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Scanning electron microscope investigation of copper oxides formed electrochemically in alkaline solutions

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SCANNING ELECTRON MICROSCOPE

INVESTIGATION OF COPPER OXIDES

FORMED ELECTROCHEMICALLY IN

ALKALINE SOLUTIONS

by

Michael F. Costantino

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Metallurgy and Materials Science

Lehigh University

1973

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

April 17, 1973
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ACKNOWLEDGEMENTS

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ABSTRACT

One step in the manufacture of millimeter waveguide involves the oxidation of electroplated copper in order to provide a more durable interface for the adhesive bonding of a polyethylene dielectric liner. The oxidation is performed electrochemically in NaOH electrolyte. From the results of previous work involving electrochemical experiments and X-ray diffraction measurements, it is possible to partially characterize the oxides and their morphology.

This thesis study examined samples from waveguides using scanning electron microscopy with the idea of gaining a better understanding of why the oxidation improves the bond interface. The results indicated the presence of two oxides; a first stage consisting of a thin film of Cu_2O, and a second stage consisting of needle-like clusters of CuO. These results were discussed in relation to the previously known description and were shown to agree in every respect. Results also indicated that the oxidation process appreciably roughens the copper by forming a porous, sponge-like surface. This is believed to be caused by a combination of the mechanisms involved in both stages of oxide formation.

From the picture thus obtained, it is postulated that the improved bonding of the liner is a result of some mechanical interlocking between the adhesive and the oxide. However, two

potential problem areas were pointed out. One is the possibility of some contaminant attacking the oxide layer resulting in separation at the copper/oxide interface. The other is that the appearance of the copper surface after oxidation suggests that there would be a significant increase in heat (I^2R) losses during waveguide use.

INTRODUCTION

This thesis investigation is related to the development of cylindrical waveguide for a long distance, high capacity transmission system. The waveguide consists of low carbon steel tubes of approximately 51 mm inside diameter with an internally electroplated copper layer approximately 0.5 mil thick. (See Figure 1.) The copper is the conductive medium for the propagation of electromagnetic energy along the waveguide at frequencies in the range of 40-110 GHz. A polyethylene dielectric liner adhesively bonded to the copper aids transmission efficiency by attenuating unwanted energy modes. However, the copper/adhesive interface is highly subject to corrosion upon exposure to moisture, causing separation of the polymer from the copper. This, in turn, results in strong degeneration of the transmission characteristics. In order to provide a more durable interface, the copper is intentionally oxidized prior to lining. The presence of the oxide results in a marked improvement in the reliability of the bond. Sumitomo Electric Industries, Ltd.,[1] working on a similar waveguide transmission system, has published results on the durability of the interface as a result of the oxidation. They studied oxides formed by both chemical and electrochemical techniques and concluded that the properties of both oxides were similar. Results of bond strength tests and liner peeling rates as a function of exposure to water were reported for the chemically formed oxides.

From a practical viewpoint, the electrochemical technique seems more suited to production applications,[2] since the oxidation can be performed immediately after electroplating with a minimum of equipment change and product handling. (However, other factors must also be considered, such as possible contamination of the different solutions used for plating and oxidizing.) For this reason, only electrochemically formed oxides were investigated in this thesis. Electrochemical growth is obtained by anodic oxidation at constant current density in a suitable electrolyte while monitoring the change in potential with time. The electrochemical growth in this case was performed in an alkaline solution.

The anodic behavior of copper in alkaline solutions has been the subject of several investigations.[3-11] The results of such experiments have at times not been in full agreement with each other, but nevertheless, they have enabled the development of a picture of the oxidation process. This picture consists of three stages to describe the oxidation. The first stage is the formation of Cu_2O.[3-8] The existence of this oxide has also been confirmed by X-ray diffraction studies.[9] The second stage involves the formation of CuO or $Cu(OH)_2$.[3-7] The existence of CuO was confirmed by X-ray diffraction,[6] but only at temperatures of 40°C and above. The reason for this behavior is attributed to the fact that while CuO is more stable, its formation is more complex and is therefore retarded, favoring the formation of a metastable $Cu(OH)_2$.[7] A third stage involves the formation of Cu_2O_3.[7,8,10] However, this

oxide has been observed only at high anodic potential near oxygen evolution[7,10] and only after repeated anodic-cathodic cycling of the same copper electrode.[7] It has been concluded[10] that the first and third stages involve film formation and growth while the second stage involves a dissolution-precipitation process.

The picture of copper oxidation in alkaline solutions just described is an overall view. The specifics of each stage, such as thickness of the oxide and the time to form it, depend on the particular solution used and the conditions of the oxidation. In the present work, however, the main objective was to gain further insight into the nature of the improved bonding of the polymer liner. Therefore, to complete the picture already described, an investigation of the structure and morphology of the copper/copper oxide region was conducted. Samples from electrochemical oxidation were examined both in plan view and in cross-section using the scanning electron microscope (SEM).

EXPERIMENTAL

The samples used in this investigation were obtained from sections of previously manufactured waveguide which were available. As already described, the waveguide consisted of a low carbon steel tube with an internally electroplated layer of copper. The copper was subsequently oxidized by electrochemical techniques. The electrochemical oxidation had been performed in 2N NaOH solution at approximately 176°F(80°C). The samples used in this investigation did not have the polyethylene liner bonded to the oxide.[2]

Prior to cutting, the samples were coated with Krylon® #1302 clear acrylic spray coating to protect the oxide during the cutting operation. The samples were then cut on an abrasive cutoff wheel with a water spray coolant. First, a ½" cylindrical ring was cut from the waveguide sections. Each ring was then divided arbitrarily into quadrants. Three samples were obtained from each quadrant, one for surface oxide studies, one for a transverse cross-section, and one for a longitudinal cross-section. This enabled a rough check to be made of uniformity around the waveguide circumference. Final sample size was approximately ½" x ½". (See Figure 2.)

Just prior to mounting, the samples were soaked in acetone for approximately 15 minutes to remove the Krylon®, and then rinsed in methyl alcohol and blown dry. Not all of the Krylon® was removed in this period of time. However, this did not create any problems during subsequent polishing and microscopic observations. The

samples were then mounted in bakelite ring forms with an epoxy mixture consisting of 100 parts by weight of Epocast H-1368 casting resin to 10 parts by weight of hardener 955. Both were purchased from Furane Plastics, Inc., Fairfield, N.J. A ceramic filler (Buehler No. 20-8148 AB, 80 mesh) was also added to aid in edge preservation during polishing. Each mount contained four samples, one from each quadrant of the waveguide. The mounted samples were cured at room temperature for three days. They were then rough ground on a 120-grit belt grinder with water coolant. Intermediate grinding was done on 240, 320, 400, and 600-grit silicon carbide abrasive paper. They were polished with 12μ and 3μ diamond paste, and finally with 1μ and 0.05μ alumina.

The samples were then studied by scanning electron microscopy and replica electron microscopy to investigate the morphology and structure at the copper/copper oxide interface. Replicas for the electron microscopy were made by a two stage Formvar/carbon technique. The angle of shadowing was 30°. Sample orientation in the SEM is usually 45° with respect to a plane normal to the electron beam. In several instances, however, the angle was increased for improved contrast.

Several samples were etched to try to aid in identification of the actual interface and to aid in identification of the oxides at the interface. Two etchants were used. Etch #I was a mixture of, by volume, 1 part NH_4OH, 1 part H_2O, and 2 parts 3% H_2O_2. Etch #II was a 1.2N NaCN solution.

Attempts also were made to examine the samples under the light microscope, but the oxide thickness was near the limit of resolution attainable with light microscopy. Because of the uncertainty of the interpretation of these photographs, they were not included.

The thickness of the copper plating was measured on a Leitz metallograph with a Vickers image splitting measuring eyepiece.

Data on oxide thickness were already available from previous studies on the waveguides from which the samples were obtained.[2] These data were obtained from chronopotentiometric analysis. The technique[12] is described briefly in the Appendix.

RESULTS AND DISCUSSION

Table I is a list of the samples used in this investigation along with information related to the characteristics of the wave-guides from which the samples were obtained. The results from the chronopotentiometric analysis given in the Table indicate the presence of two oxides of copper. These results are in agreement with the results described earlier in the Introduction.

Scanning electron micrographs of several samples are shown in Figures 3 thru 10. It should be noted at this point that the samples for cross-sectional viewing were highly polished prior to observation in the scanning electron microscope. As a result, there were very few topographic differences within a sample. Since the contrast in the secondary electron image depends heavily on topography, the photographs do not show good contrast at the interfacial area of interest. As a comparison, the reader is asked to note the particles of ceramic filler which can be seen in several of the photographs.

