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HIGH VOLTAGE TEM STUDY OF OXIDATION-INDUCED
STRESSES IN Al-Mg

S.C. Puranikmath
(M.S. Thesis)

June 1986

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High Voltage TEM Study
of Oxidation-Induced Stresses in Al-Mg

Shivayogi Channaveerswamy Puranikmath
M.S. Thesis

Lawrence Berkeley Laboratory
Univeristy of California
Berkeley, California 94720

June 1986

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High Voltage TEM Study of Oxidation-Induced Stresses in Al-Mg

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Om Nama Shiva

To My Parents, Brothers and Sisters

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1. INTRODUCTION

The use of nearly all metals and alloys at elevated temperatures is invariably limited by the way in which they react to their surrounding environment. The most common reaction is oxidation. Oxidation usually involves a chemical reaction between a dry metal surface and an oxidizing gas to form an oxide film over the exposed surface. Industrial materials without sufficient oxidation resistance frequently fail even in a short time as a result of rapid oxidation, which owing to poor adhesion of oxide layers is also accompanied by spalling of the oxide scale. As a result permissible limits of wear are often exceeded and expensive apparatus and machinery parts have to be replaced prematurely costing the metal industry millions of dollars a year in metal losses and preventive measures.

In oxidation, the reaction product frequently appears as a compact phase with the reacting substances spatially separated from each other and further reaction is possible only if at least one of the reactants diffuses through the product layer (oxide) to the other reaction partner. The two reaction partners are metal and oxygen (non-metal). The course of the reaction can be dictated by a) phase boundary reactions at the oxygen/oxide or metal/oxide interface, b) diffusion of metal ions and/or oxygen ions through the oxide, c) transport processes in space-charge boundary layers for thin oxide layers grown at low temperatures. The slowest process determines the kinetics of oxidation. The formation, composition and structure of the oxide layer

may also depend on the thermodynamic stability of oxide that is formed; and the crystal structure of the oxide layer and of the metal or alloy which determines the adhesion between the oxide layer and the underlying metal. The rate laws observed in oxidation of metals and alloys may take various forms. The oxidation processes may follow the logarithmic rate law ($x \propto \ln t$); linear rate law ($x \propto t$); parabolic rate law ($x \propto t^{1/2}$), where 'x' is the thickness of oxide formed in time 't', or as breakaway where repeated parabolic steps give an overall linear behavior. The logarithmic rate law applies mainly to highly protective thick films formed at lower temperatures. The linear rate law applies to the initial stages of oxidation, before a thick protective oxide film is formed. The parabolic rate law is obeyed at higher temperatures and high gas (oxygen) pressures. Breakaway effects are observed when the oxide film cracks or flakes which reduces its thickness. Repeated breakaway of a fine oxide scale can prevent it from increasing beyond a certain thickness. The oxidation mechanism in metals and alloys has been explained by Wagner¹, who was the first to give a complete theory of parabolic oxidation; he was able to derive the observed parabolic oxidation rate constant. Wagner's theory is applicable when diffusion processes alone are rate determining which is generally the case at high temperatures. It also assumes that metal ion and non-metal ion diffusion are equally likely. It is not applicable for low temperature oxidation and space charge boundary layer thin film oxidation where the Cabrera-Mott² theory of oxidation can be applied.

Oxidation of alloys is more complex. There may be formation of a single oxide, multiple oxides or complex oxides. In binary alloys one of the constituents is oxidized at a given time or both constituents oxidized simultaneously depending on the affinity for oxygen of the constituents. Internal oxidation and catastrophic oxidation can occur depending on the nature of the alloying elements. Alloying elements are often added to inhibit oxidation by formation of a protective oxide film on the metal.

The growth of an oxide on a metal surface may result in the generation of stresses and these stresses may eventually cause the film to rupture and thus cease to protect the metal surface. The most obvious evidence of stress generation during oxidation is that the scale (oxide) eventually fails in a manner which clearly indicates a stress system acting in the plane of the interface: blistering or shear cracking indicating compressive stresses in the film: tensile fractures indicating tensile stresses in the film. In 1947 Evans³ demonstrated the existence of stresses in oxide films grown on Ni. A number of investigators have observed dimensional changes in the substrate which they attribute to creep due to growth stresses. The first of these was Moore⁴, who oxidized a Cu tube on the outside only. The internal diameter of the tube diminished slightly. Stringer⁵ has observed increases in diameter of Ta tubes on oxidation, which can be attributed to compressive stresses in the metal. Investigators at the Berkeley Nuclear Laboratories of C.E.G.B. have observed significant extensions of steel-fuel element cans⁶ and contractions of Mg specimens⁷ as a result of oxidation.

The experimental methods used to determine stresses in oxidized films can be divided into two classes. Bending of a strip which is clamped at one end and allowed to oxidize on one side only; and expansion or contraction of a helix, again allowed usually to oxidize on one side only. Both techniques were originally used to determine stresses in electro-deposited coatings. The first method was introduced by Stoney⁸ and was first applied to oxidation of metals in a modified form by Dankov and Churaev⁹. In this experiment a thin film of metal was vapor-deposited on a thin sheet of mica, which was clamped at one end while the other end carried a pointer, which could be viewed through a telescope. When oxygen was introduced, the stresses produced during oxide growth bent the mica sheet. This experiment has been criticized¹⁰ on the basis that the morphology of the vapor-deposited metal is not known and that observed stresses may be due to growth of oxide within pores of the metal. A simple extension of the Stoney technique can be used to determine at room temperature the stresses present in films formed on metals by oxidization at elevated temperatures. A thin flat wafer is oxidized on both surfaces, and the film is subsequently etched from one side. The wafer bends as a consequence of stresses present in the film remaining on the other side. Jaccodine and Schlegel¹¹ measured the bending with a mechanical micromanipulator while Whelan et al.¹² used an X-ray method. In the wafer bending method there is difficulty in producing a flat wafer. The second major method was developed by Brenner and Senderoff¹³. In their apparatus called a spiral

contractometer, plating took place on the outer surface of a metal helix protected on the other side by an insulating lacquer. The helix was clamped at one end and as a result of stresses developing, the helix expanded or contracted, the other end consequently winding or unwinding. The technique was applied in a modified form to oxidation of metals by Engell and Wever¹⁴ who oxidized a spiral of iron at 700.C. Both surfaces of the spiral were allowed to oxidize, the differential stress arising because of the difference in length of inner and outer surfaces. The method is attractive to study stresses developed during high temperature oxidation of metals; but it is very sensitive to different oxidation rates on opposing sides, which in some cases are dependent on the curvature of the metal surface⁵.

For a metal oxidizing by anion diffusion, stresses result as new oxide is formed at the oxide-metal interface. Under these conditions the volumetric change between metal and oxide expressed via the Pilling-Bedworth Ratio (PBR)¹⁵ can be used to predict the localized stress state. For metals oxidizing by the usual case of metal ion diffusing outwards, new oxide is formed at the oxide-oxygen free surface; both oxide and metal should therefore be stress free. That this is not so has been clearly demonstrated throughout the literature, but no satisfactory explanation has been advanced, even for metals with a single oxide layer. It has been postulated¹⁶ that some inward oxygen ion diffusion occurs through the oxide to cause a reaction at the metal-oxide interface and generate stress. In thin film oxides epitaxial stresses are present. The other type of stresses present in

an oxide-metal system are a) recrystallisation stresses of the type described by Jaenicke et al.^{17,18} b) composition change stresses of type described by Richmond¹⁹ c) stresses due to oxide growth within an oxide layer^{17,18,20} and d) point defect stresses.

High Voltage Electron Microscope (HVEM) can be used to detect and study oxidation-induced surface stresses by dislocation network formation. Thin foil specimens may undergo changes in microstructure during examination in a high voltage electron microscope, as a result of specimen interaction with the electron beam and/or its surrounding gaseous environment. Useful information can be derived from the observed changes in microstructure.

In studies of Al foils electron-irradiated in a high voltage electron microscope it was observed that after a short incubation period, interstitial loops nucleated in the center of the foil and grew under continued irradiation until eventually a network was formed²¹. Stereo-microscopy confirmed that the loops were unable to nucleate within 0.2 μ m of the surface²². The surface acts as a good sink for the point defects and prevents the attainment of the necessary supersaturation for loop nucleation. During a study of the effect of surface conditions on the radiation damage in Al-11% Mg by Westmacott²³, it became apparent that the presence of oxide films on the foil surfaces completely altered the distribution of the damage in the foil. In thin foil specimens deliberately oxidized for 2-1/2 months at room temperature prior to irradiation, preferential formation of interstitial loops at the metal-oxide surface was observed, which

had grown with increase in time of irradiation (Figs. 1a and 1b). After post-irradiation annealing, the dislocation loops interacted to form an irregular dislocation network. In foils with {013} surface orientation hexagonal networks were formed. The results have been interpreted in terms of oxidation-induced stress. Oxidation of the Al-Mg alloy results in the formation of MgO surface film, consequently since the Pilling-Bedworth Ratio for MgO and Al-Mg is greater than unity, tensile stresses develop in the matrix and compressive stresses in the oxide. During electron-irradiation in the HVEM, interstitial loops nucleated and grew in the metal at the oxide-metal interface in response to the tensile stress. The formation of such interstitial networks can be used to monitor stress buildup during oxidation. Mitchell et al.²⁴ have also used electron microscopy to characterize the stress effects which occur during the oxidation of iron.

The appearance of irradiation damage in a material is affected by the magnitude of the electron flux, the temperature of the area under observation, the time of irradiation and the surface condition of the area being irradiated. These factors should be taken into consideration for proper interpretation of the results.

The aim of the present work is to study in detail the near-surface formation of dislocation network in electron-irradiated Al-Mg alloy on oxidation and to assess the possibility of monitoring the stresses produced during oxidation by the dislocation network formed. Preliminary work was done to optimize the different variables involved in the experiment such as the time and temperature of irradiation and the post-irradiation annealing conditions, for good network formation.

The specimens were then oxidized at different temperatures, for different durations of time, and stress buildup was monitored via the dislocation networks formed.

This is an exploratory study with an effort to use the high-voltage electron microscope as a tool to quantify the stresses produced at oxide-metal interface.

2. EXPERIMENTAL WORK

2.1 Material Preparation

An Al-2.5 wt.% Mg alloy was made using Al of 99.995% purity and Mg of 99.995% purity. The alloy was prepared by melting the metals in a graphite crucible in a vacuum arc melting furnace in an atmosphere of 99.998% He. The ingot was cast in a copper mold. The cast ingot was homogenized at 600°C for two days and rolled; homogenized and rolled to a final thickness of 0.003". The rolling apparatus was carefully cleaned before use to avoid any contamination of the alloy. The rolled sheet was annealed at 500°C for 1 hour and then furnace-cooled.

2.2 Electron Microscope Foil Preparation

Three mm discs for jet polishing were punched from the center portion of the sheets. Since the oxide present on the surface of the specimen hinders polishing, it was removed by dipping the specimen into a solution of 70% HPO_3 , 25% H_2SO_4 and 5% HNO_3 maintained at 80°C. followed by rinsing in distilled water. The specimens were electrolytically thinned using the Fischione twin jet polishing apparatus. An electrolyte of 95% Methanol and 5% Perchloric acid was used at room temperature and 20V. In some cases difficulty in polishing was encountered due to the formation of a white deposit. This was removed by dipping the specimen in the solution used for oxide removal.

2.3 Microscopy

Irradiation was performed in a Hitachi HU 650 high voltage electron microscope at an electron energy of 650KeV, using a Gatan double-tilt heating holder equipped with a platinum thermocouple for temperature read out. The manufacturer's calibration of the heating stage was used throughout this work. The Liquid-Nitrogen cold-trap was kept full to restrict specimen contamination.

2.4 Oxidation

The specimen was oxidized by heating it in the Gatan heating holder in the airlock of the microscope and was cooled to room temperature after completion of oxidation. The oxidation of the specimen in the holder minimizes handling whereas furnace oxidation involves many handling stages and can contribute to deformation damage. Another advantage of oxidation of the specimen in the heating holder is that it can be inserted immediately into the microscope to carry out the irradiation study. A device such as the environmental cell is very useful to perform in-situ experiments like oxidation and irradiation damage. Unfortunately the valves of the environmental cell of the Hitachi high voltage electron microscope were not functioning, and it could not be used for this study.

2.5 Irradiation Damage

The specimens were heated to the required temperature in the microscope and after selecting a suitable thin area they were irradiated by focusing the electron beam. Constant observation of the

specimen area was necessary in order to counteract the specimen drift. A visible mark close to the region being irradiated was used to identify the area. After irradiation the electron beam was defocused and micrographs were taken. The irradiated specimens were annealed by heating the specimen in the microscope and the effect of temperature on the irradiated defect structure was observed. Micrographs were taken at the required annealing temperatures. The dislocation structure formed was not stable at higher annealing temperatures and when held for longer duration of time. Sometimes dislocation defect structures annealed out before micrographs could be taken. Consequently, the condition for formation of a stable, equilibrium dislocation network could be established only after studying the effects of several experimental variables.

2.6 Experiments

In the first experiment (Table I), the irradiated defect structure formed in the oxidized alloy was analyzed as a function of time. The second series of experiments (Table II) was performed to determine the optimum conditions of (i) irradiation temperature (ii) time of irradiation (iii) annealing condition after irradiation, required for the formation of a resolvable dislocation network. The effect of oxide thickness and oxidation stresses on the dislocation network formed were studied in the third series of experiments by varying the oxidation time and temperature (Table III). The experiments were carried out with a beam direction of $[001]$ and for a foil orientation of $[001]$.

3. RESULTS

3.1 Defect structure (Dislocation Structure) generation with progress in time of irradiation

The experiment was performed to study the defect structure produced in oxidized Al-2.5%Mg alloy with progress in time of irradiation. The specimen was oxidized for 75 minutes at 350°C in the airlock of the microscope prior to irradiation. Irradiation was conducted with the specimen held at 150°C (Table I).

1. After irradiating the specimen for 20 minutes a low density of small dislocation loops was observed. The time of irradiation was insufficient for loop growth [Fig. 2a].

