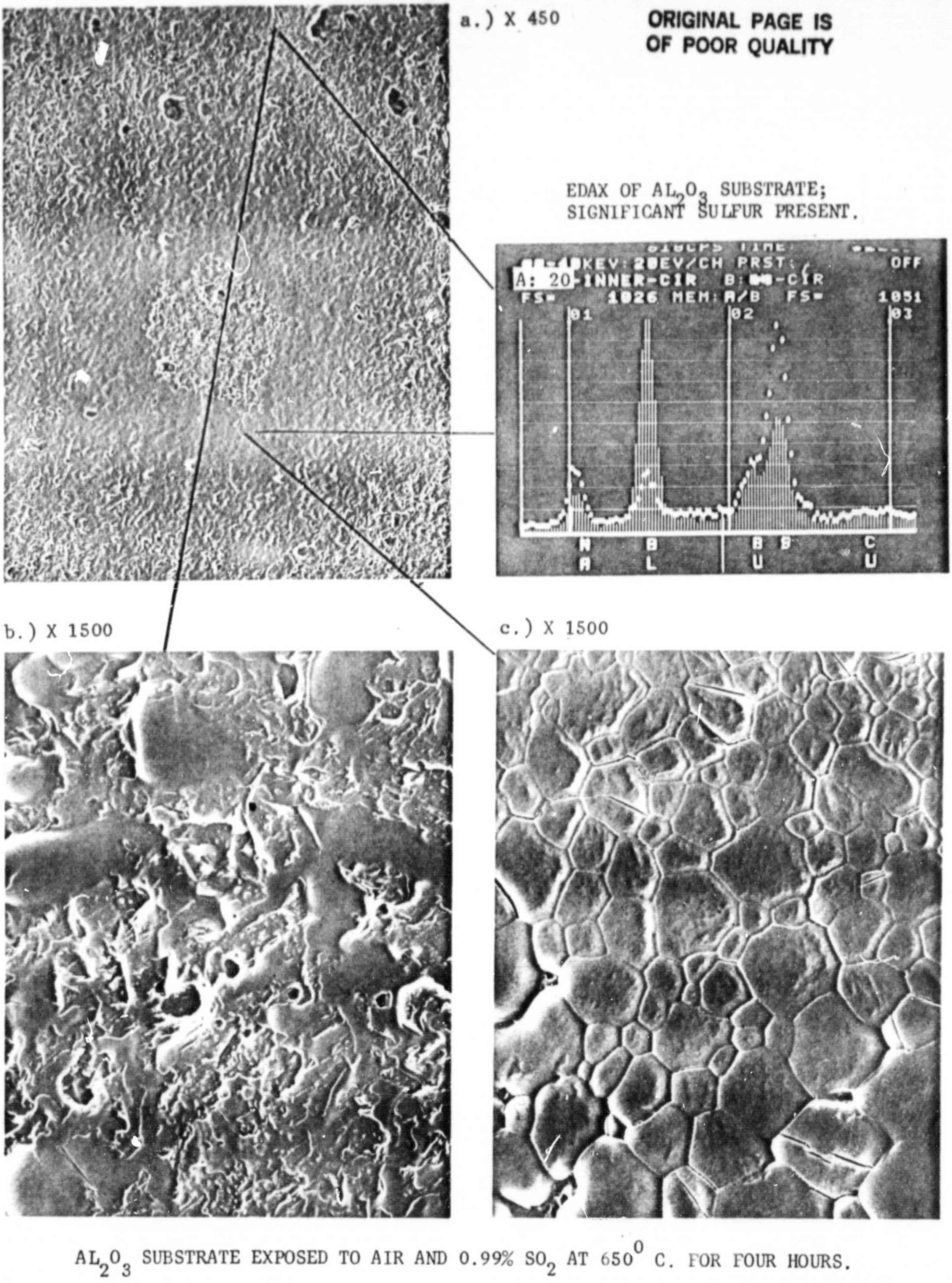


EDAX OF AL_2O_3 SUBSTRATE
IN THE DENDRITE AREA;
HIGH AL PEAKS.

EDAX OF AL_2O_3 SUBSTRATE
NEAR THE NACL PARTICLE;
HIGH SULFUR CONTENT NOTED.

