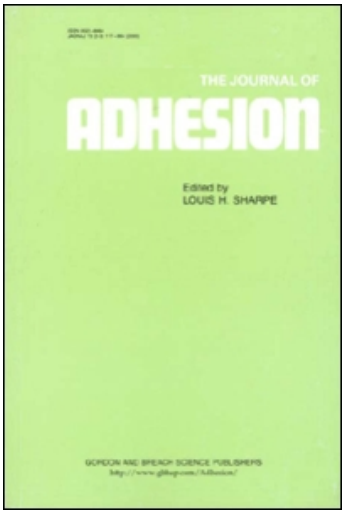

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Scanning Electron Microscopy of Fracture Surfaces†

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Scanning electron microscopy has supplied information concerning the mechanism of failure of aluminium/epoxide joints: (1) evidence for a critical concentration of A-1100 silane that inhibits stress corrosion cracking; (2) evidence of plastic deformation at a crack tip; (3) observation of aluminum corrosion products.

INTRODUCTION

Adhesive joints and composite materials are of increasing importance to design, material, and process engineers in the Aerospace Industry. As with all structural components, there are limits to the loads that can be safely applied. Fracture mechanics is an experimental and analytical means for (1) determining load limits of existing materials and structures, and (2) for extending the useful limits by learning how to inhibit the occurrence of fracture.

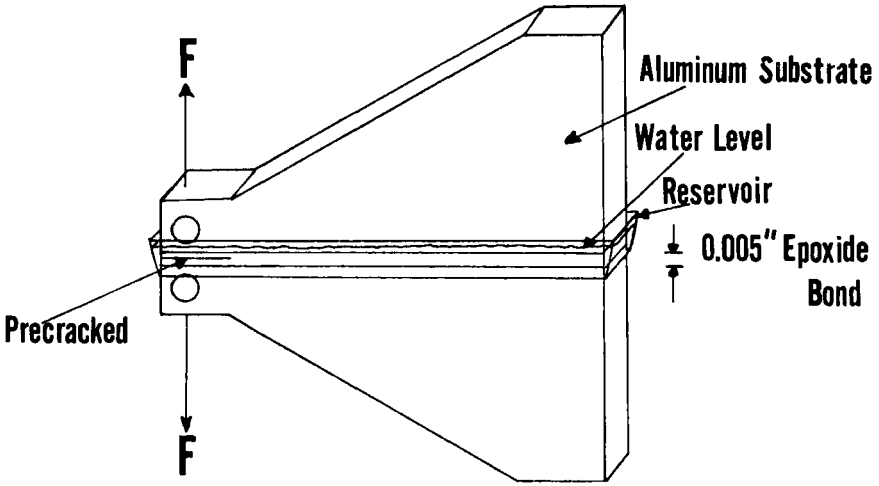
Fracture mechanics studies of aluminum/epoxide joints have been carried out for some time at Alpha Research & Development, Inc.;[1,2,3] and also, as described in the immediately preceding three papers, [4,5,6] at the Materials Research Laboratory and the University of Illinois. In addition, Alpha has used Scanning Electron Microscopy (SEM) to study the topography of fracture surfaces; and as a result has significantly increased the information gained in the fracture mechanics work.[3]

† First presented at the 2nd National SAMPE Technical Conference; Dallas, Texas, October 6–8, 1970. Copies of the preprint book may be purchased for $30 from SAMPE National Business Office, Azusa, California 91702.

The purpose of the present paper is twofold. First, we would like to give some insight into the type of information that can be gained by SEM work. Second, we would like to present a method for inhibiting stress corrosion cracking that is potentially of great practical importance to the aerospace industry.

THE NATURE OF SEM INFORMATION

The SEM information to be discussed was obtained from fracture surfaces of specimens such as the tapered double cantilever beam (TDCB) illustrated in Figure 1. Initially, a Center-of-Bond (CoB) "precrack" was introduced into the center of the epoxide adhesive by means of a rising-load stress. The stress was applied with an Instron machine which provided a measure of the strain energy release rate under *dry* conditions, $\mathcal{G}_{IC}$. The $\mathcal{G}_{ISCC}$ values were obtained by the use of static loads in the presence of water which was introduced into the reservoir around the bond-line as illustrated in Figure 1.