2. Dislocation loops were observed to grow after 40 minutes of irradiation while loop nucleation continued [Fig. 2b].

3. With increase in time of irradiation to 60 minutes, 80 minutes and 100 minutes, the loops grew further. [Figs. 2c, 2d, 2e]. Two sets of dislocation roughly perpendicular to each other were observed. There was evidence of formation of a dislocation network; but it was not a regular network. Further irradiation up to 120 minutes produced little change in the dislocation loop structure.

4. Post-irradiation annealing at 170°C for 20 minutes increased the dislocation loop size in many cases. A few of the dislocations had annealed out. The smaller dislocation loops had nucleated and grown into the larger dislocation loops. A clear geometrical network was not observed, though at some areas of the damage there was evidence of elongated loops at right angles [Fig. 2g]. Stereo microscopy confirmed that the dislocation loops were near the surfaces. Figure 2h is the diffraction condition used to observe the damage.

In this experiment irradiation was conducted at intervals of 20 minutes and micrographs were taken. It was a case of non-continuous irradiation as irradiation was interrupted to take the micrographs. There was insufficient time and insufficient continuous irradiation for nucleation and growth of dislocation loops into a resolvable network.

3.2 Effect of time and temperature of irradiation and post-irradiation annealing treatment on the defect structure (Dislocation Structure) formed

3.2.1 Effect of irradiation time

The specimen was oxidized at 250°C for an hour in the airlock of the microscope. Four different areas of the specimen, with the same [001] surface orientation were irradiated for 1/2 hour, 1 hour, 1 1/2 hours and 2 hours, respectively. The post-irradiation annealing was performed at 170°C for 20 minutes. (Table II; Expt. 1).

1. The damage produced in this specimen after 1/2 hour of irradiation was in the form of dislocation loop clusters [Fig. 3a]. The magnitude of the damage was small. The density of the loops was low. The irradiation time was too low to produce sufficient damage. A second area irradiated for 1 hour showed slightly more irradiation damage [Fig. 3b]. The density of the dislocation loop clusters was more than in the previous one. The dislocation loops had grown in size, but the time and temperature of irradiation was insufficient to produce a dislocation network. There was substantial growth of dislocations towards network formation after post-irradiation annealing [Fig. 3c]. Though dislocations used in two different directions were detected no clear evidence of a distinguishable dislocation network was seen.

2. A third area in the specimen was irradiated for 1 1/2 hours. The dislocation loop structure had grown with increase in time of irradiation with smaller dislocation loops coalescing to form larger ones. Two sets of edge dislocations were in contrast for g of $0\bar{2}0$ [Fig. 3d]. The process of dislocation network formation had been initiated. The post-irradiation annealing helped the growth of some dislocations due to enhanced diffusion, while in some cases dislocations had annealed out [Fig. 3e]. A few square units in the dislocation network could be observed.

3. A fourth area in the specimen was subjected to irradiation for 2 hours, resulting in the formation of a dislocation network [Fig. 3f]. Two sets of dislocation loops perpendicular to each other had grown and

were intersecting each other to form a resolvable network. The network was close to a square geometry near the surfaces. The post-irradiation annealing treatment improved the definition of the dislocation network [Fig. 3g]. The two sets of dislocations were found to be edge type with Burgers vectors $a/2[110]$ and $a/2[\bar{1}10]$. Both sets of dislocations were in contrast for $g[020]$ and $g[200]$.

At lower irradiation times dislocation defect clusters were seen. These grew into resolvable dislocation loops with continued irradiation, eventually intersecting and forming a dislocation network. At the specimen temperatures of 150°C an irradiation time of 1 1/2 hours to 2 hours does produce sufficient irradiation damage in the specimen, which results in dislocation network formation. The dislocation network lies close to the surface of the foil.

3.2.2 Effect of specimen temperature on the irradiated defect structure

Two specimens were used in this experiment. The specimens were oxidized at 250°C for 1 hour in the airlock of the microscope. Irradiation on one specimen was conducted while it was held at 165°C , while on the other it was done at 180°C . After irradiating for 2 hours, the samples were annealed at 170°C for 20 minutes. (Table II, Expt. 2).

1. Irradiation at 165°C :

A dislocation network was observed after 2 hours of irradiation. Two sets of dislocations perpendicular to one another were in contrast

for g of 020 [Fig. 3h]. There was no evidence of formation of clusters of dislocation loops. At the temperature of study, the smaller dislocation loops had grown, joining one another to form larger dislocations, and subsequently a network. The geometry of the dislocation network was not well-developed although in certain regions the network units seemed closer to a square shape. Figure 3i shows one set of edge dislocations with Burgers vector $a/2[1\bar{1}0]$ in contrast for g of $\bar{2}20$. The post-irradiation annealing enhanced the growth of some dislocations, while a few annealed out [Fig. 3j]. The diffraction pattern of the irradiated area is shown in Fig. 3k.

2. Irradiation at 180°C:

After 2 hours of irradiation, radiation damage in the specimen was observed in the form of small dislocation loop clusters. Very few of these clusters had grown into detectable larger dislocation loops, [Fig. 3l]. After a post-irradiation annealing treatment at 170°C for 10 minutes, it was observed that the smaller dislocation loops (clusters) combined with one another to form larger dislocation loops [Fig. 3m]. The absence of irradiation during annealing at a temperature of 170°C had led to the growth of dislocation loops. Figure 3n shows the dislocation structure after 20 minutes of annealing. Figure 3o shows the diffraction pattern of the area studied.

During irradiation, the temperature is a very important factor. It is probable that during the first experiment, irradiation of the specimen at 165°C, the temperature during oxidation of the specimen was higher than that shown on the monitor, which might have given a thicker

oxide which gave rise to dislocation network formation after irradiation. The second factor is the nature of the experimental conditions used. A pseudo-static condition was used in the present study. The use of dynamic in-situ conditions like the ones which exist in the environmental cell might better help to arrive at conclusive results. From the results of the irradiation study at 180°C specimen temperature it seems that the temperature was too high for stable dislocation network formation to occur.

3.2.3 Effect of annealing conditions on the dislocation loop structure

The specimen was oxidized at 250°C for 1 hour in the airlock of the microscope. Three different areas of the specimen were chosen for this study. Each area was irradiated at a temperature of 150°C for 1 1/2 hours. They received a subsequent annealing treatment in the microscope at 160°C, 180°C and 200°C respectively (Table II; Expt. 3).

1. The first area showed a dislocation network structure after completion of irradiation. As observed in previous experiments, two sets of edge dislocations with Burgers vectors $a/2[110]$ and $a/2[\bar{1}\bar{1}0]$ were seen. The network had an approximately square geometry [Fig. 3p]. A subsequent annealing of the specimen at 160°C for 20 minutes showed growth of dislocations as well as an increase in the network size. The dislocation density had decreased. The annealing time and temperature were sufficient to produce a resolvable dislocation

network. The size of the network unit was approximately 300 nm x 266 nm [Fig. 3q].

2. A second irradiated area also showed a square dislocation network, with network unit size of 215 nm x 215 nm [Fig. 3r]. The post-irradiation annealing of the specimen was carried out at 180°C for 20 minutes. The dislocation network structure had disappeared leaving a few dislocations [Fig. 3s]. After annealing the specimen at 180°C for 30 minutes the dislocations had disappeared completely [Fig. 3t]. The temperature and time of anneal were clearly too high and the dislocations were unstable.

3. The irradiation of a third area was performed. As before a dislocation network was observed [Fig. 3u]. The dislocation network grew in size on subsequent annealing at 200°C for 5 minutes. The smaller dislocation loops had grown into the larger dislocations [Fig. 3v]. The process of annealing out of the dislocations had been initiated. After 15 minutes of annealing at 200°C, the network of dislocations had disappeared completely [Fig. 3w].

A dislocation network approximately of a square geometry is formed after irradiating the specimens at 150°C for 1 1/2 hours. The post-irradiation annealing increases the size of the dislocation network. If a higher annealing temperature and/or longer annealing time is used, it is found that the dislocation network is unstable. A post-irradiation anneal of 160°C-180°C for 10 to 20 minutes may be suitable for a resolvable dislocation network to be observed.

3.3 Effect of Oxidation Conditions (Oxide Thickness, Oxide-Metal Stresses) on the Dislocation Network Structure

1. The specimen for the first experiment was oxidized at 300°C for 75 minutes in the airlock of the microscope. The irradiation of the specimen was performed at a temperature of 150°C for 75 minutes. The post-irradiation annealing of the specimen was carried out at 180°C. (Table III; Expt. A).

After completion of irradiation it was observed (Fig. 4a) that a dislocation network had formed. The dislocation network was of square geometry, with a network unit size of 283 nm x 283 nm. There was evidence of two dislocation networks at two surfaces of the specimen. Two sets of dislocations, perpendicular to one another were seen in contrast for g of $0\bar{2}0$. Figure 4b shows one set of edge dislocations of Burgers vector $a/2[\bar{1}10]$ observed in contrast for a g of $2\bar{2}0$. Figure 4c shows the other set of edge dislocations of Burgers vectors $a/2[110]$ observed in contrast for g of $\bar{2}\bar{2}0$. The distance between adjacent dislocations was 283 nm. Stereo microscopy confirmed that the dislocation network had formed at the oxide-metal interface [Figs. 4c and 4d]. The post-irradiation annealing of the specimen at 180°C for 10 minutes showed that the dislocation network had grown slightly [Fig. 4e]. An annealing of the specimen for 20 minutes at 180°C enlarged the dislocation network squares to 333 nm x 333 nm [Fig. 4f]. An annealing of the specimen for 30 minutes did not increase the size of the dislocation network appreciably. The dislocations had begun to anneal out [Fig. 4g]. Figure 4h shows the area at a bright field condition

with a g of 220, with a post-irradiation anneal of 30 minutes at 180°C. By comparing figures 4h and 4b it can be observed that the total number of dislocations had decreased, while the distance between the adjacent dislocations had increased. Figure 4i is the diffraction pattern of the irradiated area.

2. The oxidation of the specimen for the second experiment was carried at 250°C for 60 minutes in the airlock of the microscope. The irradiation of the specimen was performed at 150°C for 60 minutes, temperatures raised to 165°C and irradiated for another 15 minutes. The post-irradiation annealing was done at 180°C (Table III, Expt. B).

After irradiating the specimen at 150°C for 60 minutes, it was observed that a dislocation network had not yet formed at the oxide-metal interface. The irradiation damage was insufficient to produce dislocation growth into a network [Fig. 4j]. A further irradiation of the specimen at 165°C for 15 minutes was necessary to produce a resolvable, clear dislocation network [Fig. 4k]. The dislocation network formed was of approximately square geometry. Two sets of edge dislocations of Burgers vectors $b = a/2[110]$ and $b = a/2[\bar{1}10]$ were observed in contrast for g of 020. The size of the dislocation network unit was 300 nm x 300 nm. A post-irradiation annealing of the specimen at 180°C for 20 minutes, showed growth of the network; the network unit size was found to be 330 nm x 330 nm [Fig. 4l]. The diffraction pattern of the irradiated area is shown in Fig. 4m.

3. A third specimen was oxidized at 250°C for 15 minutes in the airlock of the microscope. It was irradiated at 150°C for 60 minutes. The post-irradiation annealing of the specimen was conducted at 165°C and 180°C (Table III, Expt. C).

On completion of irradiation, small dislocation loop clusters along with some larger dislocation loops were observed. The dislocations had not coalesced into larger dislocations to form a dislocation network (Fig. 4n). As observed in previous experiments (Experiments A and B) two sets of edge dislocations $b = a/2[110]$ and $b = a/2[\bar{1}10]$ were seen in contrast for g of 200. Figure 4o shows edge dislocation with $b = a/2[\bar{1}10]$ seen in contrast for g of $\bar{2}20$. On annealing the specimen at 165°C for 20 minutes a resolvable dislocation network could be detected, which was approximately of square geometry [Fig. 4p]. A magnified image of the annealed area is shown in Fig. 4q. The network unit size was 150 nm x 180 nm. The annealing of the specimen at 180°C for 20 minutes showed the network growth [Fig. 4r]. The density of the dislocations had decreased. Figure 4s shows the annealed area at a higher magnification. The size of the dislocation network unit was 180 nm x 245 nm [44100 sq. nm].

4. DISCUSSION

4.1 Oxidation Stresses

During the oxidation of a metal two solid phases are in contact; one is formed by consumption of the other. Therefore one has to expect mechanical forces in the metal-oxide system. The components of forces which are directed parallel to the surface of the oxide layer are able to bend a thin metal strip which is oxidized at one side and protected against oxidation at the other side¹⁷. Equilibrium is reached if along the cross-section of the strip all longitudinal forces and simultaneously the internal bending moments are compensated. If these forces are related to a suitable area on which they work, they are called stresses. In Fig. 5 some examples of bent strips in equilibrium are shown (from work of Jaenicke et al.¹⁸). Resulting compressive stresses between the layer surface and axis of zero stress give a convex equilibrium shape of the initially straight oxide layer (Fig. 5a) and resulting tensile stresses a concave shape (Fig. 5b). The bending which is observed therefore is an integral phenomenon; it gives no information on the distribution of stresses along the cross-section. If the volume of the oxide formed is more than that of the metal consumed ($PBR > 1$), a compressive stress is observed in the oxide layer and a tensile stress in the underlying metal (Fig. 5a); but if the volume of oxide formed is less than the volume of metal consumed ($PBR < 1$), a tensile stress is observed in the oxide and a compressive stress in the metal. A tensile stress in the oxide may give rise to a

cracking of the oxide (Fig. 5b). For thicker oxides a complicated system of stresses may exist, and the source of the observed stress effects can be situated in the oxide layer, at the phase boundary or inside the metal.

The origin of stresses in growing oxide films has been considered by a number of investigators. Jaenicke and Leistikow¹⁷ suggested that recrystallization in the oxide scale results in the development of stresses, but the recrystallization process in itself is thought to be a stress relief mechanism. Similarly Rhines and Wolfe²⁰ have developed a growth stress theory based on observations with Nickel, whereby internal growth occurs within an already continuous oxide layer. It was assumed that oxygen diffuses along the oxide grain boundaries or cracks in the oxide and reacted with Ni^{2+} ions diffusing in the bulk oxide. They reasoned that this causes excess oxide to form at the grain boundaries and creates a compressive stress in the oxide. Speight and Harris²⁵ have clearly demonstrated that this mechanism is untenable; such boundary oxides can relax existing applied external stress but cannot create stress nor augment existing ones. They proposed that formation of new oxide in cracks or pores of the oxide generated compressive stresses in the oxide and tensile stresses in the metal substrate.