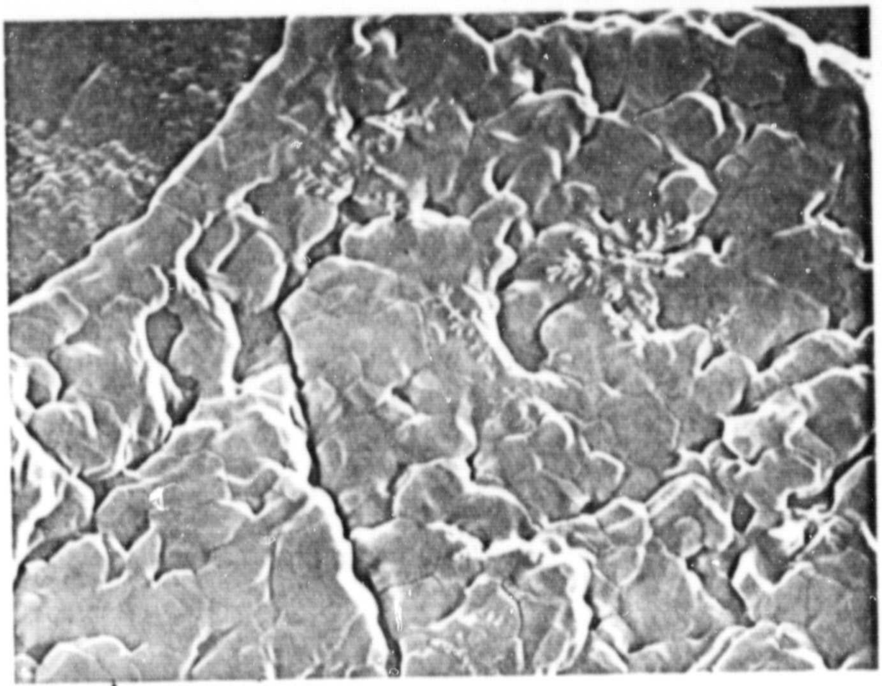
AL_2O_3 SUBSTRATE IN THE VICINITY OF THE NACL PARTICLE AFTER EXPOSURE TO AIR AND 0.99% SO_2 AT 650^0 C. FOR 30 MINUTES.

Figure 4



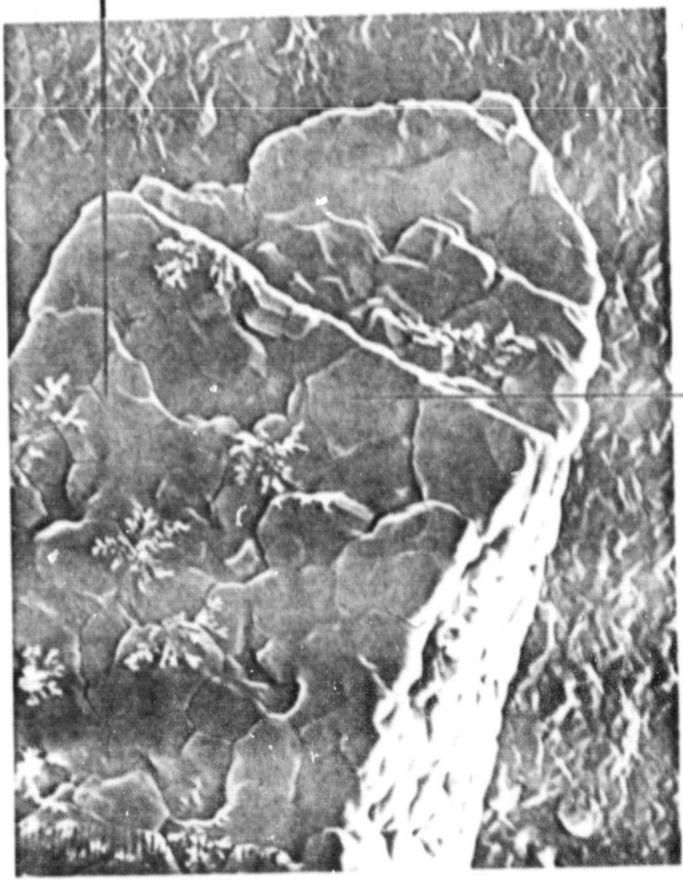
AL_2O_3 SUBSTRATE EXPOSED TO AIR AND 0.99% SO_2 AT 650^0 C. FOR FOUR HOURS.