Figure 3 is a photograph showing the surface topography of oxide sample no. 125. This is typical of the electrochemically formed oxides investigated in this work. The visible morphology consists of needle-like clusters. From the earlier description, this oxide could be either second stage CuO, second stage $Cu(OH)_2$, or third stage Cu_2O_3. However, Cu_2O_3 has been observed only upon repeated anodic-cathodic cycling.[7] Since the oxidation in this case was only a one-time anodic half cycle, it seems reasonable to

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assume that Cu_2O_3 is not present. Also, since the oxidation was performed above 40°C, it seems reasonable to assume that this oxide is second stage CuO.[6] The appearance of this oxide also seems to be consistent with the dissolution-precipitation mechanism of formation. One possible reaction[1,13] in the formation of CuO involves the dissolution of the copper, the formation (in NaOH electrolyte) of $CuO_2^=$ in solution near the copper, and then the precipitation of CuO given by the following reaction:

$$CuO_2^= \; + \; H_2O \; \longrightarrow \; CuO \; + \; 2OH^- \qquad\qquad (1)$$

The dissolution of the copper occurs in two ways.[11] One is the oxidation of Cu(+1) to Cu(+2), and the other is the oxidation of Cu(0) to Cu(+2) as shown in equation (2). Some of the Cu(+2) then dissolves into the solution.

$$Cu(0)solid \rightarrow Cu(+1)solid \rightarrow Cu(+2)solid \rightarrow Cu(+2)solution \qquad (2)$$
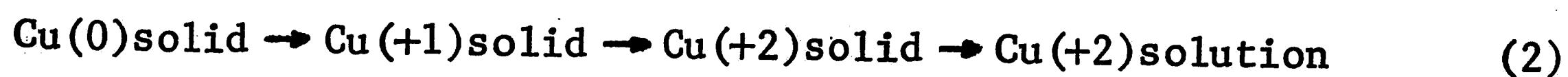
At this point it should be noted that, considering the complex nature of most electrochemical reactions, it is possible that some reaction other than (1) may also account for the formation of CuO.[14]

Figures 4 and 5 are SEM photographs of longitudinal cross-sections of electrolytic oxide sample no. 125. A somewhat needle-like structure is apparent, and the oxide layer is non-uniform across the copper surface. These observations are consistent with the surface topography in Figure 3. A faint white line following the oxide edge of the copper is also visible in Figures 4 and 5. This could be attributed to either or both of two things. One is a charging

effect due to the electron beam striking a non-conductive oxide at the copper edge. The other is a possible "edge" effect which arises when the electron beam strikes a sharp edge resulting in a greater intensity of secondary electron emission at the edge. It is this effect which enables the high contrast to be obtained in the SEM. Of itself, it is very difficult to say what the cause of the white line is. However, the etching studies to be described later, and observations at higher magnifications such as in Figure 6, indicate that it is most likely due to a layer of oxide.

Figure 6 shows photographs of a transverse cross-section of electrolytic oxide sample no. 125. One can again observe the non-uniform covering and the clusters of needle-like structure. Again the faint white line is visible, but in these higher magnification photographs, there does not appear to be much of an edge. This would lead one to suspect that the line is due to an oxide. If this is the case, then a logical assumption is that the oxide is a thin film of the first stage Cu_2O. This, along with the evidence for two oxides given in Table I, makes the picture developed thus far consistent with the description mentioned earlier in the Introduction.

Figure 7 shows photographs of a transverse cross-section of electrolytic oxide sample no. 725. The oxide appears more dense and uniform compared to sample no. 125, but otherwise the observations are the same. The more uniform appearance was expected because upon visual examination of the surface of these two samples

-11-

prior to mounting it was noted that sample 725 was very black in appearance while sample 125 was grey. This difference in color is directly related to the density of the oxide covering. The more dense the oxide covering, the blacker the surface appearance. The observations on these two samples are not consistent with the thickness data in Table I in that the chronopotentiometric analysis showed sample 125 to have a thicker oxide. However, it should be noted that the chronopotentiometry was performed on a larger (1 foot long) section of the waveguide, which would tend to average out any non-uniformity in thickness. The particular samples used in this investigation were chosen at random, thus there was a real possibility of obtaining samples of varying oxide density. It is seen then, that caution must be exercised in interpreting the thickness data in Table I. The thicknesses obtained from the chronopotentiometric technique are average thicknesses, assuming a dense, uniform film of oxide. Although the technique is well established, the assumption made is not a very good one in this case as can be seen from Figure 3.

It is known from the results of the coulometric reduction technique given in Table I that two oxides are present in the samples. Unfortunately, these oxides are not readily distinguishable in cross-section, although one can speculate on the basis of the description presented in the Introduction. For this reason, two etches were tried in an attempt to delineate the structure at the interface and to try and distinguish between the

oxides. These results are given in Figures 8a and 8b which show etched cross-sections of electrolytic oxide sample 125. Figure 8a shows the results of a 1-2 second swab in etch #I (ammonium hydroxide-hydrogen peroxide). This etch has not brought out any significant structure in the copper, however, it does appear to have lightly attacked the oxide/metal interface, delineating a very porous or spongy surface. Also evident in the photograph are clusters of surface oxide which are embedded in the epoxy mount. Figure 8b shows the results of a 1-2 second swab in etch #II (NaCN). Again, no significant structure of the copper is evident, however, the etch appears to have heavily attacked the interface. There even appears to be a uniform separation all along the sample between the copper and the mounting epoxy. It is known that NaCN will dissolve both cuprous and cupric oxides of copper. However, its rate of attack on each is different. It will dissolve Cu_2O usually in less than 1 second, but takes several minutes to dissolve CuO. With this in mind, returning to Figure 8b it appears that this etch has not only delineated the oxide/metal interface, but has dis- tinguished between the two oxides by preferentially dissolving one of them, namely the Cu_2O. It then appears that the separation was caused by a thin layer of Cu_2O which had been dissolved away. The layer of CuO is still present in the epoxy. With these results then, along with the results described previously, it appears that the visual picture of the morphology of electrochemical oxides is consistent with that predicted from electrochemical measurements

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as described in the Introduction. The uniform separation at the metal/oxide interface just described also suggests a potential problem in delamination of the waveguide dielectric liner even after oxidation. Any contaminant which has an effect on the oxides of copper similar to the effect of NaCN will result in separation of the liner at the copper/oxide interface.

Figure 9 shows a photograph of an electrolytic oxide sample from which the oxide had been completely dissolved in etch #II. Note the sponge-like porosity of the copper surface. This is consistent with the cross-sectional observations in Figure 8a. Figure 10 shows a partially etched sample. The etch loosened the oxide (by dissolving the underlying Cu_2O) such that it flaked off when blown with nitrogen. It is felt that Figures 9 and 10 are representative of the effect of the oxidation on the copper surface. Preliminary experiments on unoxidized copper plated waveguide sections showed that the NaCN etch does not appreciably roughen the copper surface even after an 8 minute etch. The results in these photos also suggest that, since the copper is the conductive medium in the waveguide, the surface roughening due to the oxidation process will result in some increase in heat (I^2R) losses. Surface roughness has been shown[15-21] to have a significant effect on the attenuation characteristics of waveguides. Morgan[15] showed theoretically that for grooves transverse to the direction of induced current flow, losses may increase anywhere from zero to 100%, depending on the ratio of r.m.s. surface roughness to skin

depth. Increases in attenuation of up to 22% were observed in copper waveguides that had been exposed to atmospheric corrosion for several months.[16]

It is not known what causes the porosity observed on the copper surface when the oxide is dissolved away. It could result from the formation of the film of Cu_2O, the rate of which is controlled by the diffusion of ionic species in the solid.[11] It could also result from the dissolution-precipitation process of CuO formation discussed previously. However, the complexities which usually exist in electrochemical reactions suggest that the porosity might be the result of some combination of all the reaction stages of the oxidation. Additional investigation into this aspect could involve the oxidation of some samples only to the point of Cu_2O formation, then stripping the oxide and examining in the SEM.

Some results from the replica electron microscopy are shown in Figures 11 and 12. The dark areas with light tails on the photos represent depressions on the samples. These photographs are difficult to interpret and do not show much information, but they are presented as a matter of record. Figure 11 shows an interface between the copper and the epoxy mount. The fact that this interface is rougher than either the copper or the mount suggests that this might be evidence for the existence of an oxide layer. A similar sample etched in NaCN is shown in Figure 12. There appears to be a separation similar to that discussed with

respect to Figure 8b.

Photographs of all samples were not included in this thesis. This seemed unnecessary in view of the fact that no significant differences between samples were observed other than those already described.

SUMMARY AND CONCLUSION

Copper oxides formed electrochemically in alkaline solution were investigated using scanning electron microscopy. The morphology of the oxide as observed in plan and in cross-section appeared to be consistent with the proposed description for the formation of such oxides. The results indicated the presence of two oxides; a first stage thin film of Cu_2O, and a second stage of CuO consisting of needle-like clusters.

Data from the chronopotentiometric analysis showed the presence of two oxides on the samples. These results, combined with the results from the etching studies on cross-sections, were in agreement with the proposed description.

The results from the etched cross-sections suggested a potential delamination problem due to contaminants which might attack the oxide layer.

It was demonstrated that caution should be exercised when interpreting the oxide thickness measurements. The results from this technique may not always correlate with photographic observations.

The effect of the oxidation on the surface of the copper was determined by chemically stripping the oxide. This revealed a spongy, porous surface. The mechanism which causes this is unknown at this time, but it seems most likely due to some combination of the reactions involved in both stages of oxide formation. The appearance of the copper surface also suggested that there might be

a significant increase in heat (I^2R) losses as a result of the oxidation.

The visual picture that has been put forth concerning the morphology of the oxides gives some insight into why oxidation of the copper would improve its bondability with the polyethylene dielectric. The adhesive used to bond the dielectric can easily surround the needle-like fibers to form a good mechanical type of bond. With this in mind, then, a future project might be to attempt a mechanical type of analysis involving the strength characteristics of the oxides, particularly the strength of the bond between the CuO needles and the Cu_2O.