The movement of vacancies and cations in the metal is interpreted as a contributory source of stress during oxidation²⁶. The vacancy movement is the result of cation movement from the metal towards the metal-oxide interface. This vacancy and cation flux across the neutral

axis contributes to the observed deformation of unilaterally oxidized specimens. The vacancies subsequently condense in grain boundaries under the influence of grain boundary stress in the manner proposed for the formation of cavities during creep²⁷. Another stress generation mechanism is based on an orientation relationship between an oxide and its substrate. If adherence is to be maintained at an interface between two phases, i.e., oxide-metal, elastic strain will exist in both phases at the interface.

4.2 Pilling-Bedworth Model

Epitaxially induced stresses which originate at the interface led to the development of the growth stress theory by Pilling and Bedworth¹⁵. This model assumes that only the oxygen ion is mobile in the oxide and that consequently the transition of the metal lattice to the cation lattice in the oxide is produced by homogeneous dilation. If one further assumes that the dilation is isotropic then the sign and magnitude of stress are related to (1-PBR), where PBR, the Pilling-Bedworth Ratio is given by

$$\text{PBR} = \frac{\text{Volume per metal ion in oxide}}{\text{Volume per metal atom in the metal}} \quad (1)$$

If the process of ionization of a metal atom and its incorporation into the new oxide lattice produces just sufficient space to accommodate the oxygen ion, the system is free from stress and PBR is unity. A PBR greater than unity predicts tensile stresses in the metal substrate and compressive stresses in the oxide. Here additional space

is required to accommodate the new oxide, which may be provided by plastic deformation or elastic strain. A PBR less than unity indicates a cellular porous oxide in tension and metal substrate in compression. The formation of MgO on Al-Mg substrate in the present study gives a $PBR > 1$.

4.3 Growth of Dislocation Loops

4.3.1 Vacancy Injection Model

Previous studies of the climb of dislocations in dilute Al-Mg alloys have shown that prismatic loops grow rather than shrink. Initial growth observations were made by Eikum and Thomas²⁸ in Al-5% Mg and these workers suggested that the excess vacancies necessary for the growth process were released from magnesium-vacancy complexes during annealing. They concluded loop growth was not possible in a solid solution alloy. Harris and Masters²⁹ suggested that excess vacancies are retained in solution and prevented from being absorbed at the foil surface by an impervious oxide layer. Kritzing, Dobson and Smallman³⁰ have shown that loop growth occurred in a solid solution of Al-Mg alloys containing 0.65% Mg and that the vacancy supersaturation in the foil increased continuously during annealing. They suggested a mechanism of loop growth based on the growth of a magnesium oxide film on the surface of the thin foil. The transfer of magnesium atoms from the metal foil to the oxide film then gives rise to vacancies in the foil which subsequently migrate inwards to the loops causing their growth. The oxide-metal interface may act as a source or sink of vacancies. Hales, Dobson and Smallman³¹ have shown

that the vacancy injection mechanism accounts for growth of loops in pure zinc and magnesium and as a consequence of the oxidation process, vacancies are no longer annihilated at the foil surface, the oxide film effectively operating as a source rather than a sink for vacancies. Kritzing et al.³⁰ gave the rate of growth of a prismatic dislocation loop of radius r and Burgers vector b as

$$\frac{dr}{dt} = A \left(\frac{\Delta c}{c_0} - \frac{\alpha b}{r} \right) \quad (2)$$

where $\Delta c = c - c_0$ = difference between actual vacancy concentration at the surface and the equilibrium concentration.

α = constant, derived from line energy of dislocation, opposing motion.

A = constant, involving diffusion coefficient and geometrical factors.

In another study of the Al-Mg alloy Dobson et al.³² showed that growth of dislocation loops depended on the concentration of Mg. In dilute Al-Mg alloys the vacancy concentration was increasing with increasing annealing time, whereas for the more concentrated alloys, the concentration was constant during the anneal except possibly in the early stages of loop growth.

In a study of loop growth in Al-3%Mg alloys, Spalding et al.³³ supported the oxidation vacancy injection model of Kritzing. They also found that the rate of growth of loops varied by up to a factor of three from point to point within a grain in the thin foil; and that only a fraction of the vacancies emitted by the oxidation process contributed to dislocation loop climb.

4.3.2 Induced Stress Model

Hales et al.³¹ discovered that the rate of loop growth in zinc and magnesium was influenced by whether the annealing atmosphere was air or vacuum. The rate of vacancy loop growth was increased in magnesium but decreased in zinc, when the annealing atmosphere was changed from vacuum to air. The Pilling-Bedworth Ratio for the Mg-MgO system is less than unity whereas it is greater than unity for the Zn-ZnO system. Accordingly the oxidation of each system will induce stress systems of differing signs in the oxide and the metal; in the case of magnesium the oxide will be in tension and the metal in compression but with zinc the opposite will occur. Harris³⁴ proposed an alternate mechanism to explain Hales' observations. In this model the driving force for loop growth is influenced by the existence of a stress field due to oxidation of the foil as the following demonstrates. Consider a large faulted loop lying normal to the plane of a thin foil in which the vacancy concentration above the equilibrium value is of sufficient magnitude that the overall energy of the system decreases if the loop grows. If 's' is the stacking fault energy per unit area, 'b' is the interatomic spacing, ' σ ' is the compressive stress acting normal to the plane of the loop, the energy change opposing growth is $sb^2 - \sigma b^3$. Thus it can be seen that a compressive stress which might exist in a magnesium foil during oxidation would increase the rate of vacancy loop growth. In contrast, with zinc the induced tensile stress in the foil would increase the energy change opposing growth, thereby decreasing the growth rate. Thus a model involving a significant role for induced stress is in qualitative

agreement with the observations of Hales et al. The equation for the rate of growth of a loop, as given by Harris to take into account the effect of a stress σ in the plane of the foil is

$$\dot{r} = \frac{dr}{dt} = A \left[\frac{c}{c_0} - \exp \frac{sb^2 + \sigma b^3 \cos^2 \alpha}{kT} \right] \quad (3)$$

where $A = 2\pi D/b \ln (L/b)$

D = lattice self diffusion coefficient

L = half the foil thickness

α = angle between the stress and the plane of loop

c_0 = ratio of actual vacancy concentration and thermal equilibrium value

The change in stress $\Delta\sigma$ to cause a change in loop growth Δr can be derived from the following expression given by Harris

$$\Delta\sigma = \frac{kT}{b^3 \cos^2 \alpha} \ln \left[\frac{\Delta r}{A} \exp \left(\frac{-sb^2}{kT} \right) + 1 \right] \quad (4)$$

Harris derived that for magnesium oxidation changing the atmosphere from vacuum to air, the induced compressive stress in the foil increased by $8 \times 10^6 \text{ N/mm}^2$ which could account for the observed increase in rate of growth of vacancy loops. As Si/SiO₂ has a PBR>1, the observations by Sanders and Dobson³⁵ of the enhanced growth rates of interstitial loops in silicon foils is in accord with the induced stress model. In the present study for the MgO/Al-Mg system in which PBR>1, it was observed that the interstitial loops formed at the interface showed enhanced growth.

4.4 Growth of Loops in Al-Mg

Earlier preliminary studies have been done by Westmacott²³ on the near surface formation of dislocation loops in electron-irradiated Al-11%Mg. Here loops nucleated and grew at 150°C in a manner suggesting little difference from other studies. However when the specimen temperature was increased to 180°C and irradiation continued, long half loops developed and grew preferentially in directions parallel to the foil surface. After further heating of the sample to 230°C the loops in different planes interacted to form a dislocation network. The loops were interstitial in nature and were lying near the surfaces.

Figures 1a and 1b demonstrate the formation of the interstitial loops on irradiation and their growth as a function of time. It can be observed from these figures that the loops are intersecting the surfaces, thus confirming that they lie at the oxide-metal interfaces. Loop growth occurs rapidly parallel to the foil surface as a function of time.

The electron irradiation of oxidized Al-2.5%Mg in the present study supports the results of earlier work by Westmacott. After irradiating the oxidized sample at 150°C for 60 to 75 minutes a geometrically square dislocation network had formed at the oxide-metal interface. Two sets of edge dislocations with Burger vectors $a/2[\bar{1}10]$ and $a/2[110]$ were observed to be in contrast for g. of $0\bar{2}0$ (Fig. 4b). Stereo microscopy confirmed the interstitial dislocation to loops lie near the surface. A post-irradiation annealing of the specimen increases the

dislocation network spacing (Fig. 4f). The foil orientation in the present study was [001]. The foil orientation in the study by Westmacott was {013}, where nearly hexagonal network formation was observed.

The formation of a dislocation network near the interface can be explained in terms of the foil surface condition. Previous work by De Brouckere³⁵ has shown that MgO films form on the surface of Al-Mg alloys during oxidation. MgO has a cubic rock salt structure with a lattice parameter of $4.212\text{\AA}$. The unit cell volume is $74.7\text{\AA}^3$. When Mg oxidizes to form MgO, each Mg atom collects an oxygen atom. Therefore the volume per Mg atom now becomes equal to $74.7/4$ or $18.7\text{\AA}^3$. For a typical Al-Mg alloy the volume per atom is $16.98\text{\AA}^3$. Thus the Pilling-Bedworth Ratio is equal to 1.1. As the Pilling-Bedworth Ratio is greater than unity, the epitaxial growth of an oxide layer will generate tensile stresses in the metal substrate and compressive stresses in the oxide. These conditions favor the formation of interstitial half loops in the Al-Mg lattice at the oxide-substrate interface (Fig. 6). The dislocation loops interact to give a dislocation network. The enhanced growth rate of interstitial dislocation loops in Al-Mg is also consistent with the Harris model of stress-induced loop growth. The results in the oxidized foil appear to be analogous to the reported observations of dislocation network formation in partially reduced MoO_3 ³⁷ although the formation mechanism is different.

4.5 Model for Stress Calculation

The formation of an oxide on the surface of a foil introduces stress in the foil as well as in the oxide. A strain is present due to these stresses. The Pilling-Bedworth Volume Ratio gives the condition of the stress at the interface. It can also be used to calculate the strain

$$\epsilon = \frac{1}{3} \frac{\text{Volume of oxide} - \text{Volume of metal consumed}}{\text{Volume of metal consumed}} \quad (5)$$

If the oxide and the substrate have the same crystal structure

$$\epsilon = \frac{a_{\text{oxide}} - a_{\text{substrate}}}{a_{\text{substrate}}} \quad (6)$$

where a is the lattice parameter. For the MgO/Al-Mg system the above expression becomes

$$\epsilon = \frac{a_{\text{MgO}} - a_{\text{Al-Mg}}}{a_{\text{Al-Mg}}} \quad (7)$$

If dislocation with Burgers vector b and spacing h form at the oxide-substrate interface the plastic strain at the substrate-oxide interface is

$$\epsilon = \frac{b}{h}, \quad (8)$$

and hence

$$h = \frac{b}{\epsilon} \quad (9)$$

and Hooke's law can be used to calculate the elastic stress that is relieved by the dislocation network. Assuming isotropy in two dimensions $\sigma_x = \sigma_y = \sigma$; $\epsilon_x = \epsilon_y = \epsilon$,

$$\sigma = \frac{E}{1-\nu} \epsilon \quad (10)$$

where σ = stress; E = Young's Modulus; ν = Poission's ratio and ϵ = strain.

4.6 Strain in Oxide-Metal System

Stresses and strains are present in the oxide and metal substrate as a consequence of oxidation. If the metal lattice is considered to be rigid, the strain in the metal substrate is zero and all of the strain is accommodated by the oxide. The Pilling-Bedworth model can be used to calculate the strain using expression (6). The other case is the one where all the strain caused by the oxide growth is accommodated by the metal lattice; the strain in the oxide being equal to zero. In actuality the growth of an oxide on a metal substrate will cause strains and stresses of opposing nature to exist in both the oxide and the metal substrate. If the dislocation network formed at the oxide-metal interface in the metal lattice completely relieves the elastic stresses, expression (8) can be used to calculate the strain. The stress in the metal substrate can be back-calculated using Hookes' law, i.e., expression (10).

4.7 Dislocation Spacing vs. Oxide Thickness

Since the strain obtained from expression (7) is constant for a particular composition of the alloy the required dislocation spacing h is independent of the oxide thickness. From Table IV and Fig. 7 it can be inferred that the dislocation spacing was constant for oxides of thickness $116\text{\AA}$ and $103\text{\AA}$, whereas the dislocation spacing was smaller for a thinner oxide ($52\text{\AA}$). Hence the stress was higher at lower

thickness of oxide and decreased with increase in oxide thickness. This may be explained in terms of stress relaxation which might have taken place as thickening of the oxide occurred, similar to Jaenicke's¹⁸ work. Figure 8 shows the results of Jaenicke et al.¹⁸ for the oxidation of copper graphically and their interpretations at the various stages of oxide growth. In this study, initially an oxide is nucleated on the surface and spreads laterally under a large compressive epitaxial constraint. However, if this were all, eventually newly formed oxide would be strain free since one would expect epitaxial stresses to be short range. In the next stage, however, vacancies are injected into the metal by the scale forming reaction and condense on internal defects. There is a certain contraction around a vacancy in a close packed lattice, amounting to approximately half an atomic volume, so that there is an effective tensile stress introduced into the metal; this will produce a high compressive stress in the oxide but the resultant stress is tensile. At this point the oxide will start to break up because of the stress and O_2 will diffuse through pores causing oxide formation within them. This internal growth of oxide produces a compressive stress which eventually dominates.

Using Jaenicke's analogy it can be proposed that the oxide thickness in this study lies in the region x-y of the graph of Fig. 8. At a lower thickness of the oxide the stress is higher, and as the oxide thickens, some stress relieving mechanisms reduce the stress, thus reducing the strain and giving a larger dislocation network spacing as per expression (9). Ideally if stresses are not relieved

and the oxide formed is compact, the dislocation network spacing should be independent of oxide thickness in Fig. 7.