Figure 5

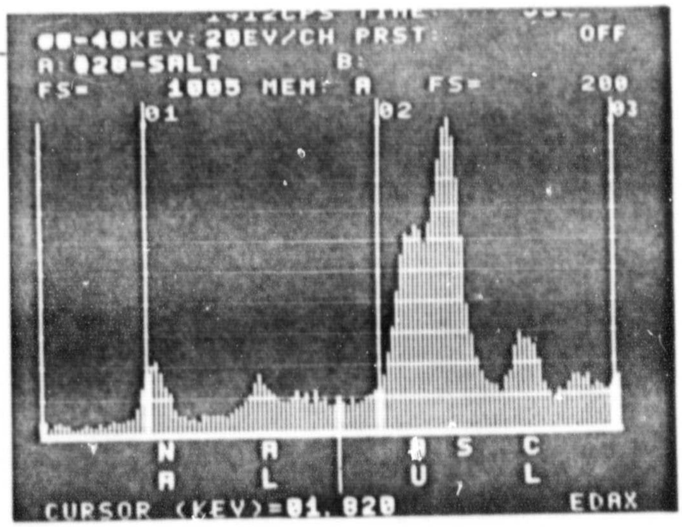


a.) X 1400

b.) X 750

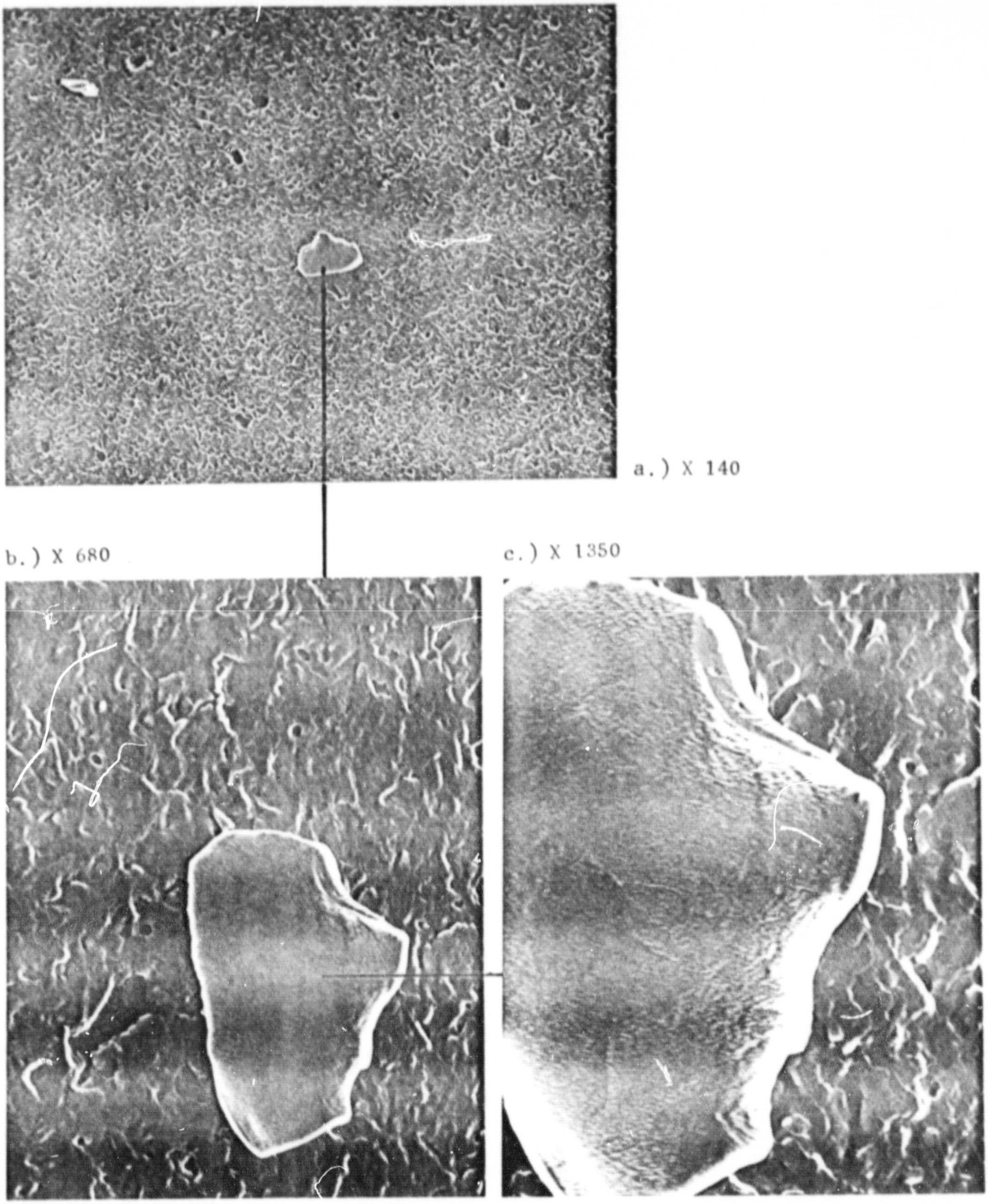


EDAX OF NACL PARTICLE;
SIGNIFICANT SULFUR PEAK.