TABLE I. WAVEGUIDE SAMPLE DATA

Sample No.	Copper Plating Thickness (mil)		Oxide Thickness (angstroms)*	
	AVERAGE	RANGE	Cu_2O	CuO
125	1.320	1.230--1.420	5693	8011**
625	1.390	1.330--1.410	3984	6379
725	0.663	0.652--0.682	2846	3560
726	0.651	0.594--0.696	N.A.***	N.A.
727	0.675	0.638--0.710	1139	3442**

* As Determined by Chronopotentiometric Analysis in $0.2M$ NH_4Cl.

** Analysis Performed by Mrs. M. Higgins of the Western Electric Co., Engineering Research Center.

*** N.A. = Not Available.

STEEL

COPPER

Cu_2O

POLYETHYLENE DIELECTRIC

CuO
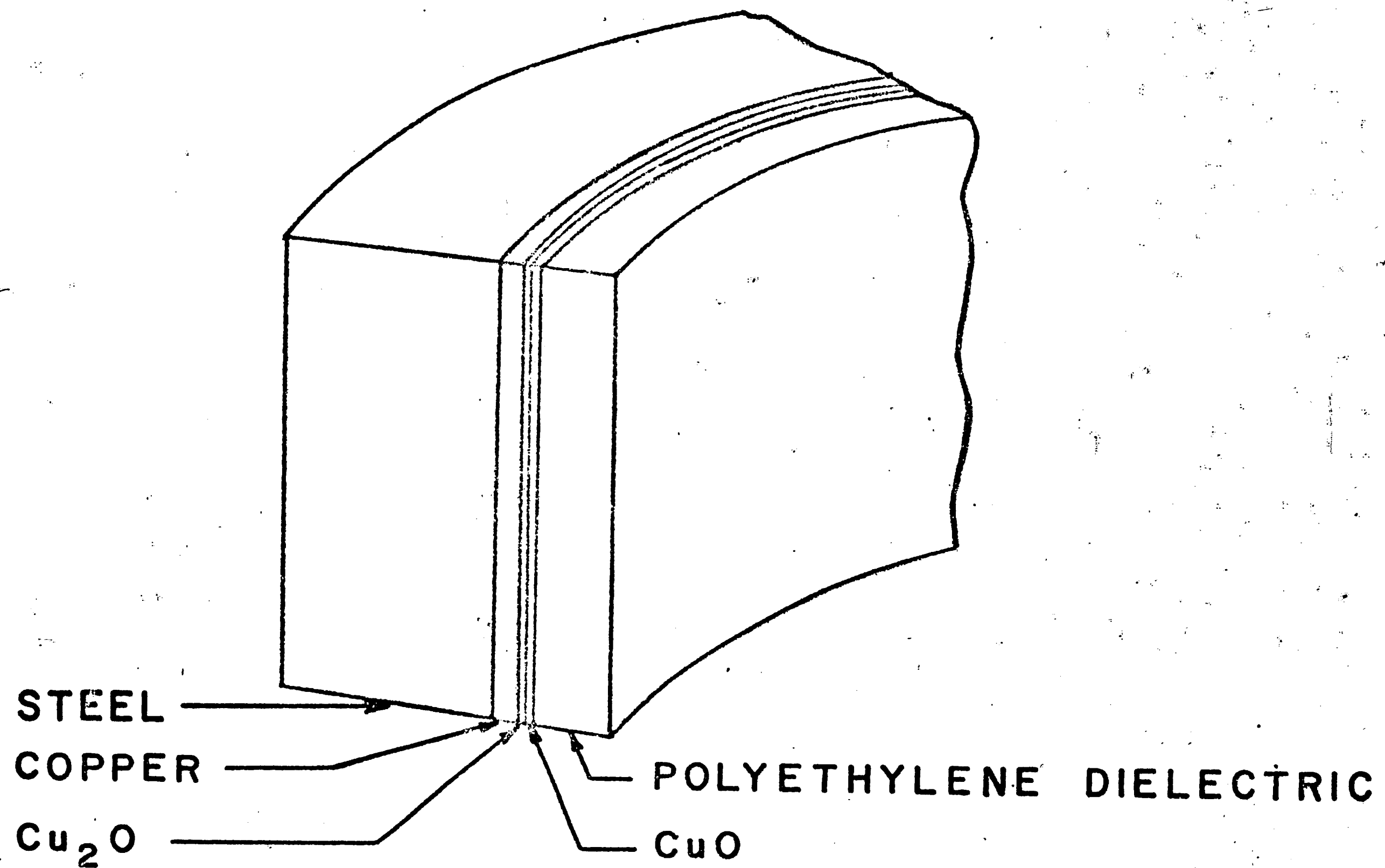
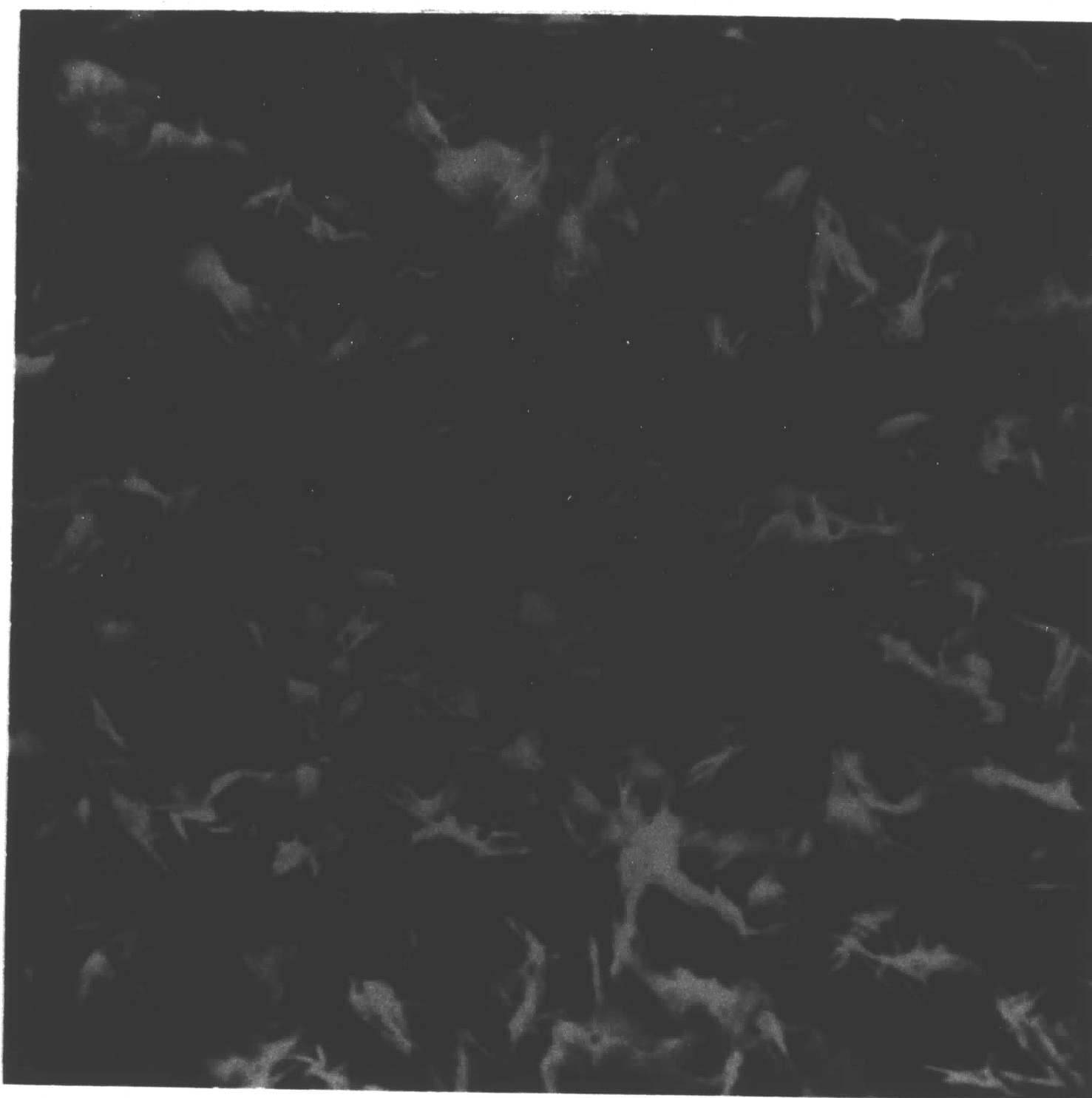CROSS SECTION OF DIELECTRIC LINED WAVEGUIDE