4.8 Stresses in Al-Mg at Oxide-Metal Interface

Table V gives the stresses calculated using expression (10). The thickness was calculated from the literature³⁸; the dislocation spacing h used in the strain calculation of expression (8) was the experimentally observed spacing obtained after a post-irradiation anneal of 180°C for 20 minutes (Table IV). The stresses calculated in Al-2.5%Mg were on the order of 1.36×10^4 to 2.19×10^4 psi. The observed stresses are thus of the same order of magnitude as those calculated by Harris³⁴ for the Ni-NiO system and by Powell et al.³⁹ for the Ta-TaO system.

4.9 Effect of Alloy Composition on the Stress at Oxide-Metal Interface

In Westmacott's²³ study of irradiated Al-11%Mg system the dislocation network spacing was found to be 5000Å. The strain for this oxide-metal system using expression (7) can be calculated to be 2.24% (Table VI). This is less than the strain of 3.36% calculated for the Al-2.5%Mg systems. Thus stress at the oxide-metal interface is greater for Al-2.5%Mg than for Al-11%Mg. From expression (9) we can conclude that the dislocation network spacing should be larger for Al-11%Mg than that for the Al-2.5%Mg system. In the Al-Mg system increasing the Mg concentration reduces the stresses at the oxide-metal interface, because the larger lattice parameter of the 11% alloy is greater than the 2.5%, and the PBR is smaller.

5. FUTURE WORK

It would be interesting to study systematically:

- (1) The oxidation-induced stresses in Al-Mg as a function of Mg concentration.
- (2) The effect of foil orientation and electron beam direction on the nature and geometry of dislocation networks formed at the oxide-metal interface.
- (3) The oxidation of Al-Mg at high temperatures ($>500^{\circ}\text{C}$), which is known to give rise to a combination of MgAl_2O_4 (spinel) and MgO; this would be expected to alter the stresses at the interface. The stress states at the oxide-metal interface should be studied in this case.
- (4) The oxidation induced stresses in the metal-oxide systems where $PBR < 1$ (e.g., MgO on Mg). The dislocation network formed at the oxide-metal interface should be of vacancy type.
- (5) Formation of in-situ oxidation-induced stresses as the oxide thickness increases in the environmental cell of the High Voltage Electron Microscope.

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TABLE I

Experiment	Object of the experiment	Oxidation Condition	Irradiation Conditions
1	Study irradiation damage with progress of time.	Specimen was oxidized at 350°C for 75 minutes at 1 atmosphere air in the airlock of the microscope.	The specimen was held at a temperature of 150°C and a specific area was irradiated. Defect generation in this area was studied at time intervals of 20 minutes up to 120 minutes. Then the sample was annealed for 20 minutes at 170°C.

TABLE II

Expt. No.	Object of the Experiment	Oxidation Condition (Performed at 1 atmosphere air in the micro- scope air lock)	Time of Irradiation	Temp. of Irradiated Specimen	Post Irradiation Annealing Temp. & Time
1	Study effect of irradiation time on defect structure	1 hour at 250°C	1/2 hour, 1 hour, 1 1/2 hours, and 2 hours	150°C	170°C for 20 min.
2	Study effect of specimen temperature on the irradiated specimen	1 hour at 250°C	2 hours	180°C; 165°C	170°C for 20 min.
3	Study effect of post- irradiation annealing condition on defect structure	1 hour at 250°C	1 1/2 hours	150°C	160°C for 20 min.; 180°C for 20 min.; 30 min. 200°C for 5 min.; 15 min.

TABLE III

Experiment No.	Oxidation Condition (Performed at 1 atmosphere air in the microscope airlock)	Irradiation Condition	Post-irradiation Annealing Condition
A	75 minutes at 300°C	75 minutes at 150°C	180°C for 10 min., 20 min., and 30 min.
B	60 minutes at 250°C	60 minutes at 150°C followed by 15 more minutes at 165°C	180°C for 20 min.
C	15 minutes at 250°C	60 minutes at 150°C	165°C for 20 min.; 180°C for 20 min.

TABLE IV

Experiment No.	Thickness of Oxide (calculated from ₃₈ oxidation curves) (Å)	Observed Dislocation spacing after post- irradiation anneal at 180°C for 20 minutes (Å)
A: Table III	116	3330
B; Table III	103	3300
C; Table III	52	2100

TABLE V

Thickness of oxide (Å)	Experimentally Observed Dislocation Spacing 'h' (Å)	Magnitude of Dislocation with Burgers Vector $a/2\{110\}_o$ 'b' (Å)	Observed Strain $\epsilon = \frac{b}{h} (\%)$	Stress in Metal $\sigma = \frac{E}{1-\nu} \times \epsilon$ (psi)
116	3330	2.899	0.087	1.36×10^4
103	3300	2.899	0.088	1.37×10^4
52	2100	2.899	0.14	2.19×10^4

TABLE VI

Composition of Alloy	a_{MgO} (Å)	$a_{\text{Al-Mg}}$ (Å)	$\epsilon = \frac{a_{\text{MgO}} - a_{\text{Al-Mg}}}{a_{\text{Al-Mg}}}$ (%)
Al - 2.5% Mg	4.238	4.10	3.36
Al - 11% Mg	4.238	4.245	2.24

FIGURE CAPTIONS

- Fig. 1. Micrographs (a) and (b) show the formation and growth of interstitial dislocation loops at the oxide-metal interface in Al-Mg on electron irradiation.
- Fig. 2. Micrographs (a) through (f) show the defect structure at intervals of 20 minutes up to 120 minutes on an oxidized sample irradiated at 150°C. (g) Micrograph of area in (f) with a post-irradiation anneal of 20 minutes at 170°C. (h) The selected area diffraction pattern of the area.
- Fig. 3. Micrographs (a) through (g) illustrate the effect of irradiation time on the defect structure (dislocation structure) of an oxidized sample held at 150°C. (a) Area after 1/2 hour of irradiation with a g of 020. (b) Area after 1 hour of irradiation. (c) Dislocation structure with a post-irradiation anneal of 20 minutes at 170°C. (d) A second area irradiated for 1 1/2 hours. (e) The irradiated area with a post-irradiation anneal. (f) A third area irradiated for 2 hours. (g) Micrograph showing the effect of post-irradiation anneal of area in (f). Two sets of edge dislocations with Burgers Vectors $a/2[110]$ and $a/2[\bar{1}10]$ are observed.

Micrographs (h) through (n) illustrate the effect of the specimen temperature on the irradiated defect structure. (h) An area irradiated at 165°C for 2 hours. (i) Micrograph of the irradiated area with edge dislocations of Burgers Vector $a/2[1\bar{1}0]$ for g of $\bar{2}20$.

(j) It shows the effect of post-irradiation anneal on the dislocation structure. (k) The selected area diffraction pattern of the irradiated area. (l) Micrograph of an area irradiated at 180°C for 2 hours. (m) Dislocation structure with a post-irradiation anneal of 10 minutes at 170°C. (n) The area with a post-irradiation anneal of 20 minutes at 170°C. (o) The selected area diffraction pattern of the irradiated area.

Micrographs (p) through (w) illustrate the effect of post-irradiation annealing conditions on the dislocation loop structure. (p) It shows an area irradiated at 150°C for 1 1/2 hours. (q) Micrograph of the area with a post-irradiation anneal of 20 minutes at 160°C. (r) An area irradiated at 150°C for 1 1/2 hours. (s) Micrograph of the area after a post-irradiation anneal of 20 minutes at 180°C. (t) The area with a post-irradiation anneal of 30 minutes at 180°C. (u) Micrograph of an area irradiated at 150°C for 1 1/2 hours. (v) The area with a post-irradiation anneal of 5 minutes at 200°C. (w) The area with a post-irradiation anneal of 15 minutes at 200°C.

Fig. 4 Micrographs (a) through (i) were taken of a sample which was oxidized at 300°C for 75 minutes in 1 atmosphere air prior to irradiation. (a) An area irradiated at 150°C for 75 minutes. (b) Micrograph of irradiated area showing dislocations with Burgers Vector $a/2[110]$ with a g of $\bar{2}20$. (c) Micrograph of irradiated area showing dislocations with Burgers Vector $a/2[110]$ observed with a g of $\bar{2}\bar{2}0$. (d) A stereo-micrograph of area shown in (c). (e) Micrograph of the area with a post-irradiation anneal of 10 minutes at 180°C. (f) The area after a post-irradiation anneal of 20 minutes at 180°C. (g) The area with a post-irradiation anneal of 30 minutes at 180°C. (h) The post-irradiated annealed area in (g) with a g of $\bar{2}20$. (i) The selected area diffraction pattern of the irradiated area.

Micrographs (j) through (m) were taken for a sample which was oxidized at 250°C for 60 minutes in 1 atmosphere air prior to irradiation. (j) Micrograph of an area irradiated at 150°C for 60 minutes. (k) The area in (j) which was further irradiated at 165°C for 15 minutes to get a clear dislocation network. (l) The irradiated area with an annealing treatment of 20 minutes at 180°C. (m) The selected area diffraction pattern of the irradiated area.

Micrographs (n) through (s) were taken for a sample which was oxidized for 15 minutes at 250°C in 1 atmosphere air prior to

irradiation. (n) Micrograph of an area irradiated for 60 minutes at 150°C. (o) It shows a set of dislocations with Burgers Vector $a/2[110]$ observed in contrast for a g of $\bar{2}20$. (p) The dislocation network with a post-irradiation anneal of 20 minutes at 165°C. (q) It is the magnified image of (p). (r) The dislocation network with a post-irradiation anneal of 20 minutes at 180°C. (s) It is the magnified image of (r).

Fig. 5. (a) and (b) show schematically the bending of a strip caused by stresses of different distribution within an oxide layer and the underlying metal (from Jaenicke et al.¹⁸).

Fig. 6. A schematic representation of the stress states and the dislocation structure in the irradiated MgO/Al-Mg system. As $PBR > 1$ for the system, there exist compressive stresses in MgO and tensile stresses in Al-Mg. The irradiation results in the formation of interstitial dislocation loops at the MgO/Al-Mg interface.

Fig. 7. Graph of dislocation network spacing as a function of oxide thickness.

Fig. 8. A schematic drawing of the results of Jaenicke et al.¹⁸ for the oxidation of copper, showing their interpretation of the various stages. x-y is the region of interest in the present study.