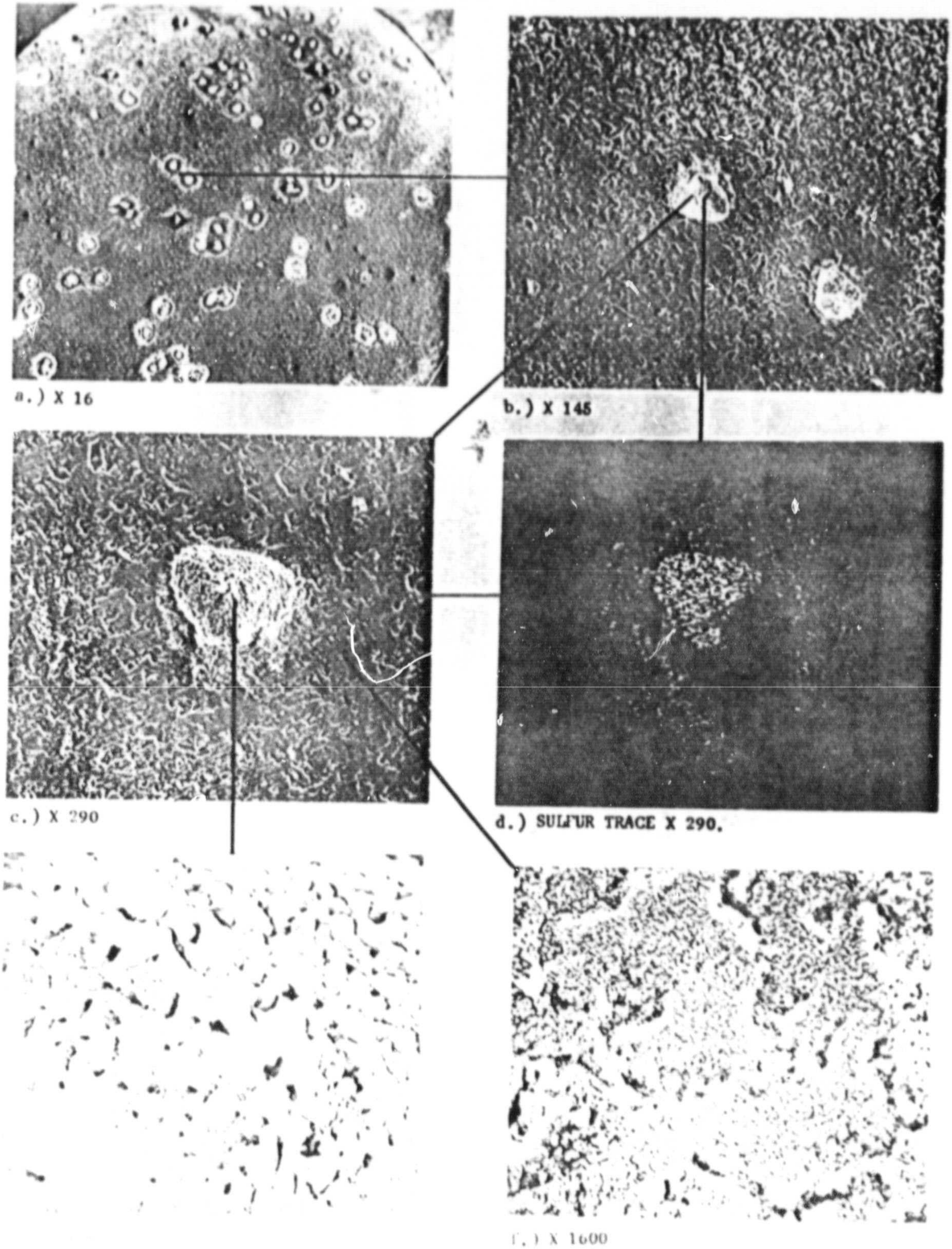
NACL PARTICLE EXPOSED TO AIR, 0.2% SO_2 AND 1.0% H_2O AT 500^0 C. FOR FOUR HOURS.