STRESS CORROSION CRACKING-SPECIMEN CONFIGURATION

FIGURE 1

Under stress corrosion cracking (SCC) conditions, our typical observation is that the CoB precrack which lies wholly inside the epoxide adhesive does not propagate. But, instead, the stress field about the tip of the CoB precrack influences the aluminum/epoxide interfaces and a new crack propagates as

an interfacial failure (IF) under stress corrosion conditions at static loads, $\mathcal{G}_{ISCC}$, that are much smaller than $\mathcal{G}_{IC}$.

Figure 2 (A) illustrates the junction between two adherend surface regions that has been treated with a 5 weight percent solution of A-1100 in water in one part (shown on the right side of the figure), and a 5 weight percent solution of A-1100 in hexane on the other part. Interestingly enough, the first stress-corrosion-induced IF crack along one aluminum/epoxide

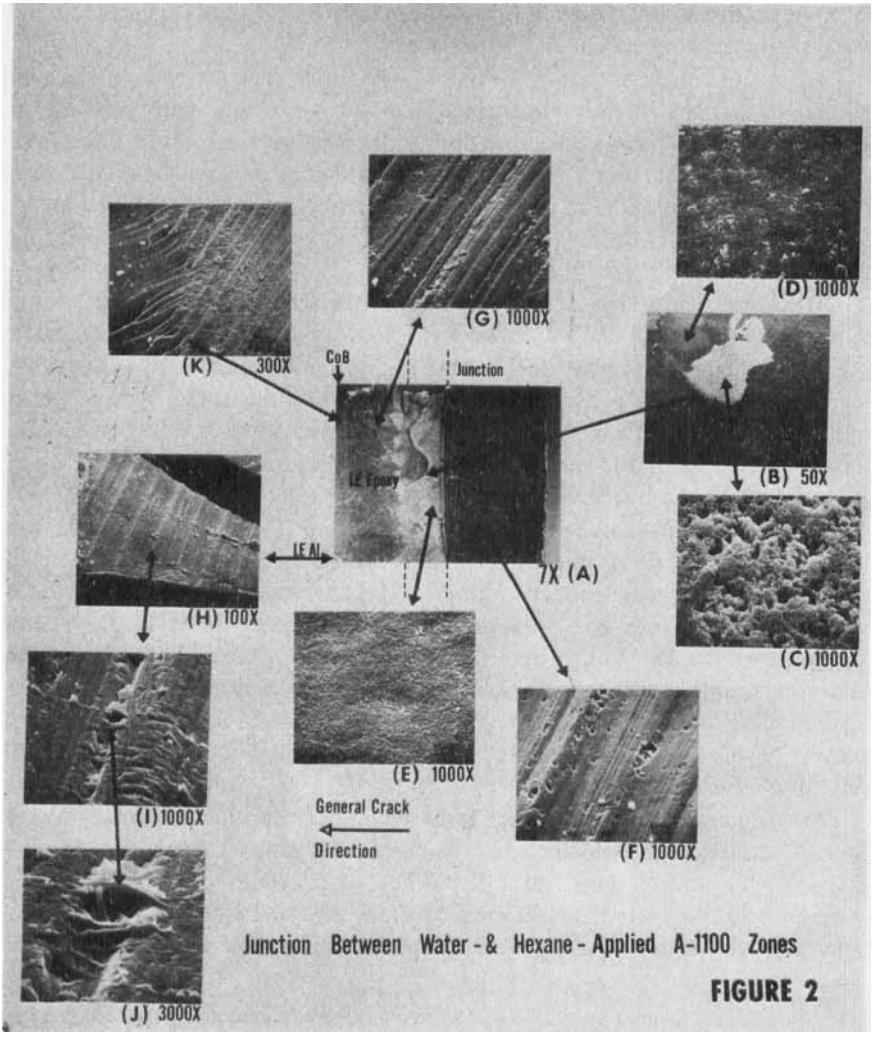


FIGURE 2

interface was arrested at a junction and, on the other side of the 5 mil adhesive layer, a new IF crack appeared and propagated along the second aluminum/epoxide interface.