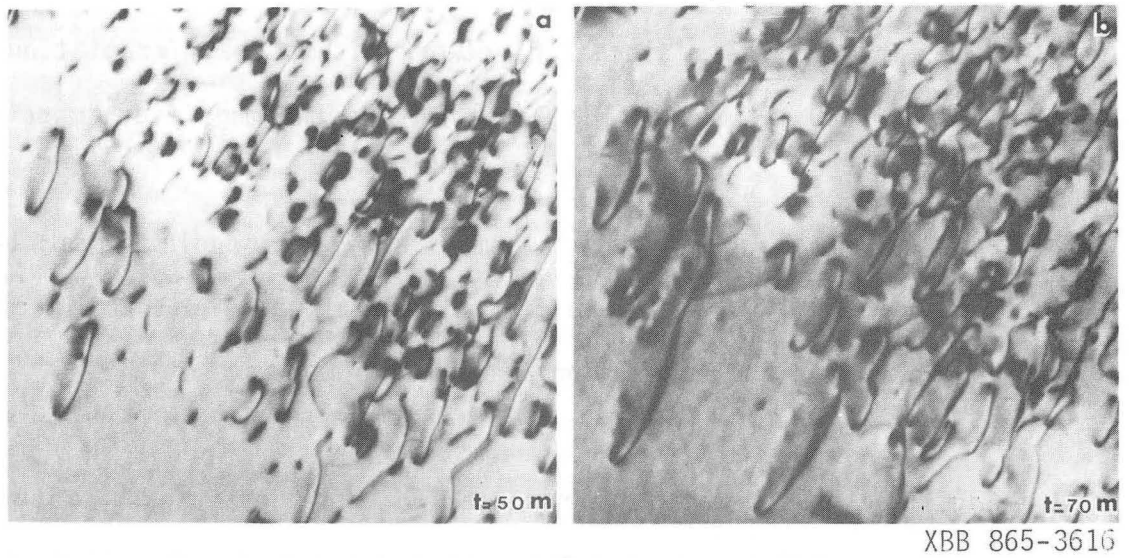
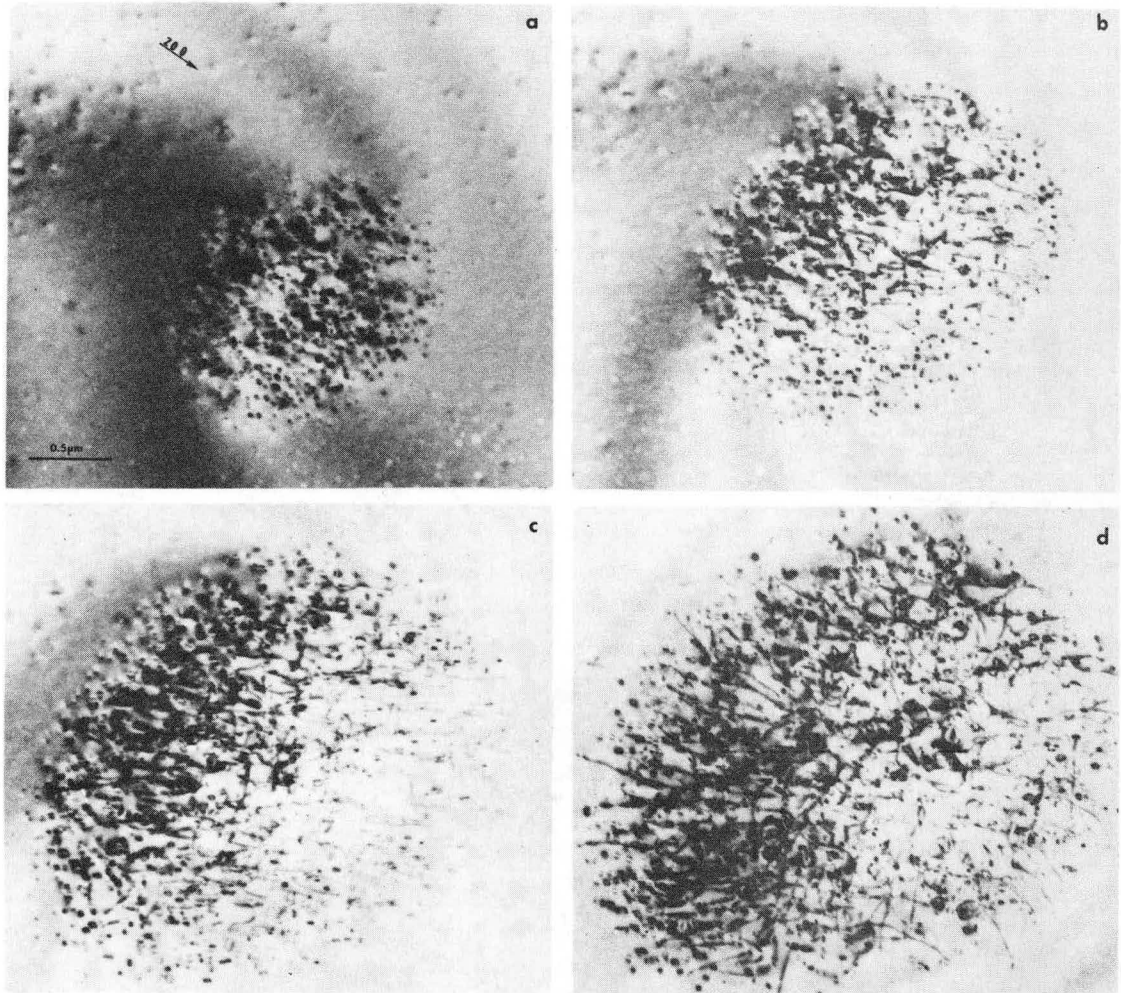
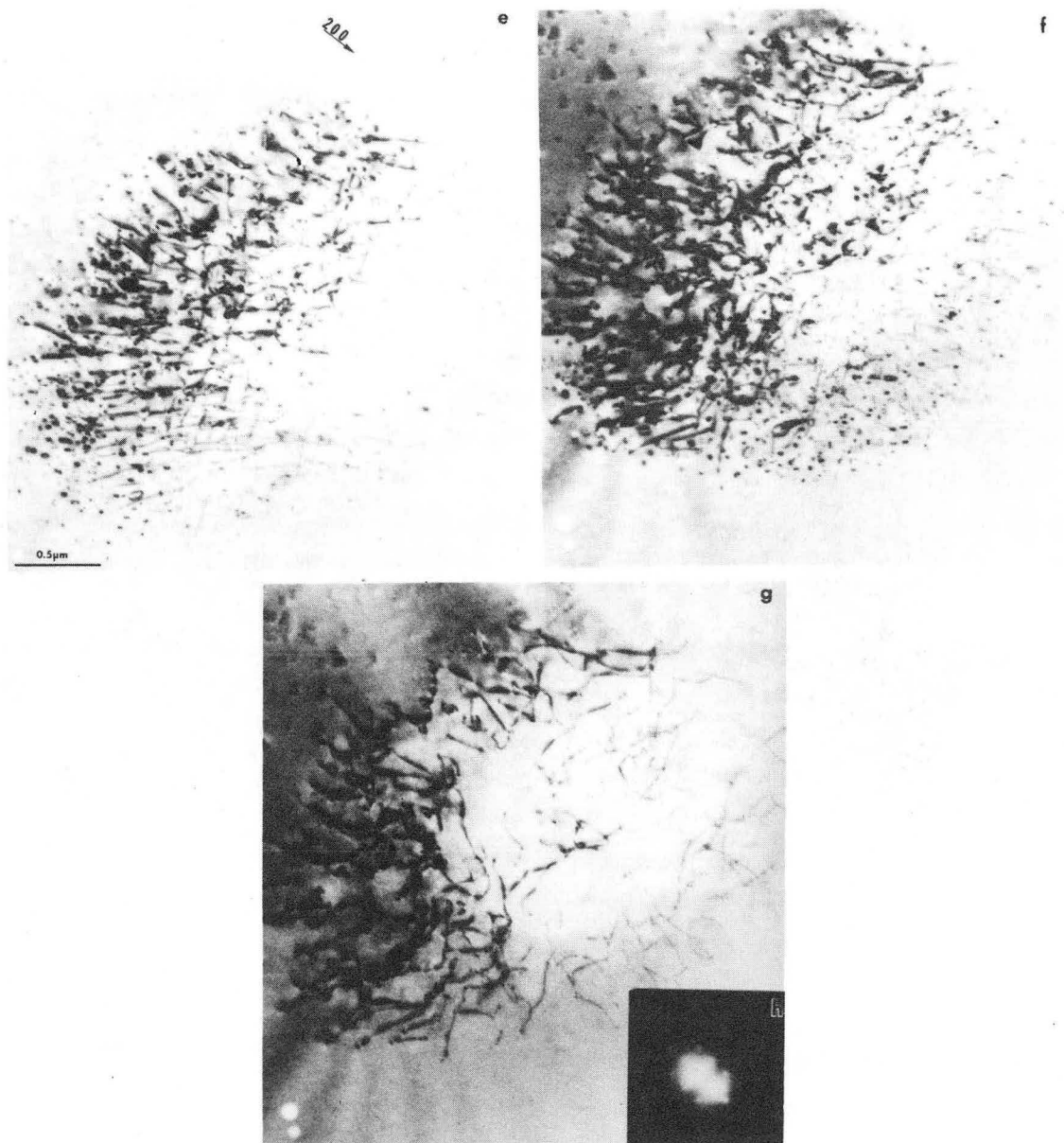


Fig. 1



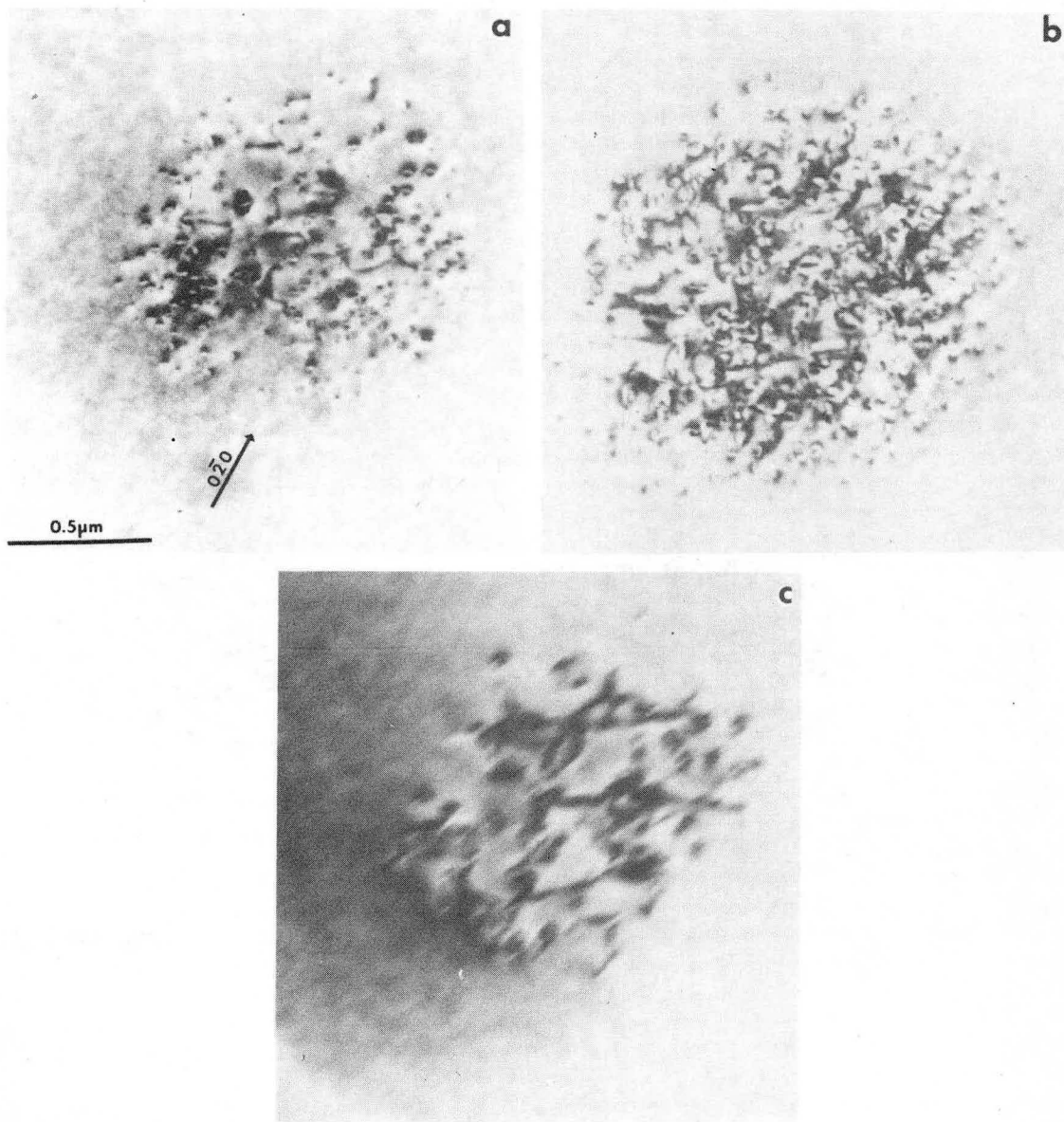
XBB 865-3617

Fig. 2



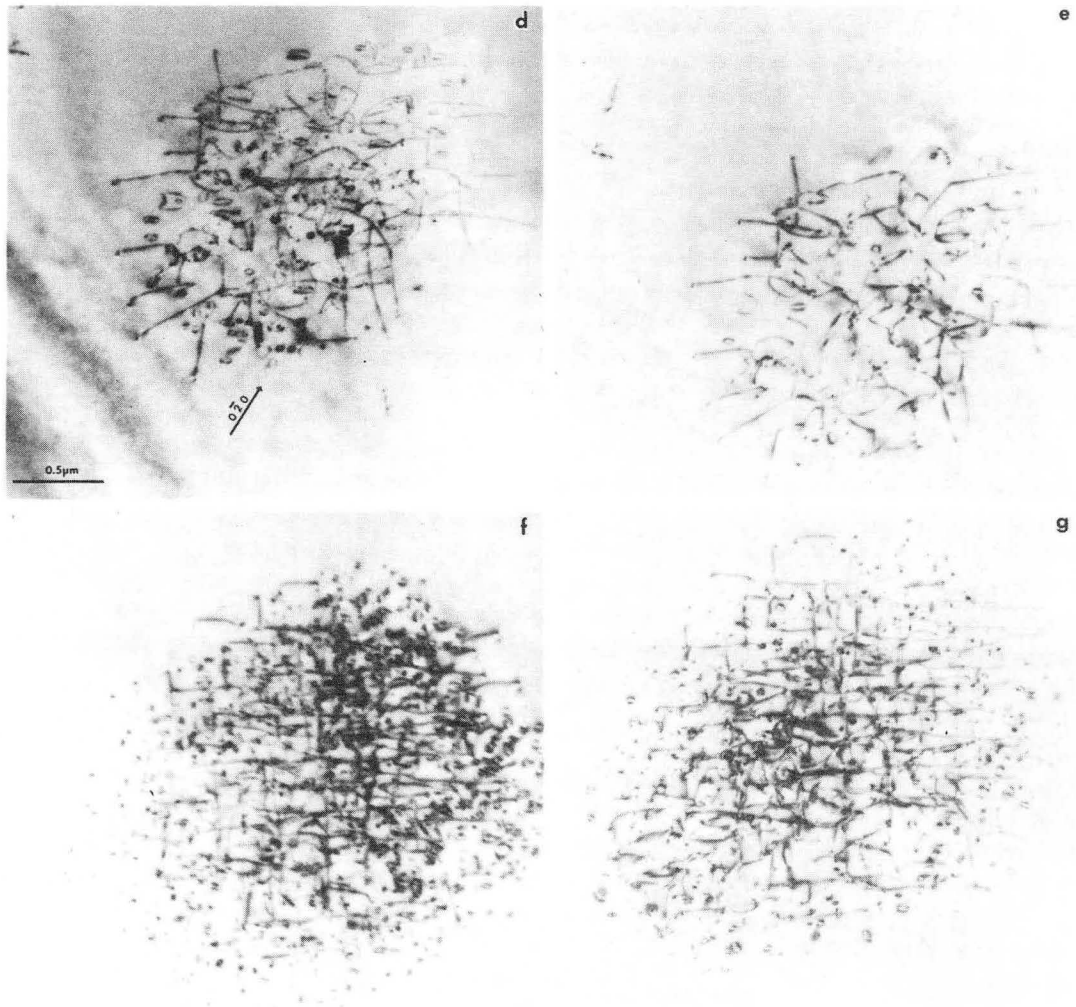
XBB 865-3618

Fig. 2
(Continued)



XBB 865-3619

Fig. 3



XBB 865-3620

Fig. 3
(Continued)