Figure 6



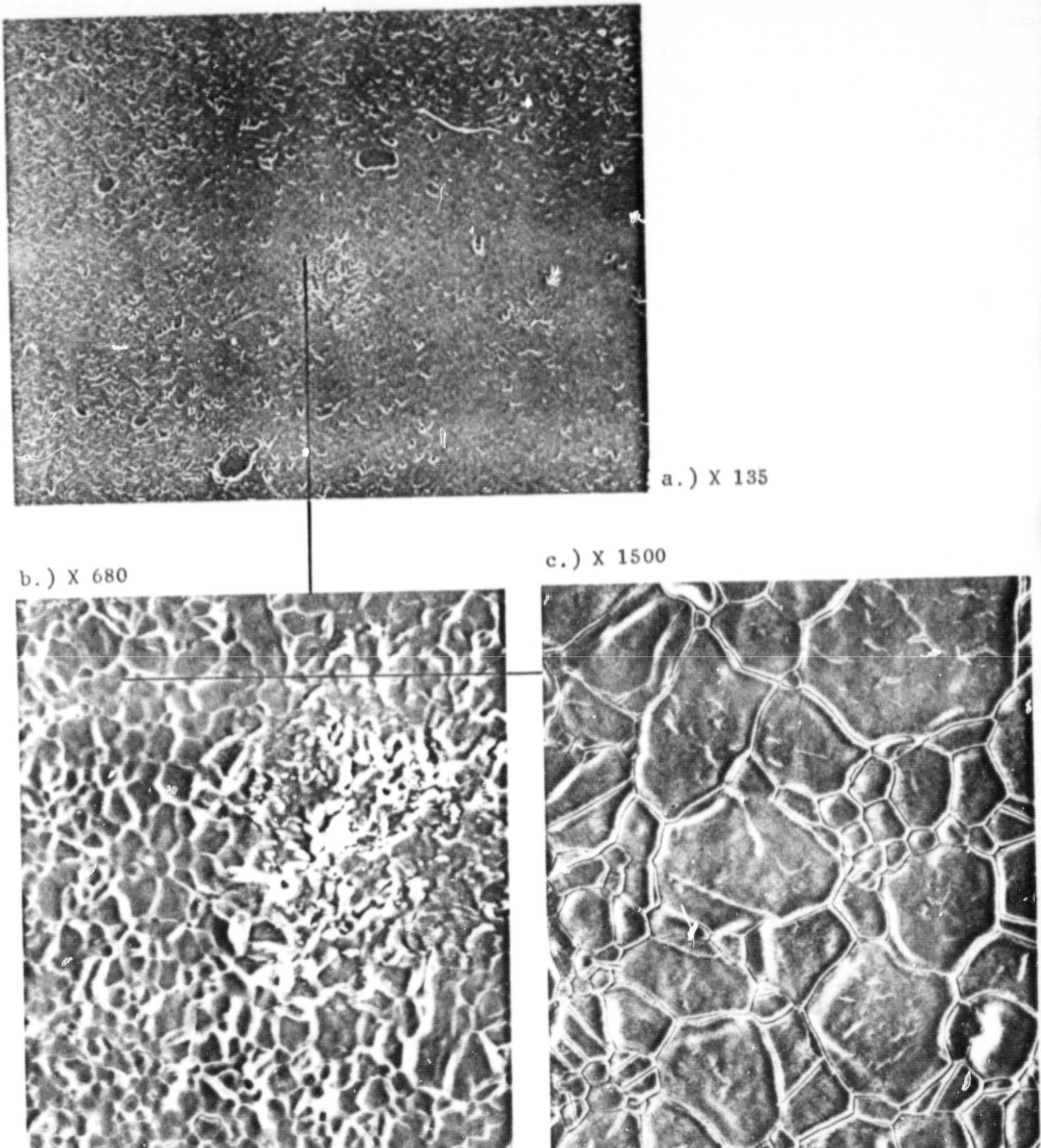
NACL PARTICLES EXPOSED TO AIR, 0.2% SO_2 AND 1.0% H_2O AT 600^0 C. FOR 10 MINUTES.