Figure 2 was chosen at random from a large number of similar montages to illustrate the scope of SEM analysis. A single specimen does not tell the whole story by any means. But, by studying many samples, certain features are seen often enough that they can be considered to be characteristic of those features, and in these cases, the SEM serves as a "fingerprint" analytical tool. Beyond this, the SEM is also a "heuristic" tool that suggests further worthwhile fracture mechanics experiments.

The 7X optical photograph of Figure 2 (A), illustrates the general features of one particular "region of interest" on one specimen. One very useful aspect of the SEM technique is its ability to focus on a region of interest at a low magnification, and then in a stepwise manner increase the magnification so at to reveal "characteristic features" that can be correlated with the lower-magnification visual observations such as might be obtained under operating conditions.

For example, in the 7X view, the junction between the water and hexane regions is not a sharp line but instead is somewhat smeared-out, as indicated by the dashed lines above and below Figure 2 (A). The 50X SEM view[a] in Figure 2 (B) is from the smeared-out region and illustrates a "spot" that one would like to be able to say more about. The SEM permits doing just this on the basis of the information illustrated by the two 1000X views of Figure 2 (C) taken inside the spot area, and the view shown in Figure 2 (D) which was taken in the smooth region outside the spot area. By comparison with other SEM photomicrographs that we have taken, we can identify the "spot" as a heavy deposit of A-1100 silane coupling agent. Previous work has shown that excess silane leads to weakened joints. Thus, we can speculate—although not prove—that this silane agglomeration had little cohesive strength and separated under the action of the stress field of the approaching crack tip. Then we can speculate further that this weak region played a role in causing the IF stress field to jump from one adherend/adhesive interface to the other.

Further insight into the use of SEM techniques to elucidate microscopic factors that control macroscopic mechanical properties can be seen by comparing Figures 2 (D) and 2 (E). These two 1000X views illustrate the difference in the spatial distribution of silane coupler, in two areas that are separated, by approximately 1500 microns. This difference illustrates the

(a) The magnification values are for 4 x 5 scanning electron photomicrographs as obtained from the machine. The ellipses shown at the lower right of each photomicrograph arrurately indicate μ dimensions in the vertical and horizontal direction.

fact that the solvent application of a silane coupler which, from a production point of view should be (apparently) homogeneous, can lead to microscopic differences. Can such small-scale differences affect the mechanical properties of macroscopic specimens? Yes is the answer strongly suggested by the evidence presented in Section 3 below. In that section we do not claim, as yet, to know the precise microscopic factor (or factors) that lead to observed mechanical property differences. However, the SEM technique is helping us elucidate methods for controlling the mechanical properties of experimental samples and production products.

Figure 2 also illustrates the replication of the surface of the aluminum adherend by the surface of the epoxide adhesive. The 1000X view of Figure 2 (F) was taken in the region of the exposed aluminum surface on the right side of the central 7X view. Other SEM work has shown that aluminum surfaces that have never been in contact with epoxide adhesive look very much like this 1000X view in Figure 2 (F). The shallow, regular machining marks typically exhibit small, deep pits as shown. Note that the epoxide surface shown in the 1000X view of Figure 2 (G) replicates the machining marks and pits, i.e. pits in the aluminum typically match up with projection in the epoxide resin.