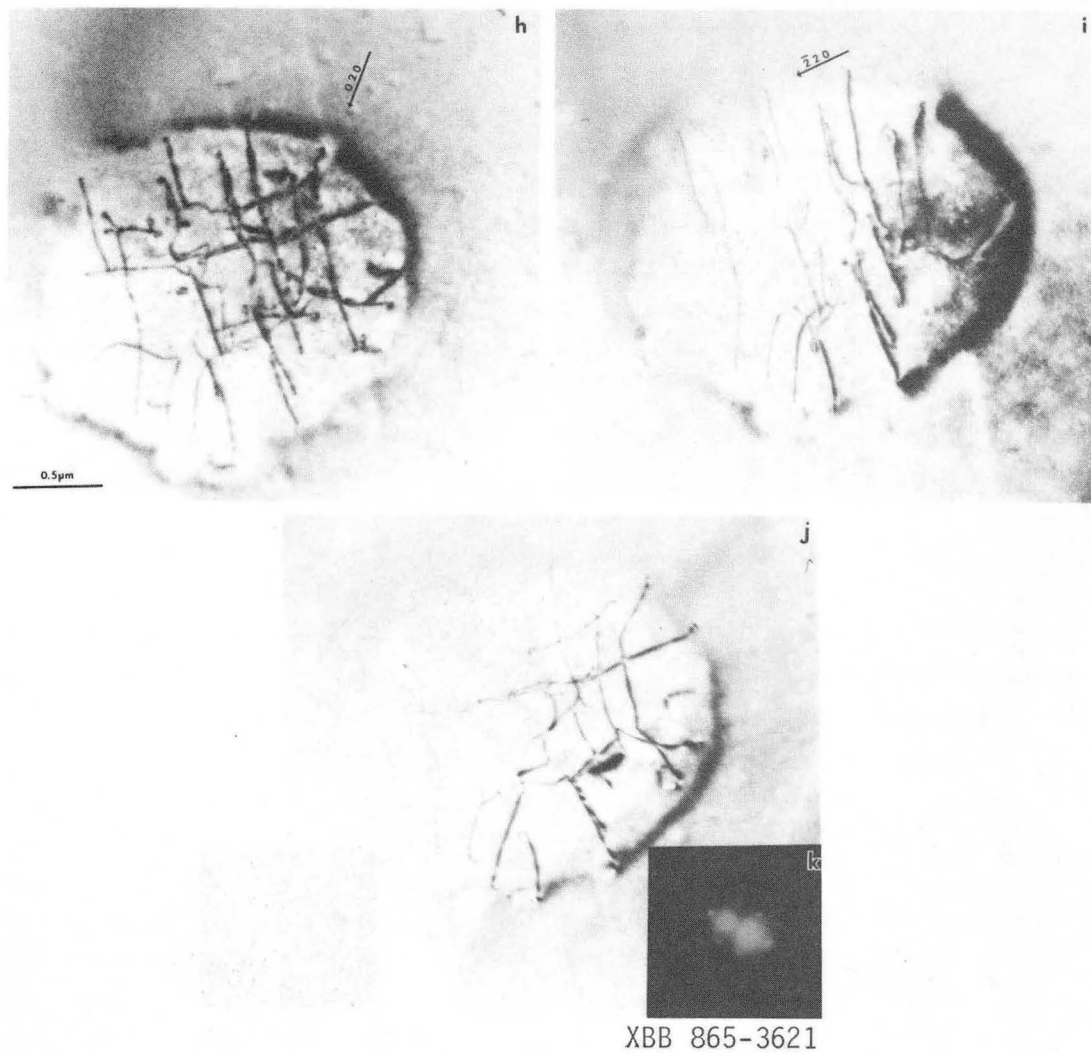


Fig. 3
(Continued)

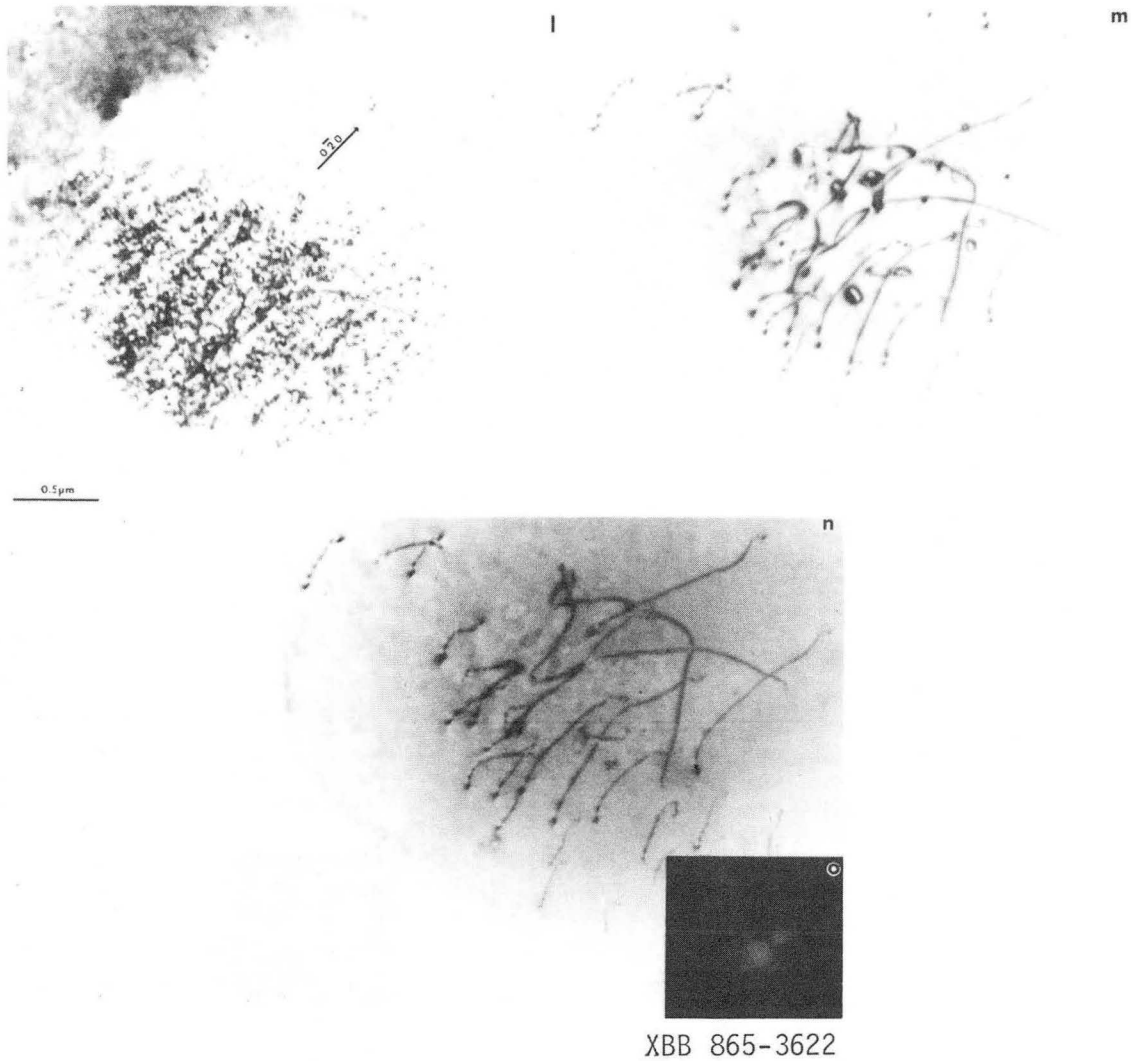
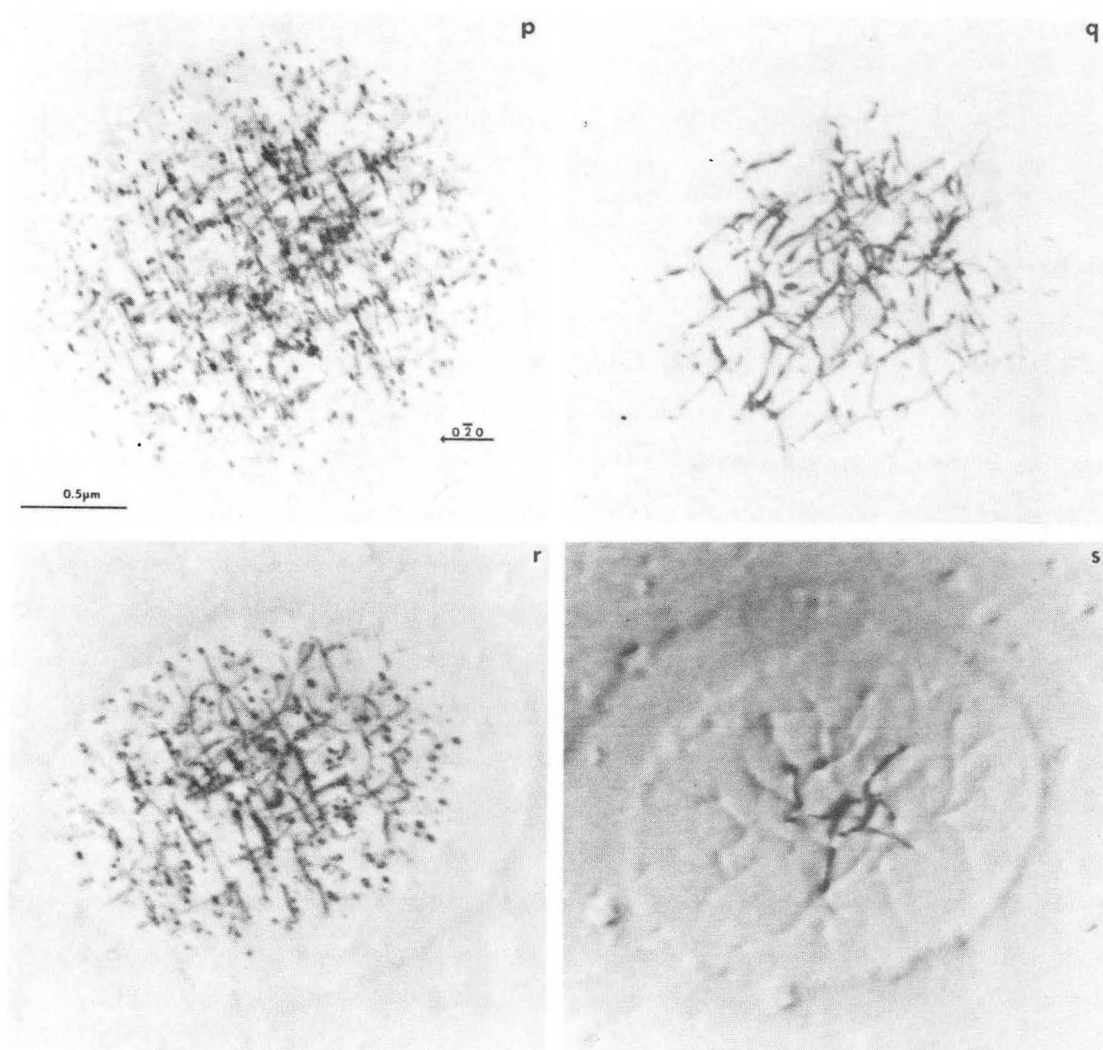
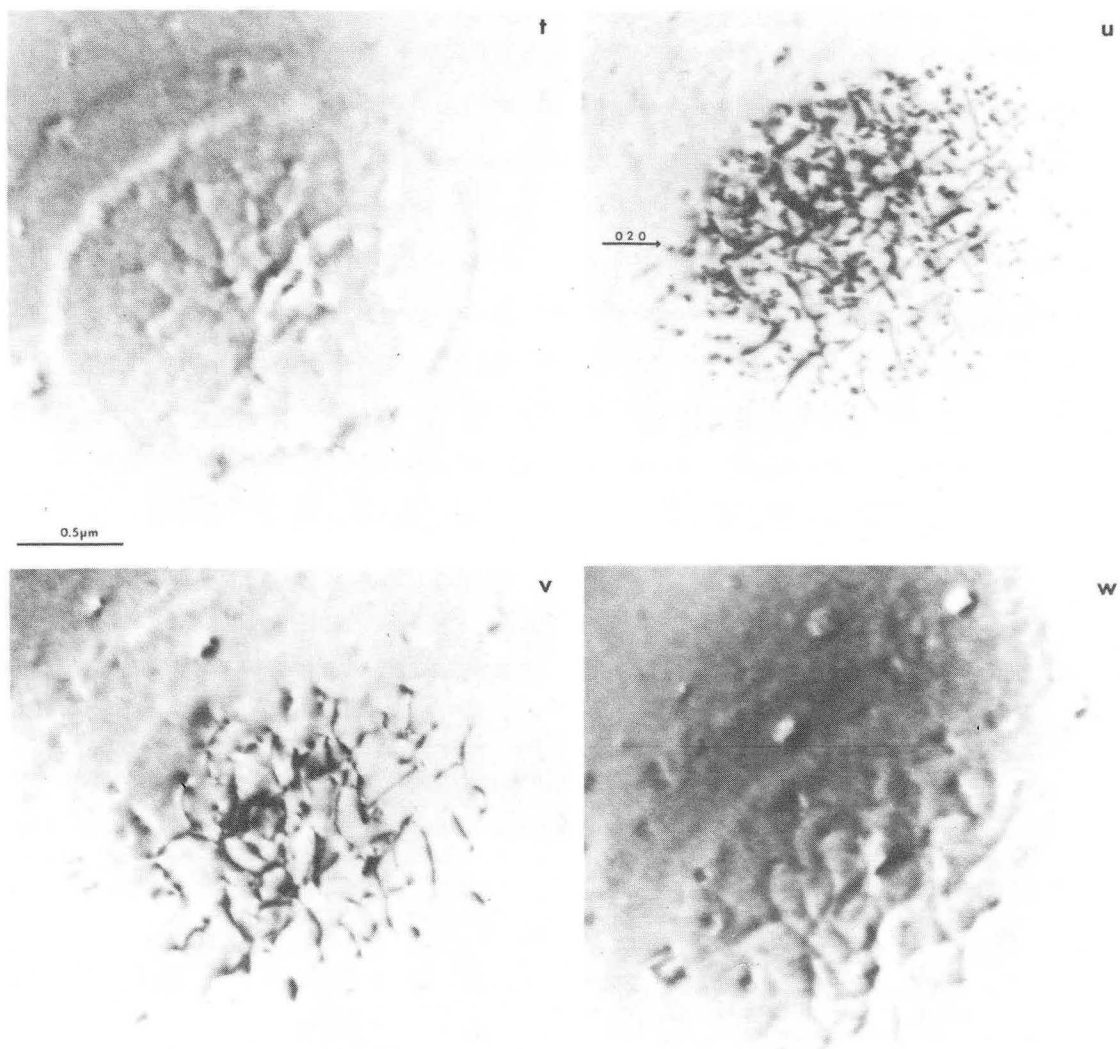


Fig. 3
(Continued)