Figure 7



NACL PARTICLES EXPOSED TO AIR, 0.1% SO_2 AND 1.0% H_2O AT 600°C FOR 30 MINUTES

Figure 8



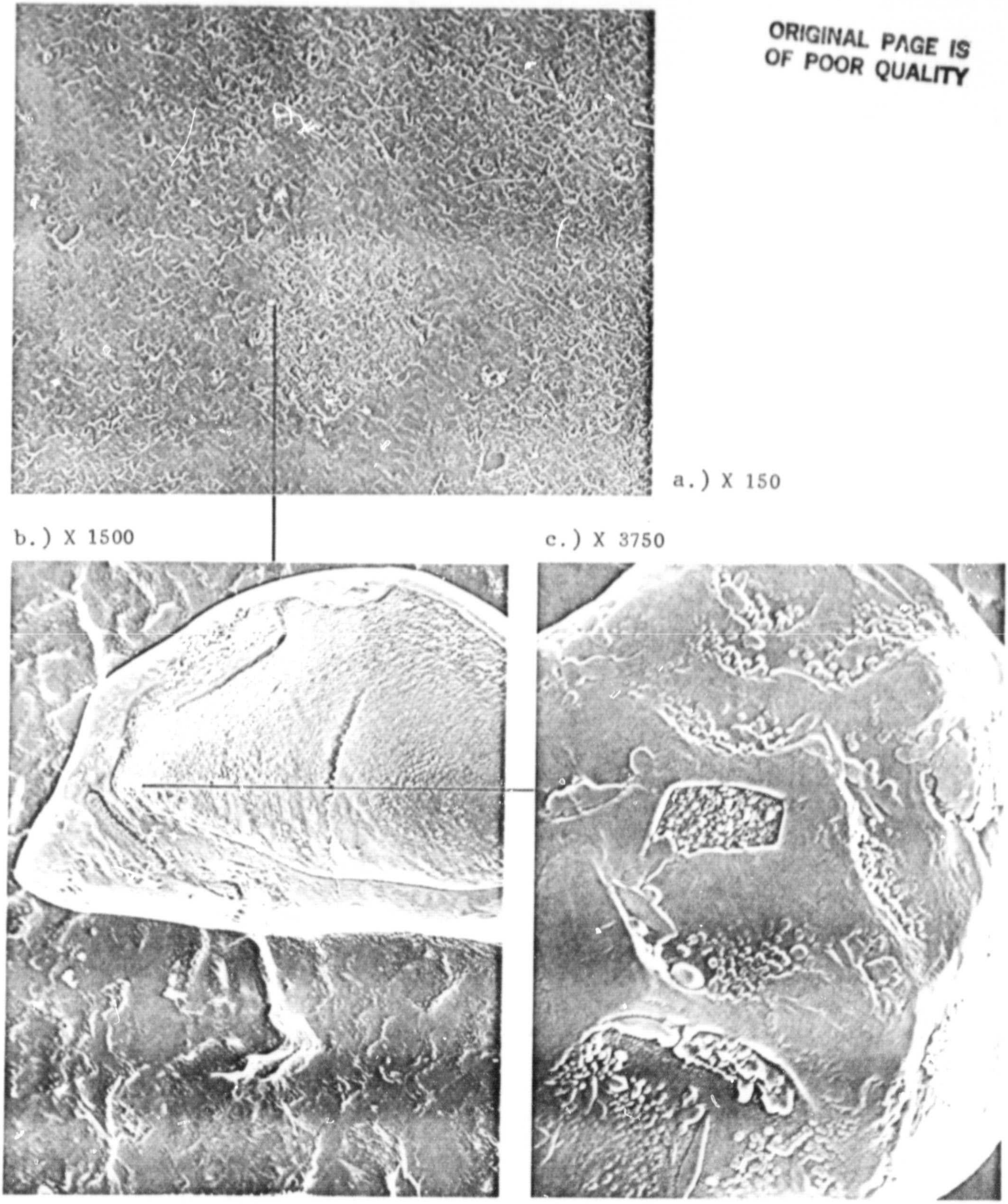
a.) X 135

b.) X 680

c.) X 1500

AL_2O_3 SUBSTRATE EXPOSED TO AIR, 0.2% SO_2 AND 1.0% H_2O AT 600^0 C. FOR ONE HOUR.