FIGURE 1
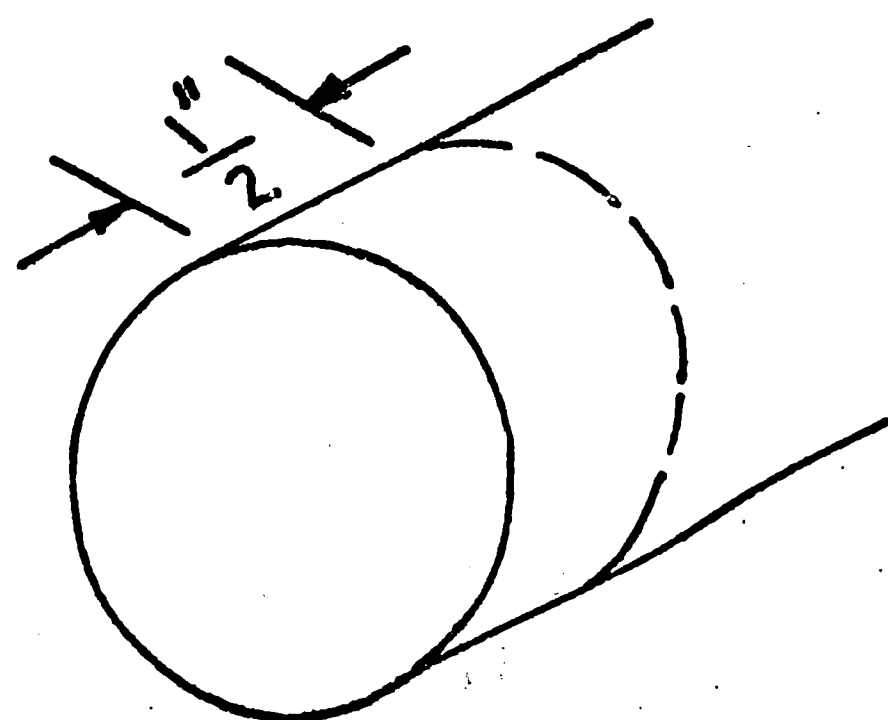
(a) CUT CYLINDRICAL RING
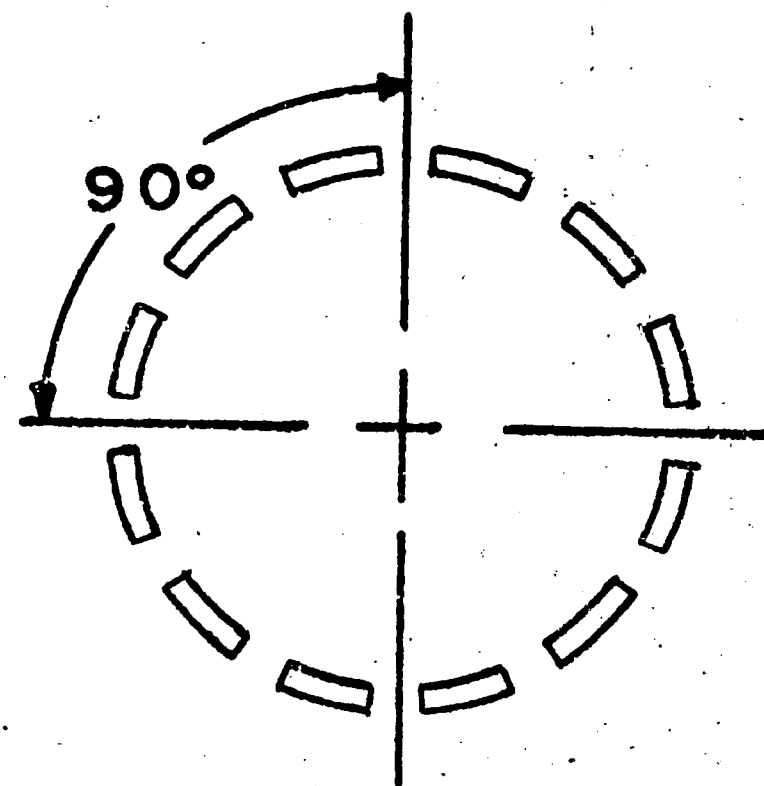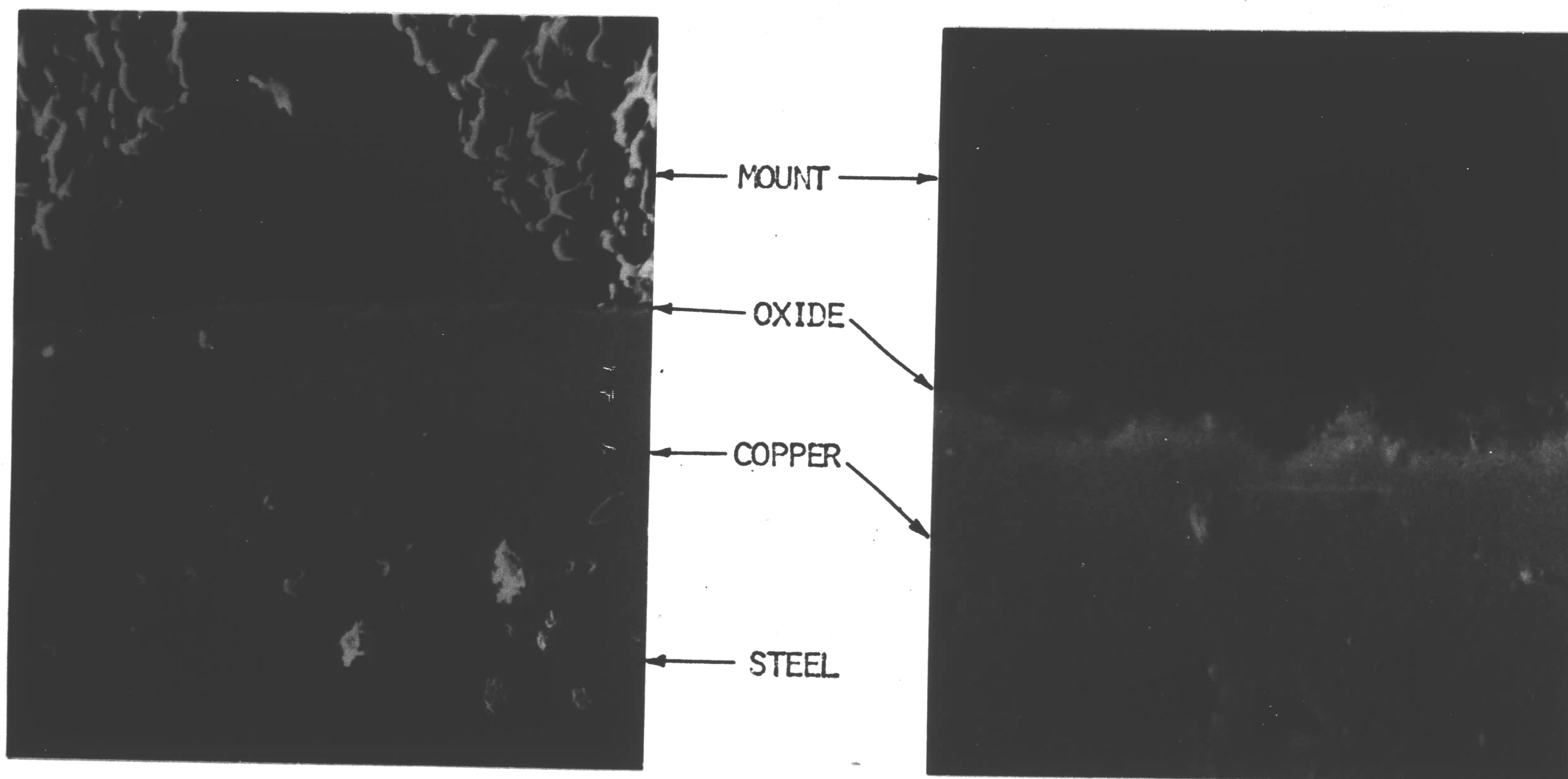
(b) DIVIDE INTO QUADRANTS AND CUT SAMPLES

SCHEMATIC SHOWING HOW SAMPLES WERE CUT

FIGURE 2

SCANNING ELECTRON MICROGRAPH OF SURFACE
TOPOGRAPHY OF OXIDE SAMPLE NO. 125
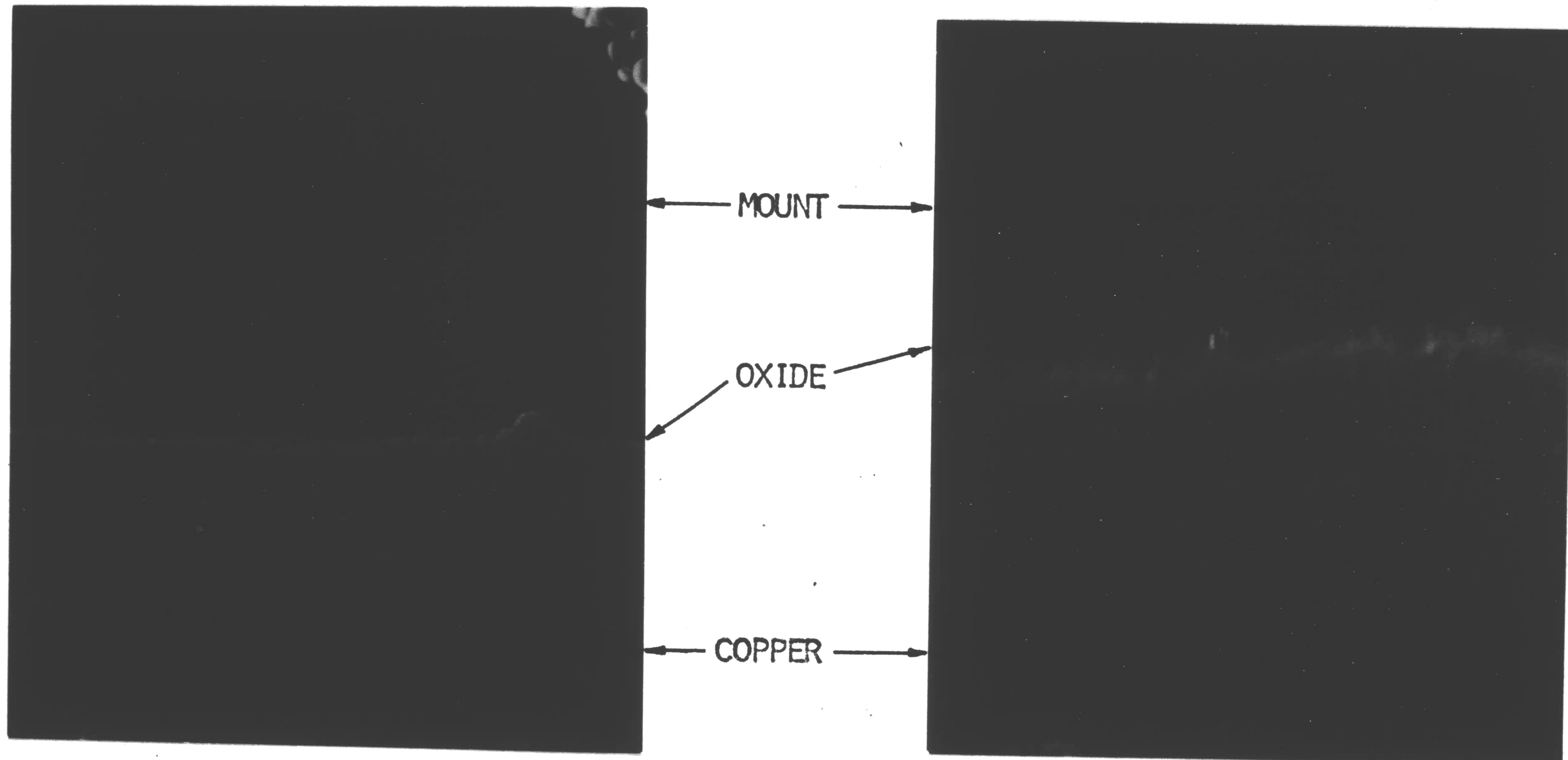(5000X -- 45°)