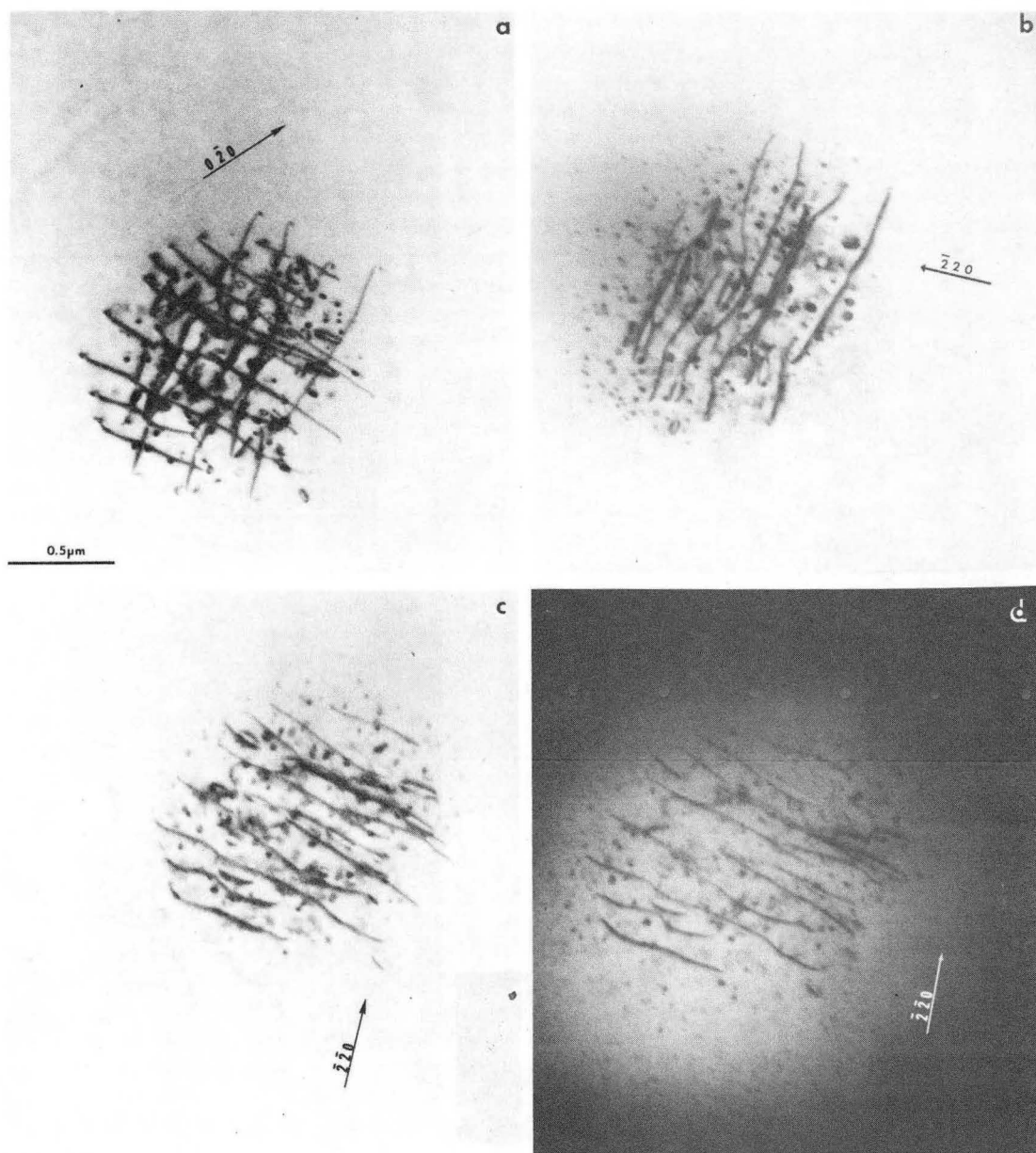
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Fig. 3
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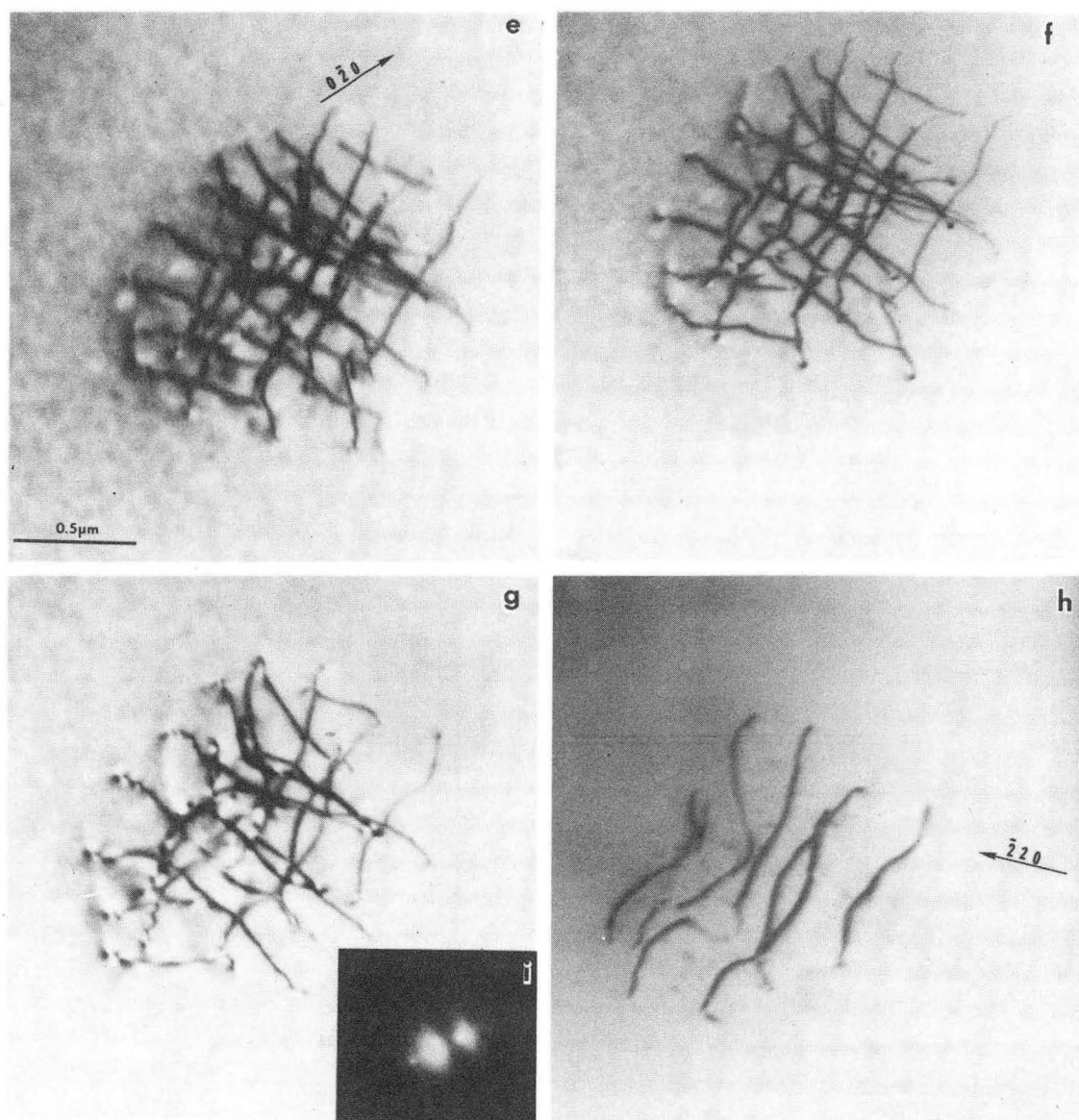
XBB 865-3624

Fig. 3
(Continued)



XBB 865-3625

Fig. 4



XBB 865-3626

Fig. 4
(Continued)

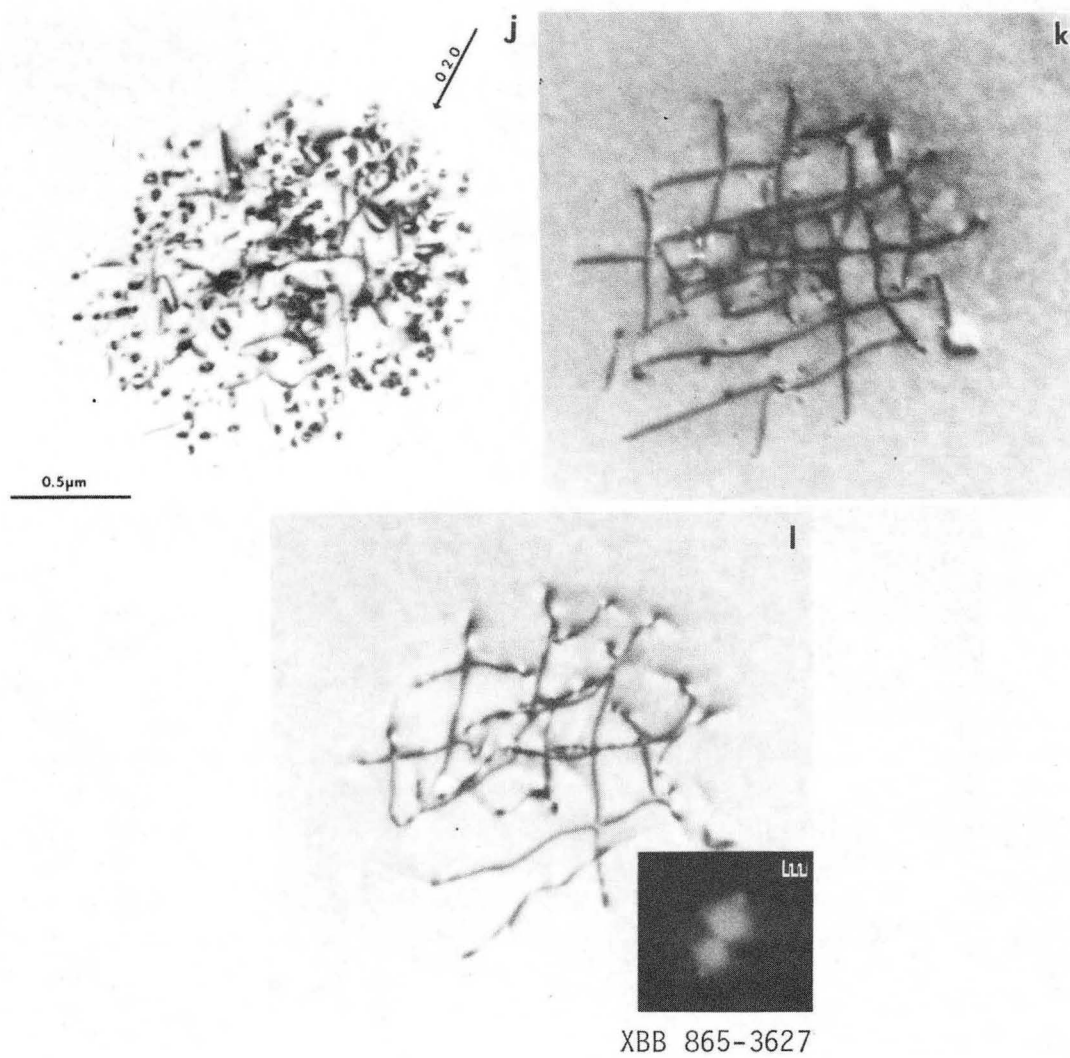
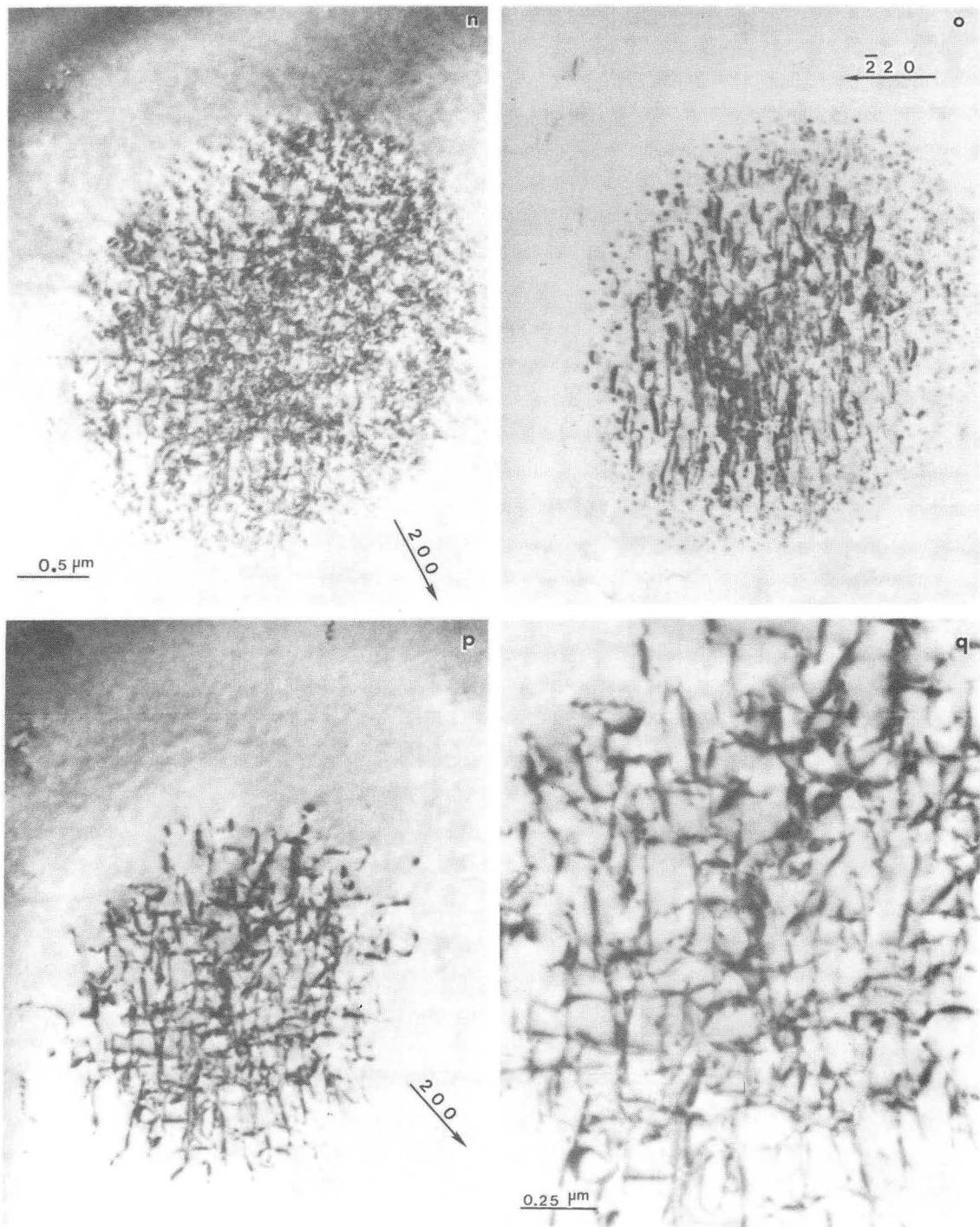
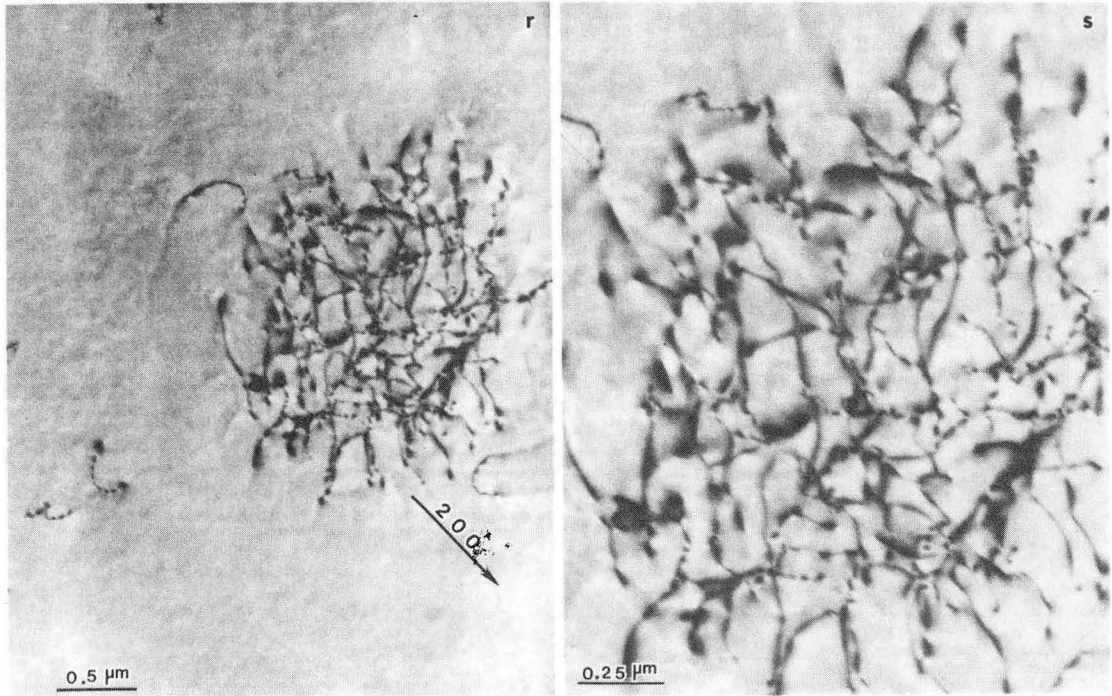