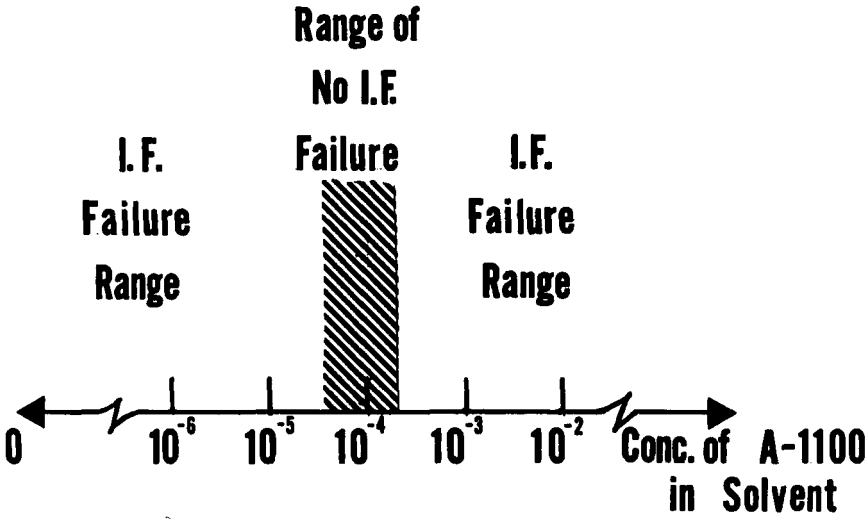
The machining marks on the aluminum surface appear somewhat different in the small IF failure region in the bottom left corner of the 7X view which is shown enlarged to 100X, 1000X, and 3000X in Figures 2 (H), (I) and (J). Here the machining marks have deposits on them which are either silane coupler or torn-out pieces of epoxide resin. Note especially the high spire of material sticking up from the aluminum surface in the 3000X view of Figure 2 (J).

One might well ask why the two "I.F. Al" regions in Figure 2 differ so much. We do not know. Some caution must be exercised, of course, in generalizing the information obtained from a single square area of approximately one mil on edge. But again, by trying to correlate the information from many SEM photos obtained from many specimens under varying conditions, one obtains valuable insight into the mechanism of adhesive-joint-failures.

Figure 2 (K) illustrates a difference in topography at the junction of the IF and CoB fracture surfaces shown in the upper left corner of Figure 2 (A). On the right side of Figure 2 (K) we see the top of the 5 mil epoxide layer which replicates the aluminum surface that the epoxide adhesive separated from. On the left side of Figure 2 (K) we see the fracture surface of the bottom half of the cohesively fractured epoxide adhesive. Thus, there is a drop-off of approximately 2.5 mils on going from the right-to-left sides of Figure 2(K). The typically observed rough marks on the CoB fracture surface on the left of Figure 2 (K) will be commented on in Section 4 below.

EVIDENCE FOR A CRITICAL CONCENTRATION OF A-1100 SILANE THAT INHIBITS STRESS CORROSION CRACKING

Recently, observations that were made with varying amounts of A-1100 silane coupler as a surface pretreatment agent suggested that there was a critical concentration of A-1100 in water that inhibited interfacial (IF) failure and, therefore, inhibited stress corrosion cracking. That work was carried out with DER 332 epoxide resin, containing 10 phr of TEPA (tetraethylenepentamine) hardener, cured for five hours at 180°F. Evidence was obtained that the critical concentration of A-1100 was 0.01 weight percent. This observation is schematically illustrated in Figure 3, and is based upon the series of photographs shown in Figure 4.[3] This series of photographs of the fractured surfaces clearly suggests that 0.01 weight percent A-1100 prohibits the occurrence of IF failure under stress-corrosion cracking conditions.



SCHEMATIC REPRESENTATION OF EFFECT OF CONCENTRATION OF SILANE SOLUTIONS ON THE MODE OF FAILURE

FIGURE 3

In the case of silane couplers the efficiency of their action is a sensitive function, not only of (1) concentration, but also of (2) the nature of the solvent, (3) the temperature of the solution and the length of time the solution has been at that temperature prior to use, and (4) the temperature and time of the silane treatment itself. This sensitivity is due to the existence