FIGURE 3

MOUNT

OXIDE

COPPER

STEEL

(A) 1000X -- 45°   (B) 5000X -- 45°

SCANNING ELECTRON MICROGRAPHS OF A LONGITUDINAL
CROSS-SECTION OF OXIDE SAMPLE NO. 125

FIGURE 4

MOUNT

OXIDE

COPPER

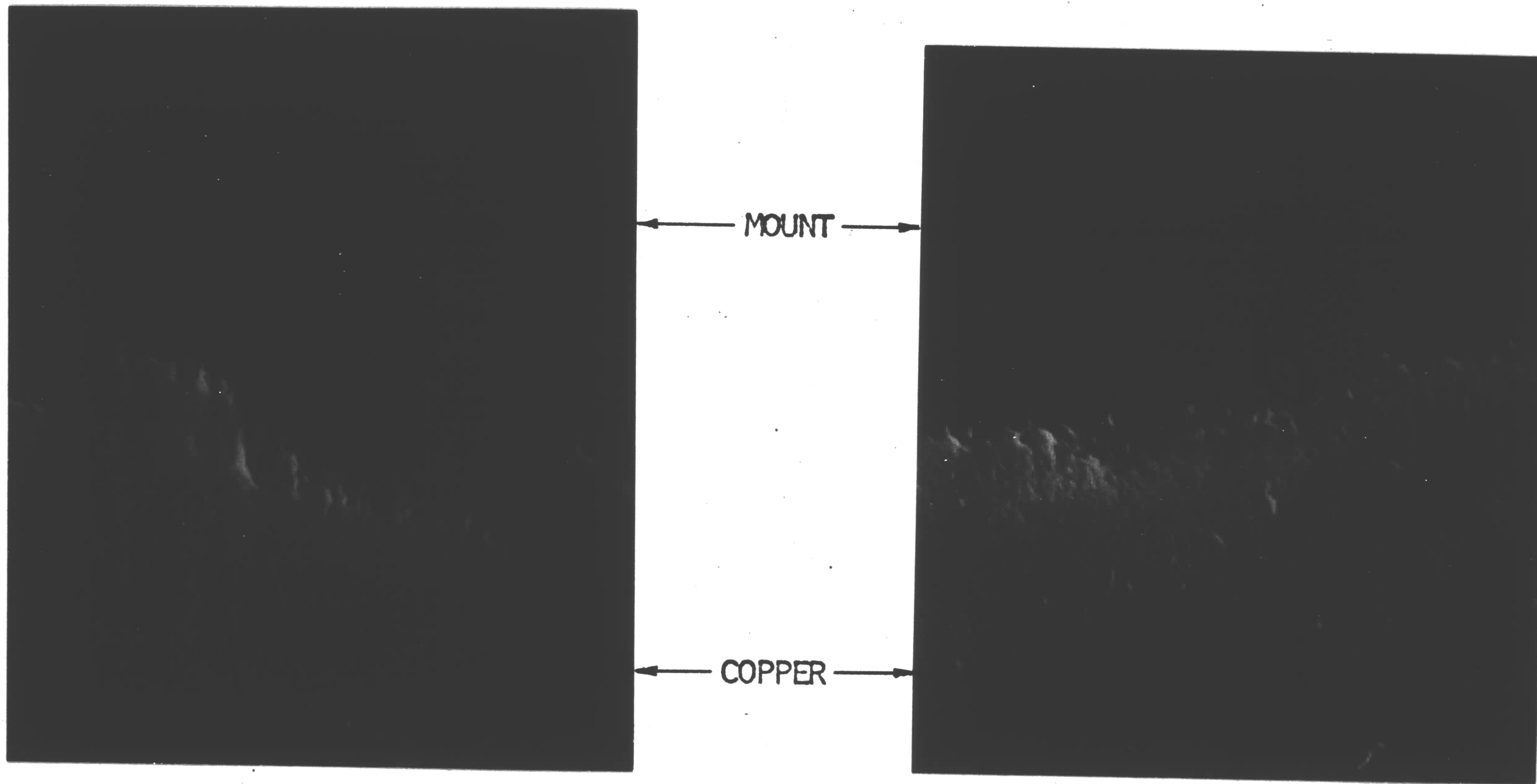(A) 1200X --45°   (B) 6000X -- 45°

SCANNING ELECTRON MICROGRAPHS OF A LONGITUDINAL
CROSS-SECTION OF OXIDE SAMPLE NO. 125

FIGURE 5
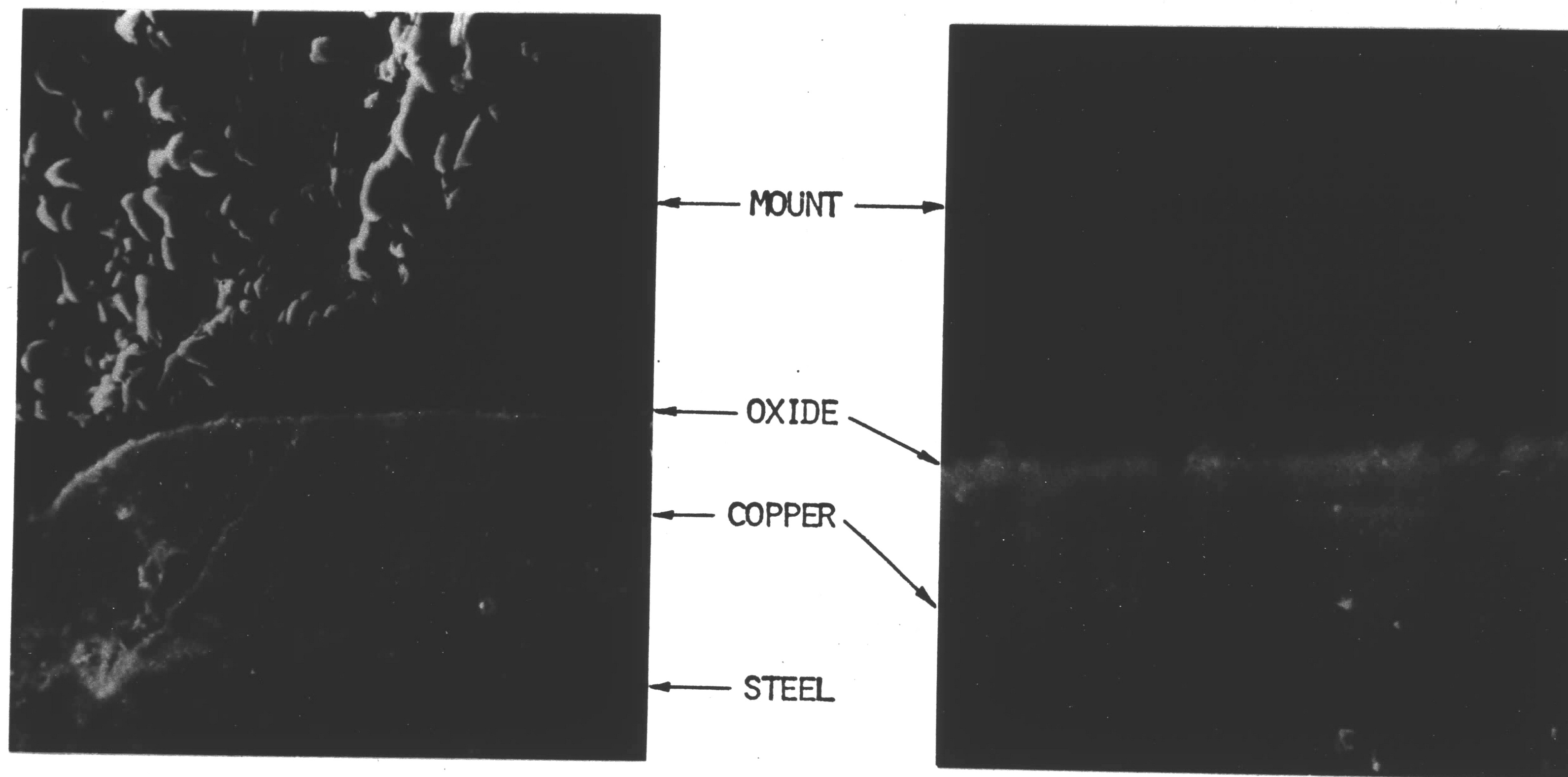
(A) 11000X -- 65°   (B) 11000X -- 45°