Figure 9



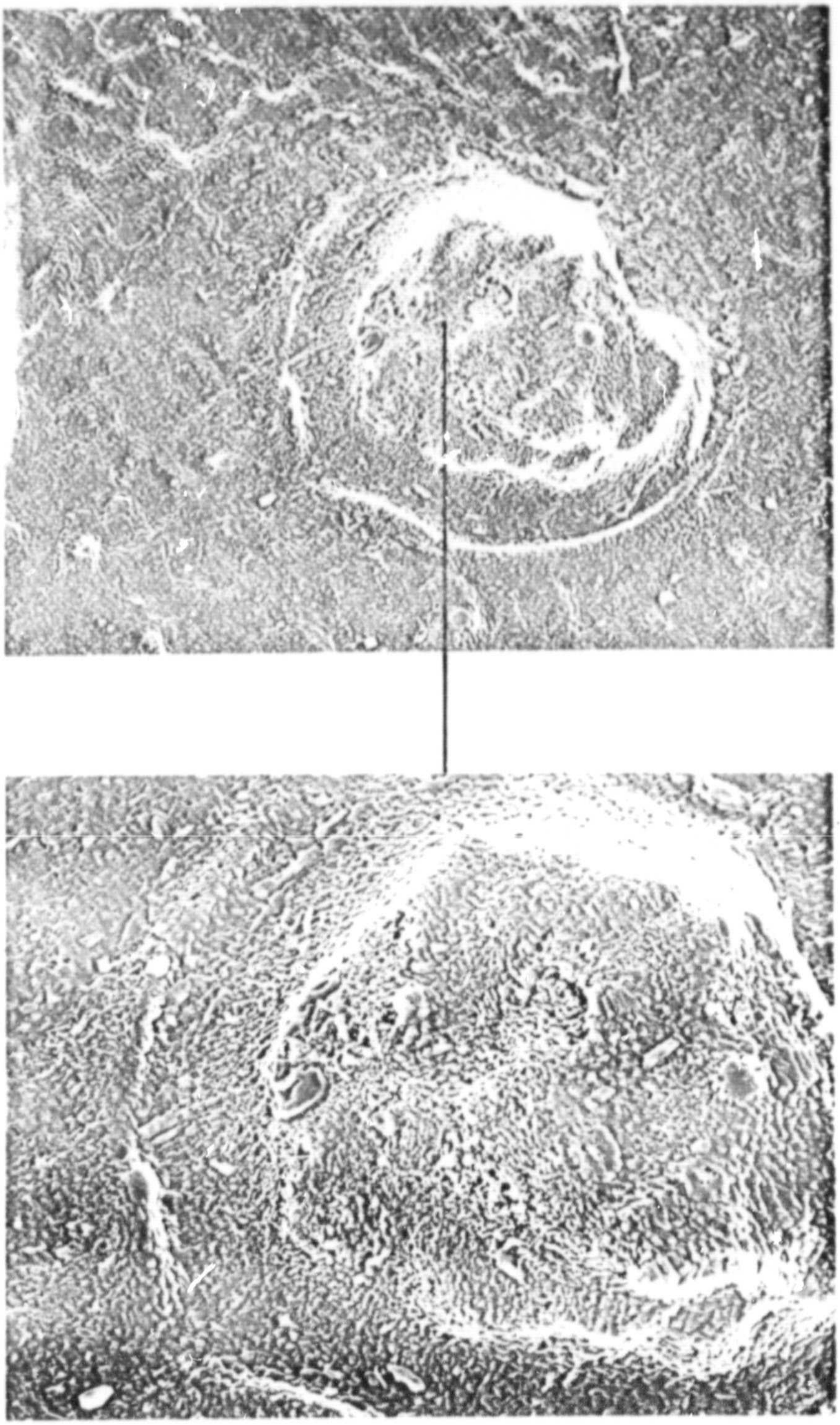
a.) X 150

b.) X 1500

c.) X 3750

NACL PARTICLES EXPOSED TO AIR, 0.2% SO_2 AND 1.0% H_2O AT 700^0 C.
FOR 10 MINUTES.