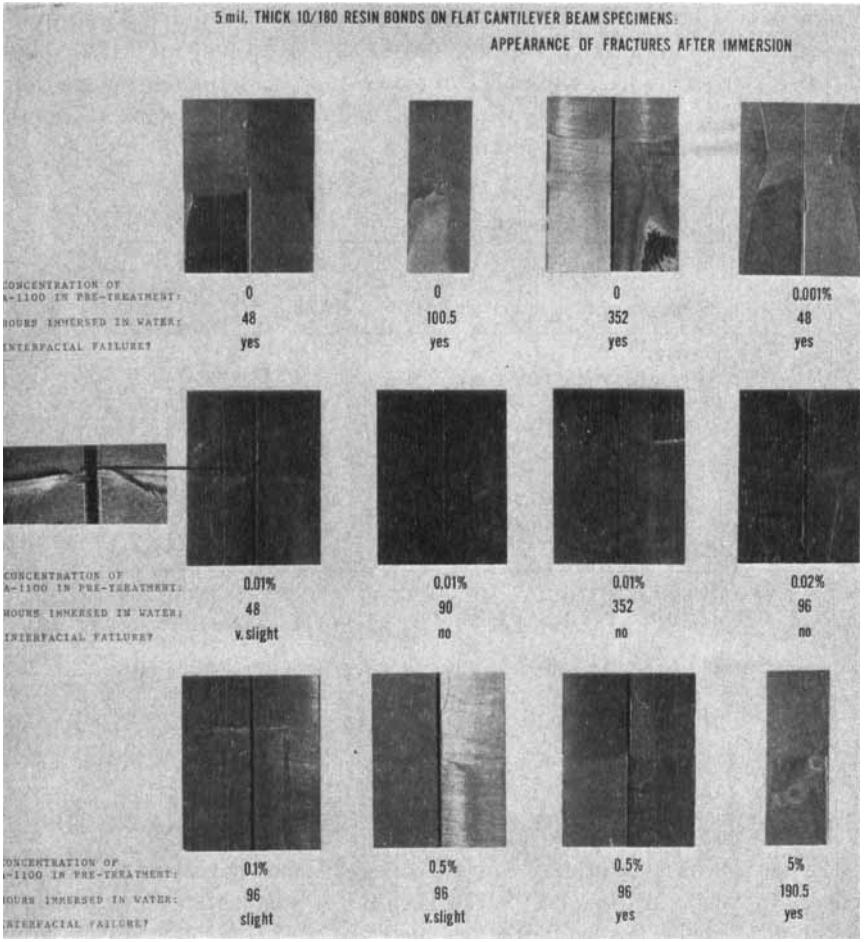


FIGURE 4

of a complicated set of solvolytic reactions (hydrolysis in the case of aqueous solvents) that the silane couplers undergo.

In the present work a lack of reproducibility plagued us for a few months. By instituting the most rigid controls in the experimental procedure we restored reproducibility. We have confirmed the inhibitory effect on I.F. failure of 0.01 weight percent A-1100 with two other hardeners: (TETA) triethylenetetramine, (10/180), and (DETA) diethylenetriamine, (8/180) respectively.

Table I lists some of our recent detailed results which can be summarized as follows: Typically, we have found that with zero or one weight percent A-1100, I.F. failure occurs within 24 hours. But with 0.01 weight percent I.F.

failure does not occur after 120 hours exposure to liquid water. This inhibitory effect has even been observed by Dr. S. Mostovoy of MRL, after 120 hours exposure in the presence of Photo-Flo†, a wetting agent that had been observed to accelerate the onset of I.F. failure. Long time tests, 832 hours, resulted in I.F. failure of all specimens.

TABLE I
Inhibition of I.F. fracture

A-1100 Conc. Weight Percent	Hardener	Exposure Time (Hours)	I.F. Fracture
0.00	A	24	Yes
0.01	A	136	No
0.01	A	120	No
0.01	A	832	Yes
1.00	A	24	Yes
0.01	A*	125	No
0.00	B	24	Yes
0.01	B	135	No
1.00	B	24	Yes

A = 10/180 TETA
A* = 10/180 TETA plus Photo-Flo
B = 8/180 DETA
10/180 = 10 parts of TETA per hundred parts of epoxide resin cured at 180°F.

Figure 4 is a series of optical photographs of beam specimens following fracture.