Scanning Electron Micrographs of a Transverse
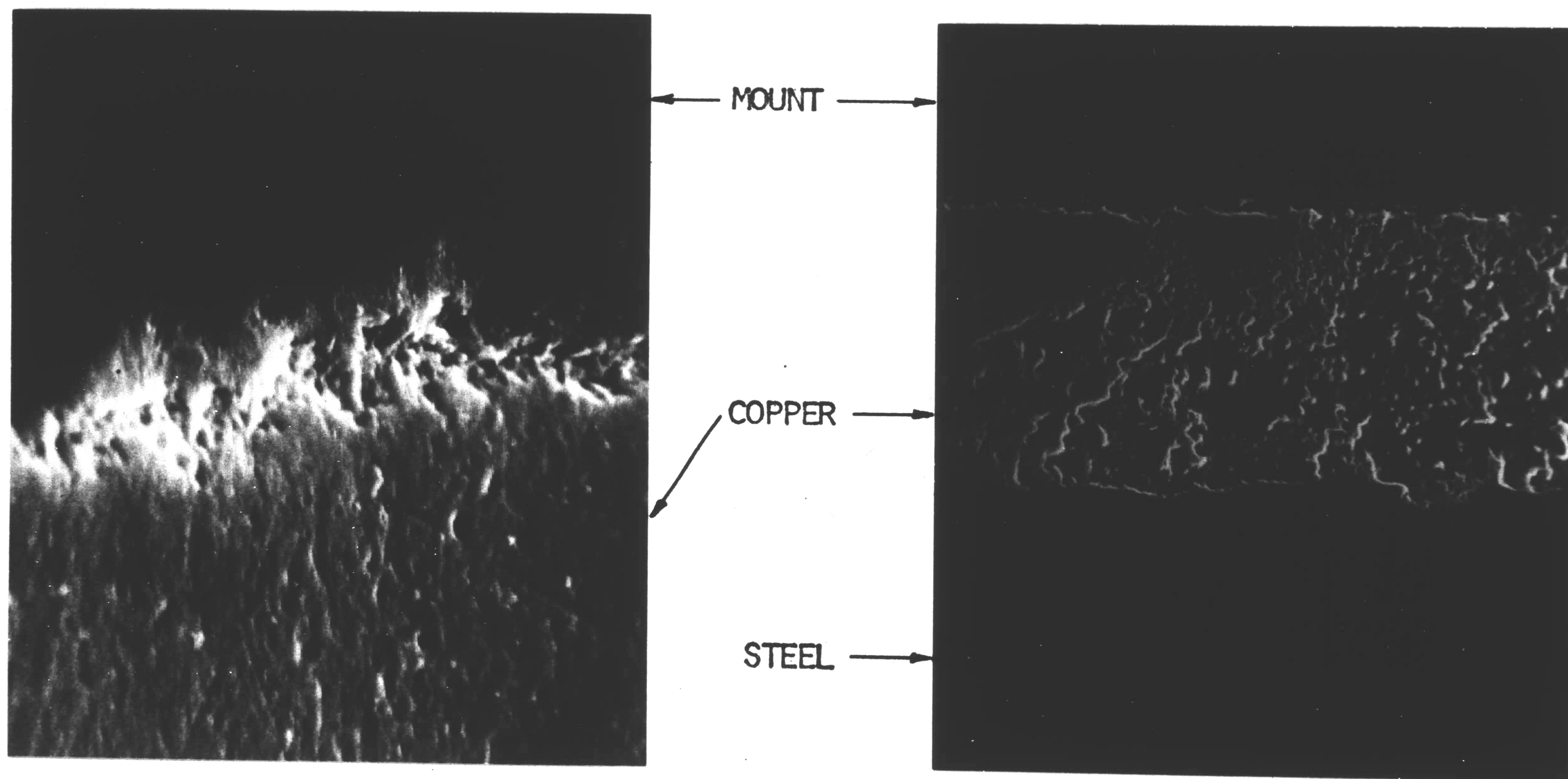Cross-Section of Oxide Sample No. 125

Figure 6

(A) 1200X -- 45°   (B) 6000X -- 45°

SCANNING ELECTRON MICROGRAPHS OF A TRANSVERSE
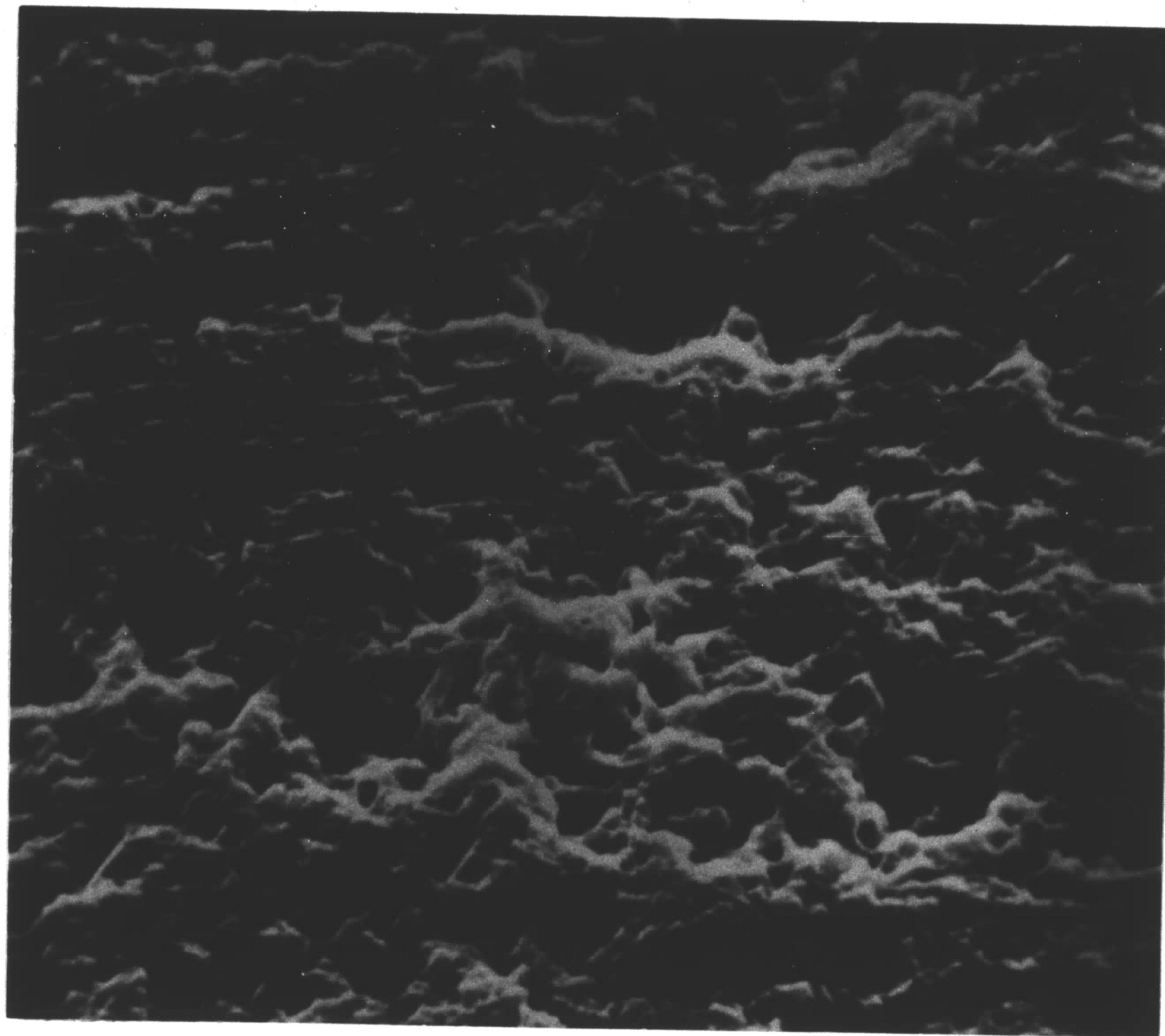CROSS-SECTION OF OXIDE SAMPLE NO. 725