Figure 10

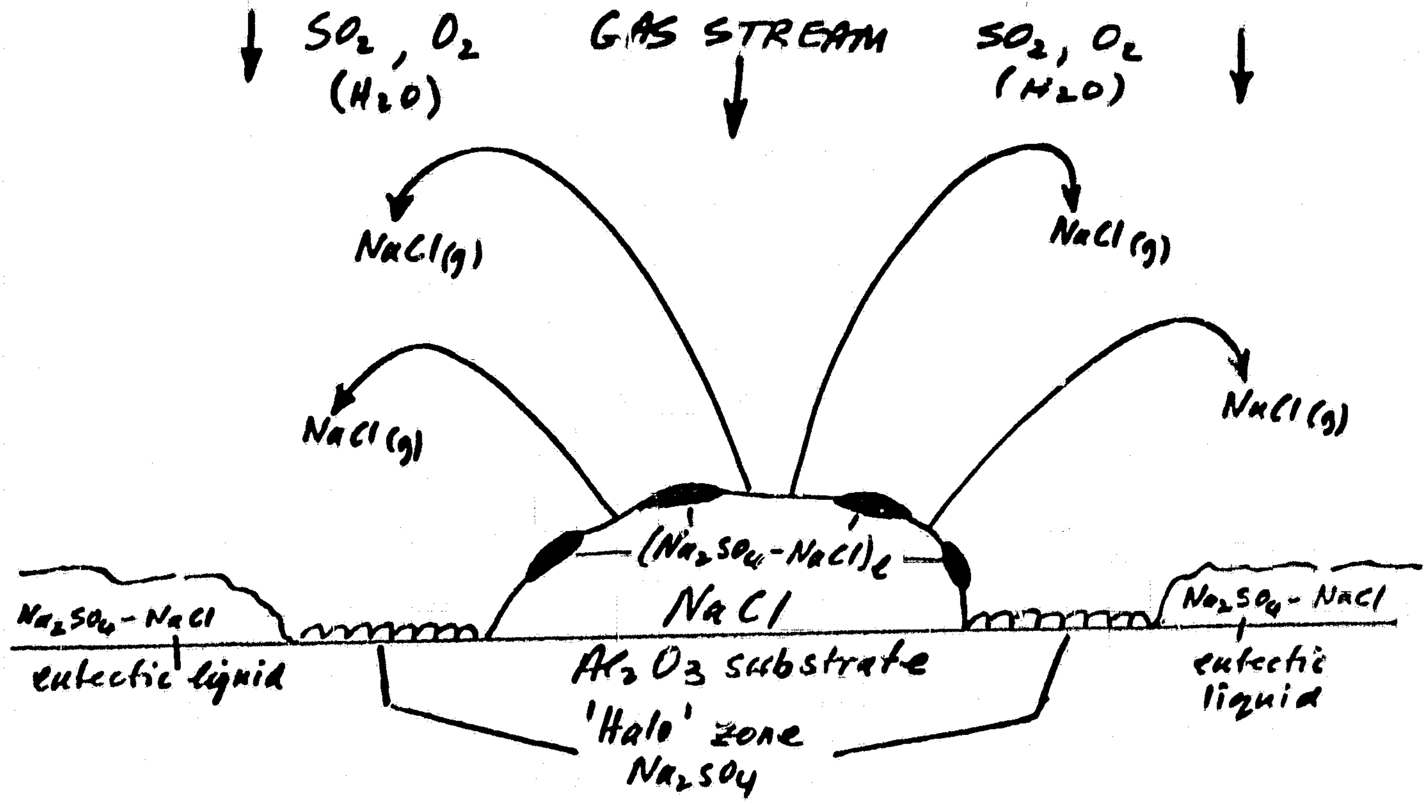


a.) X 375

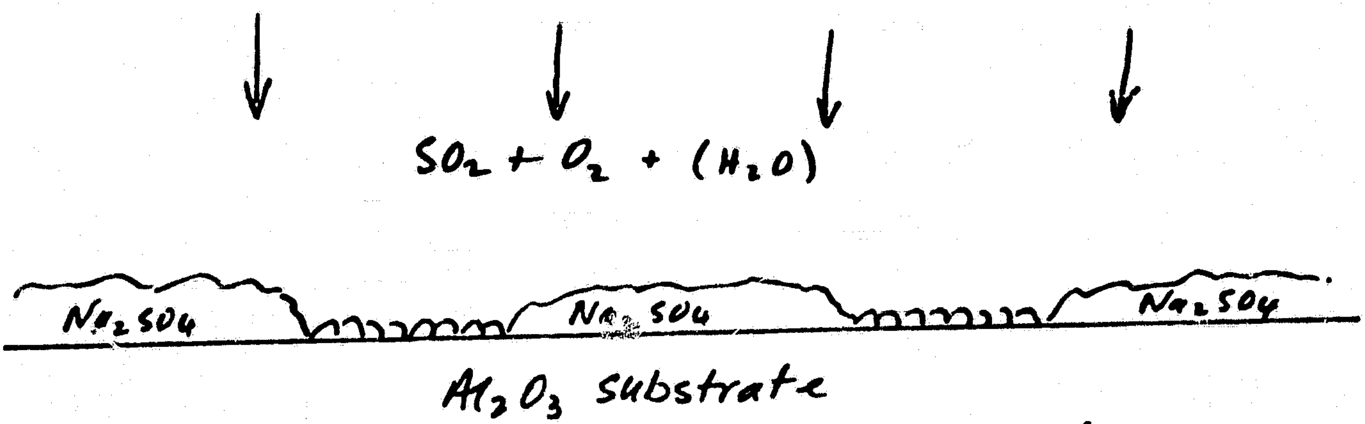
b.) X 750

NACL PARTICLE EXPOSED TO AIR, 0.2% SO_2 AND 1.0% H_2O AT 700^0 C. FOR ONE HOUR.

Figure 11



a. EARLY STAGES IN PRESENCE OF NaCl PARTICLE



NaCl in eutectic liquid reacts to form Na_2SO_4, solidification by reaction occurs

b. AFTER COMPLETE EVAPORATION OF ORIGINAL NaCl PARTICLES

REACTION MECHANISMS ABOVE 625°C

Figure 12