EVIDENCE OF PLASTIC DEFORMATION AT A CRACK TIP

A key question in fracture mechanics concerns the characterization of the energy state at the tip of a crack. Because of some of the mathematical difficulties, most fracture mechanics analyses are based upon linear-elastic theories and tend to ignore quantitative treatments of the non-linear effects that would accompany plastic deformation. Typically, some cognizance of plastic deformation is introduced in a simplified fashion to provide an energy balance at the crack tip.

The SEM technique provides topographic evidence that is highly suggestive of the occurrence of plastic deformation in the region of the crack tip. One example is shown in Figure 5 which shows views in the region of an arrest mark in a center-of-bond (CoB) crack. A CoB crack is an example of what is often called "a cohesive failure in the adhesive" in the literature. The SEM views show surfaces of the epoxide adhesive attached to both of

† Trade Name: Eastman Kodak Company, Rochester, New York. 10/180 = 10 phr cured at 180°F.

the aluminum adherends which had been joined together by the originally intact 5 mil thick epoxide adhesive. The general direction of crack propagation is from the smooth toward the rough regions in the individual photos, i.e., from the center of Figure 5 toward its left and right vertical edges, respectively.

The occurrence of plastic deformation is strongly suggested by the rough regions of the SEM micrographs in Figure 5. These views are quite reminiscent

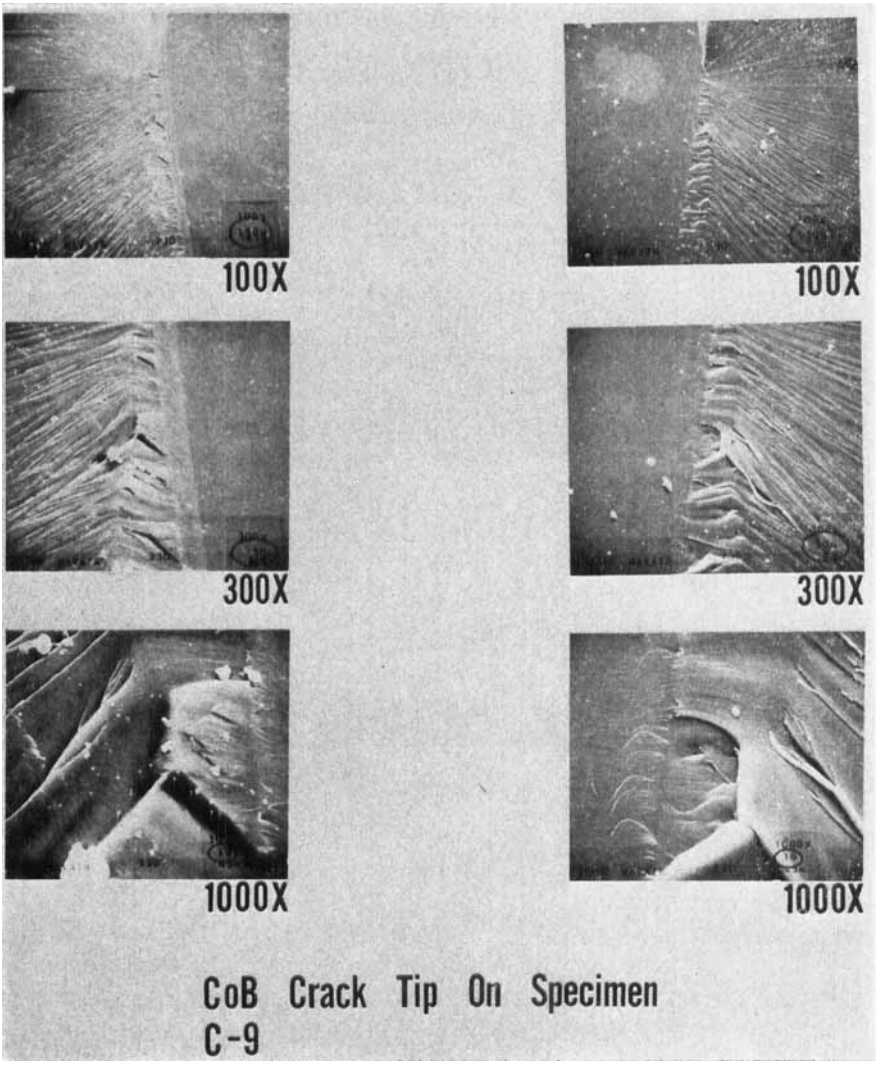


FIGURE 5

of the mirror-to-mist-to-hackle regions that are characteristic of polymer fractures, as was recently reviewed in some detail by Andrews.[7]