FIGURE 7

MOUNT

COPPER

STEEL

(A) NH$_4$OH-H$_2$O$_2$ ETCH -- 10500X -- 65°   (B) NaCN ETCH -- 1100X -- 45°
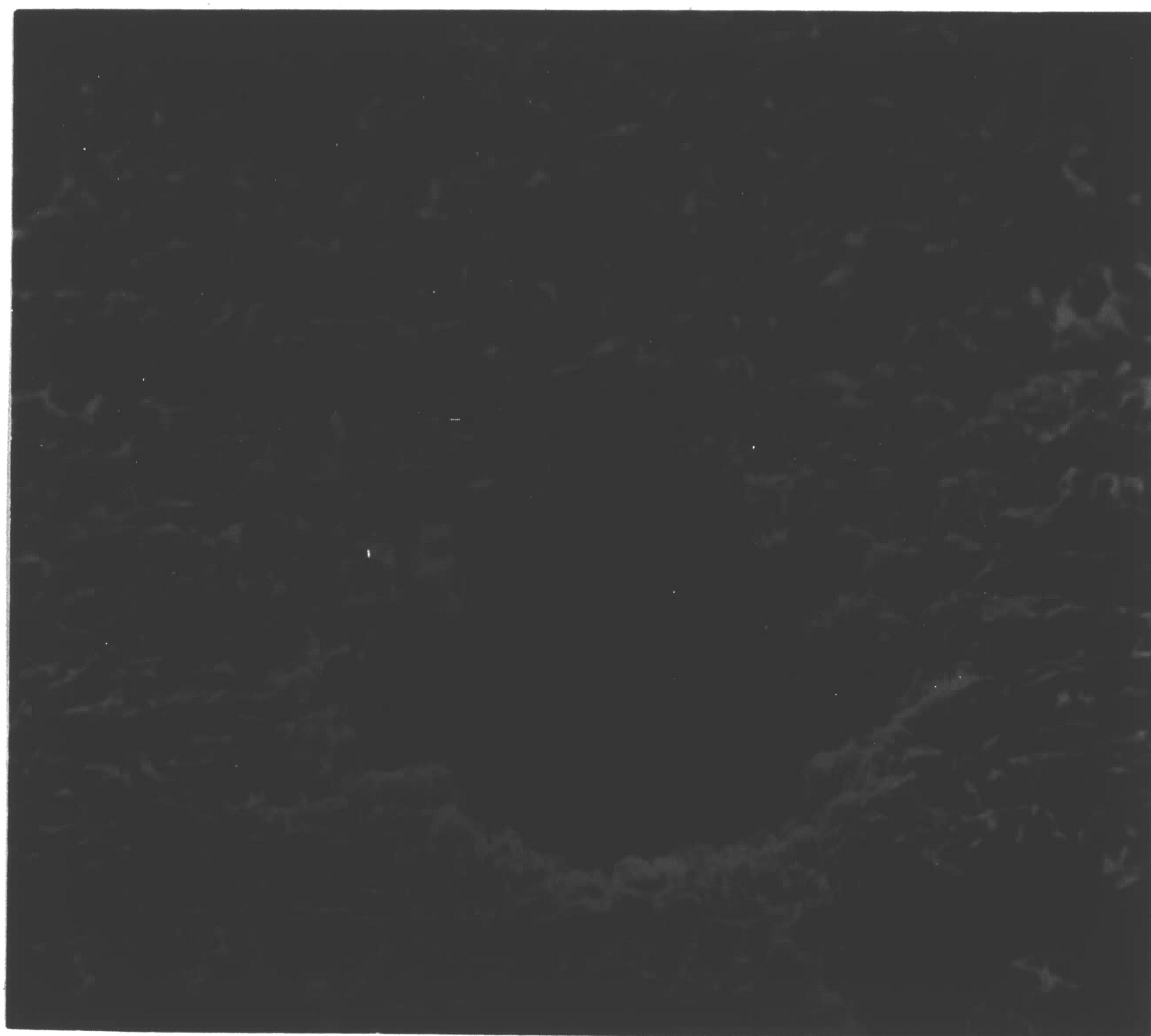
SCANNING ELECTRON MICROGRAPHS OF ETCHED CROSS-SECTIONS

OF OXIDE SAMPLE No. 125
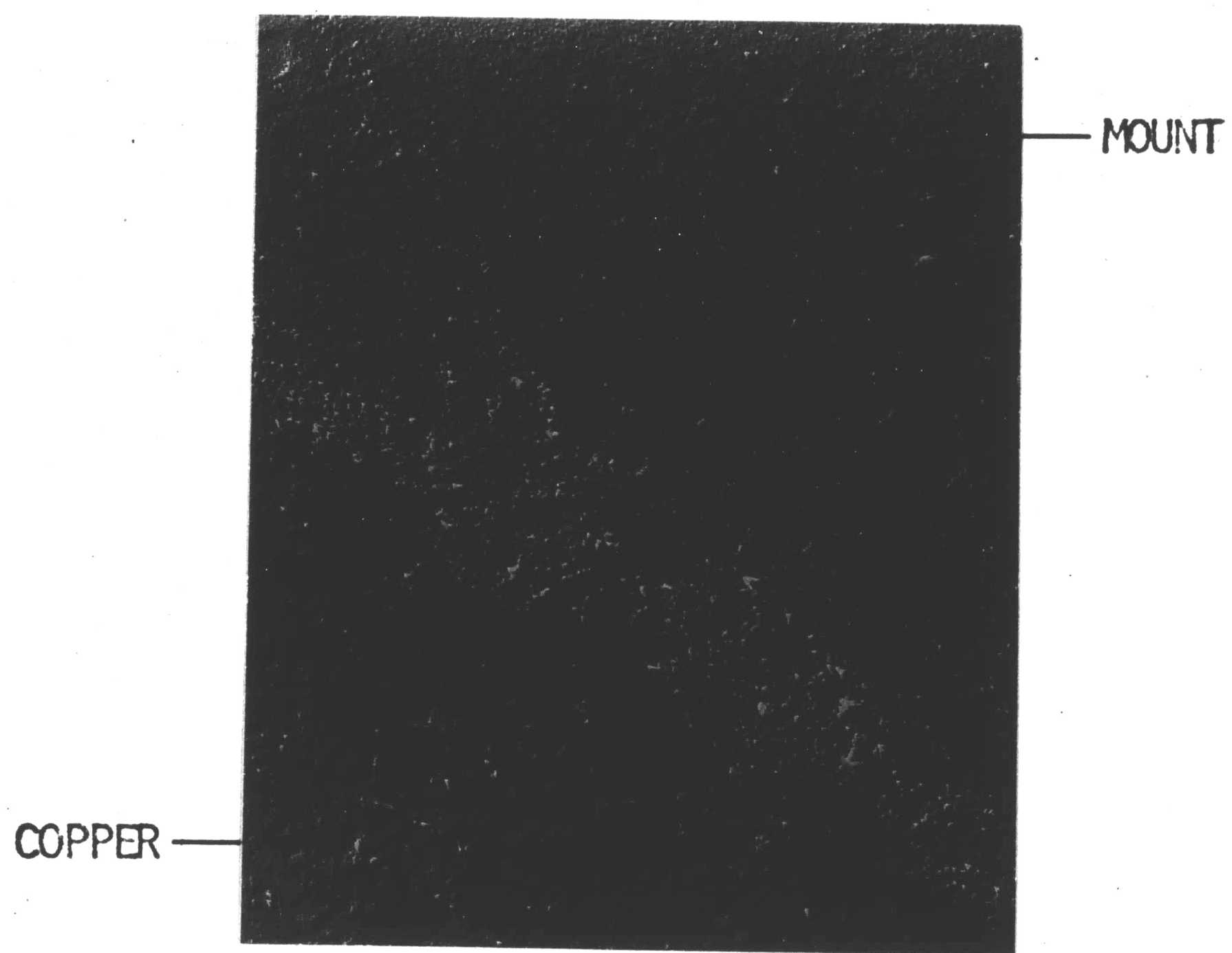
FIGURE 8

SCANNING ELECTRON MICROGRAPH OF SURFACE
TOPOGRAPHY OF OXIDE SAMPLE No. 625 AFTER
COMPLETE ETCH IN NaCN
(9000X -- 45°)