Fig. 4
(Continued)



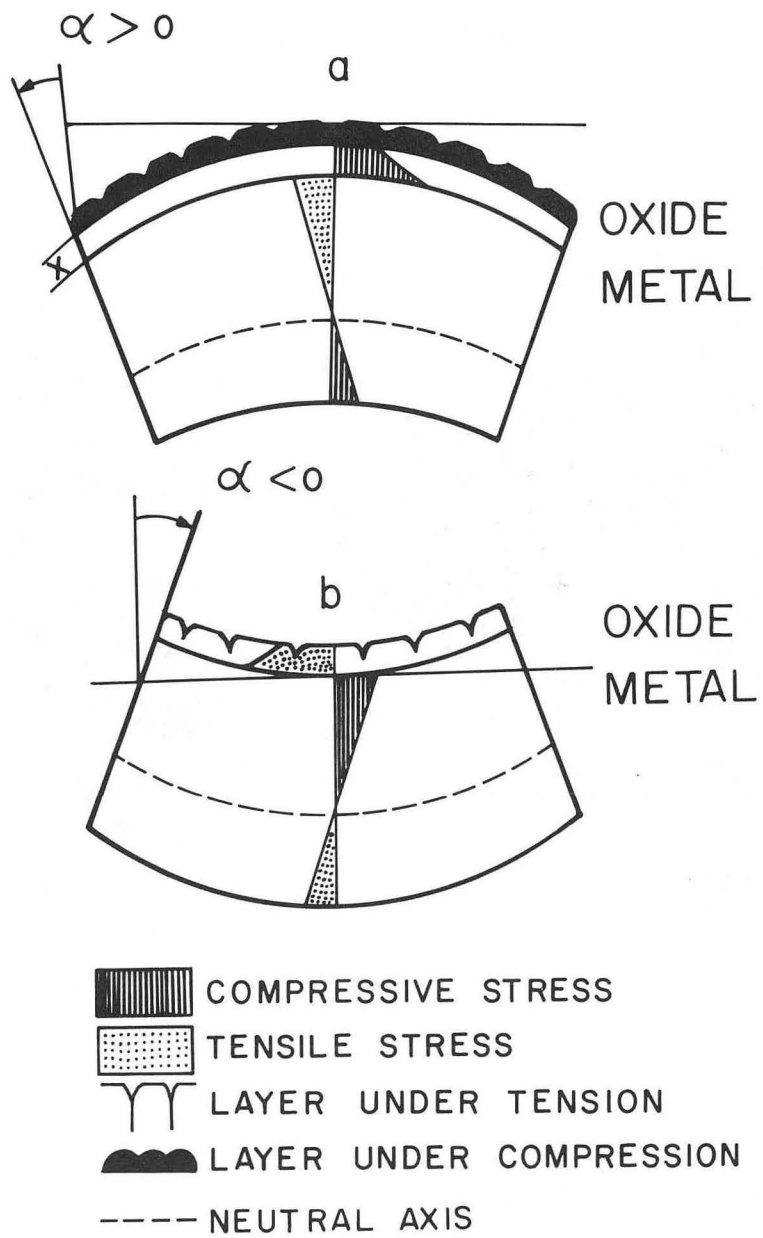
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Fig. 4
(Continued)



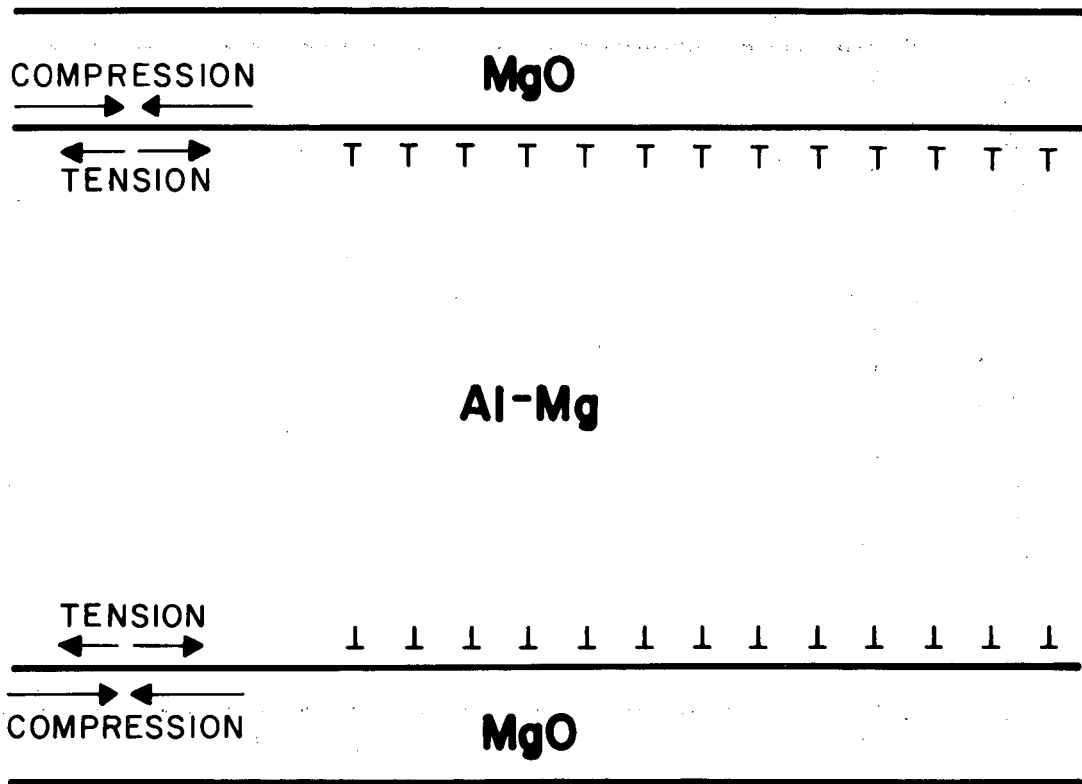
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Fig. 4
(Continued)



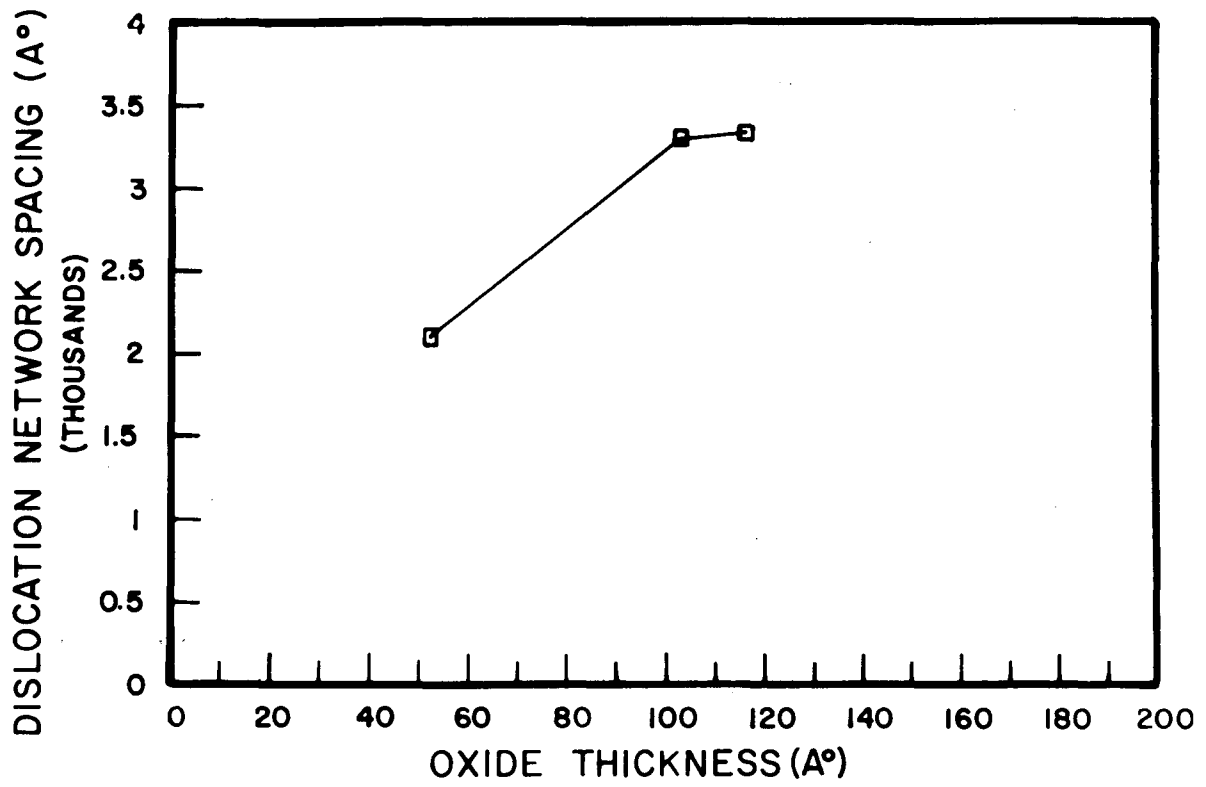
XBL 865-1824

Fig. 5



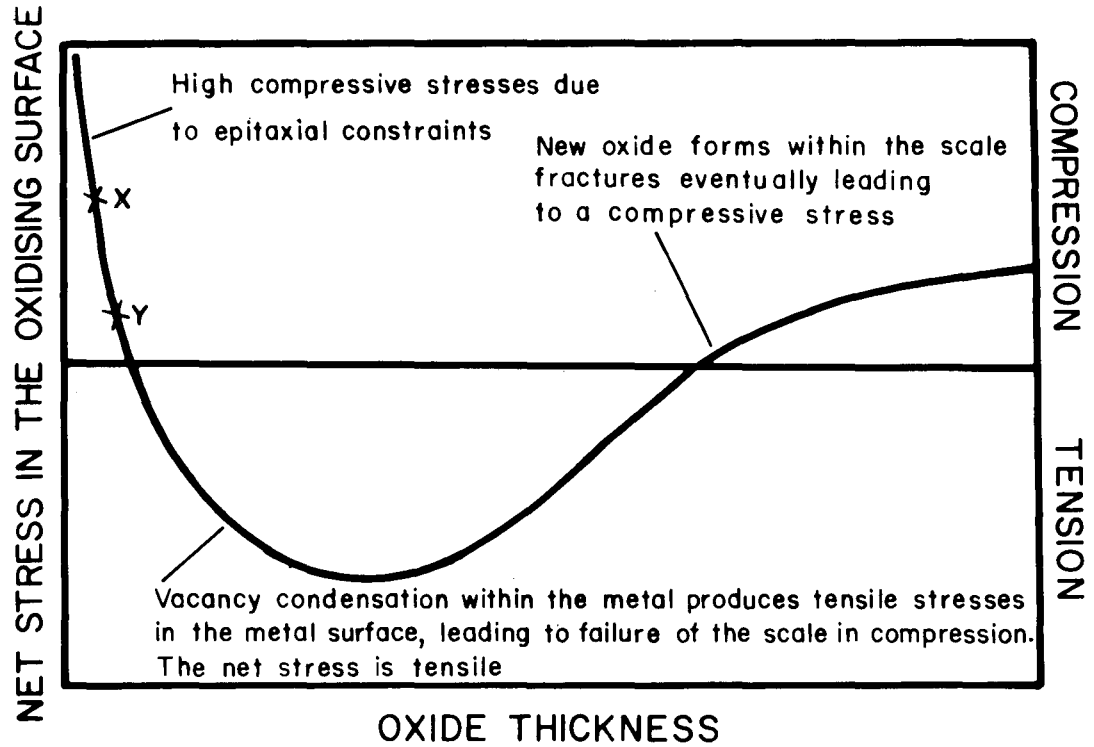
XBL 865-1825

Fig. 6



XBL 865-1822

Fig. 7



XBL 865-1823

Fig. 8

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*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*