OBSERVATION OF ALUMINUM CORROSION PRODUCTS

Another area where the SEM technique has uncovered interesting information involves the mechano-chemistry of stressed adhesive joints. Specifically, Figure 6 illustrates SEM evidence for a hydroxide corrosion product of

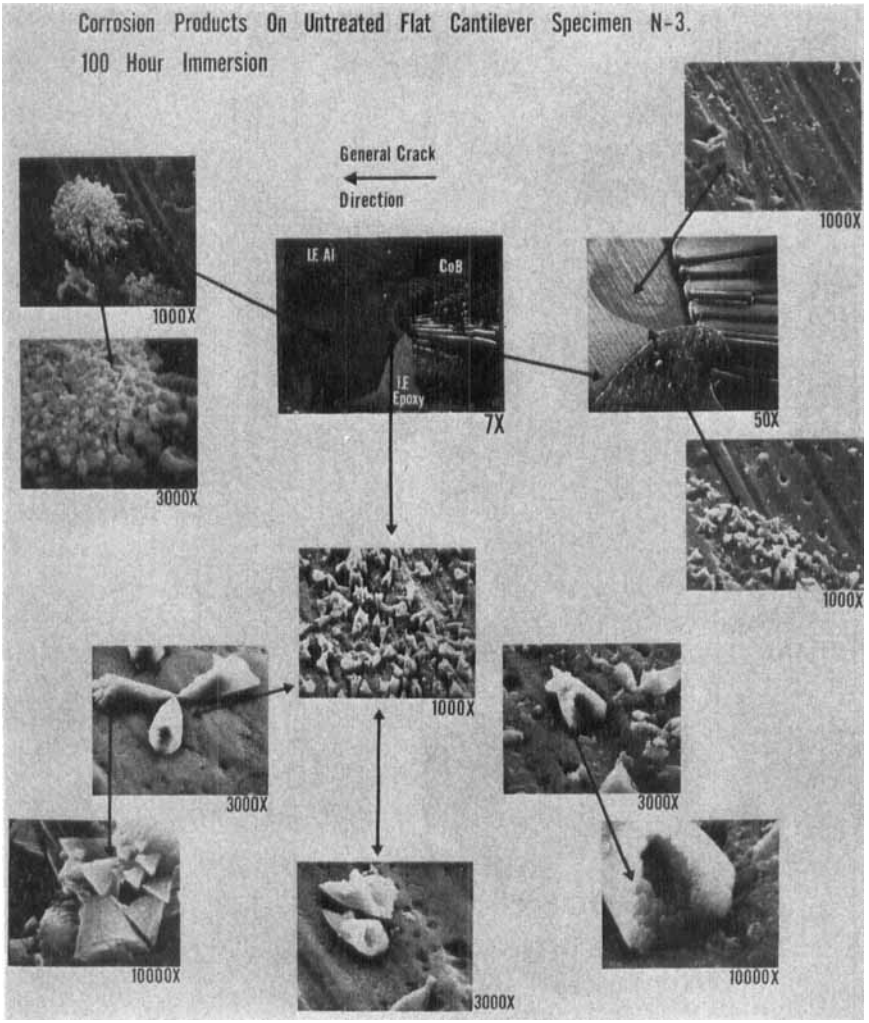


FIGURE 6

aluminum. The conical crystalline deposits in the bottom views are identified as Bayerite, beta-aluminum hydroxide, based on their morphological similarity to the Bayerite crystals which Watson and his co-workers studied by Transmission Electron Microscopy.[8]† However, the SEM methods provide much more detailed structural information than the earlier transmission work which was able to only show the gross conical shape of the crystals.

Acknowledgement

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† Recently confirmed by X-Ray diffraction as beta-aluminum hydroxide.