FIGURE 9
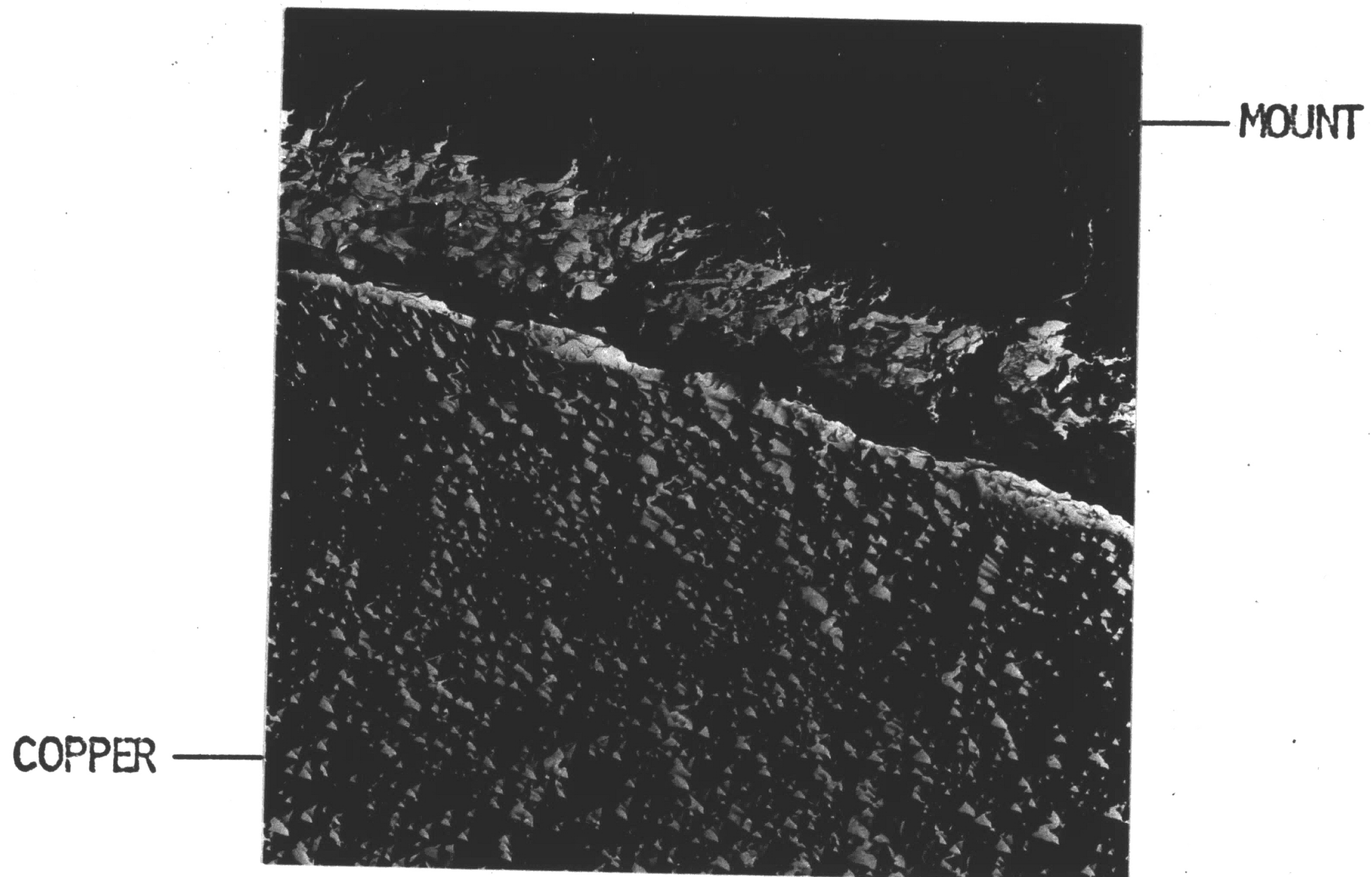
SCANNING ELECTRON MICROGRAPH OF SURFACE
TOPOGRAPHY OF OXIDE SAMPLE No. 625 AFTER
PARTIAL ETCH IN NaCN
(4500X -- 76°)

FIGURE 10

MOUNT

COPPER

REPLICA ELECTRON MICROGRAPH OF A LONGITUDINAL
CROSS-SECTION OF OXIDE SAMPLE NO. 125
(10000X)

FIGURE 11

MOUNT

COPPER

Replica Electron Micrograph of Etched
Cross-Section of Oxide Sample No. 125
(NaCN Etch -- 5000X)

Figure 12

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APPENDIX

The chronopotentiometric technique was first developed by Evans and Bannister[22] and by Miley[23,24], and was modified by Campbell and Thomas[25]. It involves cathodic reduction of the oxide film at constant current density while monitoring the change in potential with time. A sudden change in potential indicates that the film is gone and another process, usually hydrogen evolution, must occur to maintain the flow of current. A typical potential-time curve is shown in Figure A1. When the current is turned on, the potential jumps to the value characteristic of the film being reduced. When the film has been reduced, the potential then jumps to another value characteristic of another reaction, usually hydrogen evolution. The time, τ, for reduction of the film is measured from the time the current is turned on to the inflection point of the potential transition. The thickness of the film can then be calculated using the following equation:

$$T = \frac{(10^5)(M)(i)(\tau)}{(n)(F)(d)} \qquad (A1)$$

where

T = calculated thickness in Angstroms.

M = molecular weight of film.

i = current density (ma/cm^2).

F = Faraday's constant = 96,493 coul.

d = density of the film (g/cm^3).

τ = transition time (sec).

n = number of Faradays required to reduce one
gram formula weight of the film.

In some instances, as with the cuprous and cupric oxides of copper, two separate, successive transitions are observed allowing individual thickness calculations for each.

There are several assumptions inherent in the use of equation A1. It is assumed that the reduction reaction occurs with 100% current efficiency, i.e., that all the current goes toward reduction of the film and none toward side reactions. It assumes that the inflection point represents reduction of all the film. The current density, i, implies a knowledge of the true area of the specimen although the usual procedure is to use the apparent area. Use of the equation also assumes that the density of the film is equal to the bulk density.
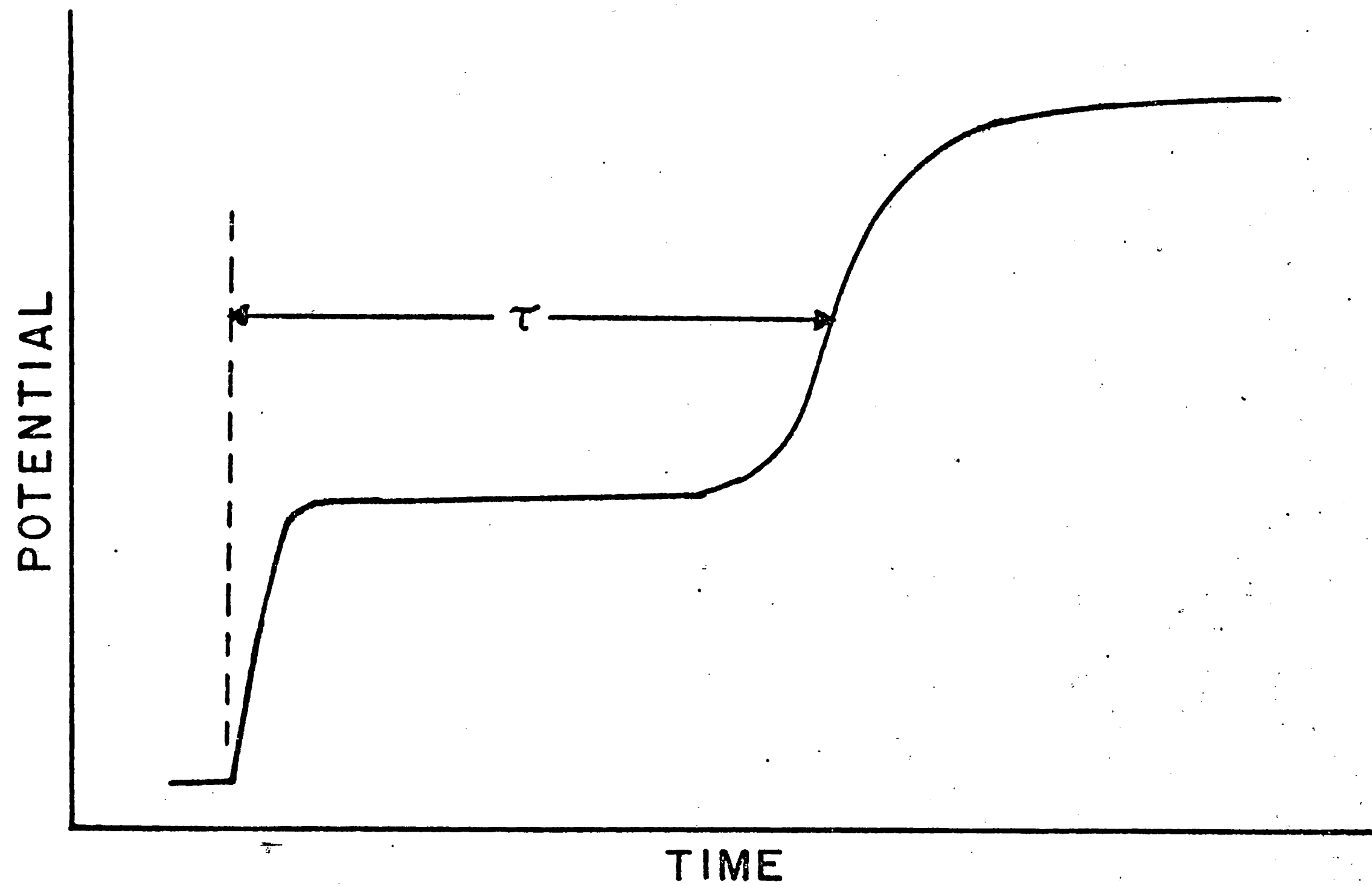
COULOMETRIC REDUCTION CURVE OF POTENTIAL VS TIME
AT CONSTANT CURRENT DENSITY

FIGURE AI

VITA

Michael F. Costantino was born on December 25, 1946 to Mr. and Mrs. Angelo M. Costantino of Lilly, Pa. He was graduated from Bishop Carroll High School in 1964, and the same year began studies in engineering at Penn State University. He was graduated from Penn State in 1968 with a Bachelor of Science degree in Electrical Engineering.

Upon graduation he accepted a position as engineer with the Western Electric Company in Allentown, Pa. While at Allentown, his assignments were in the areas of both development and manufacturing engineering for thin film hybrid integrated circuits.

In 1971 he married the former Regina Ann Williams. The same year, he was transferred to the Western Electric Engineering Research Center to pursue a Master of Science degree in Metallurgy and Materials Science in the Lehigh-Western Electric Fellowship Program.