THE UNIVERSITY OF MICHIGAN

COLLEGE OF LITERATURE, SCIENCE, AND THE ARTS
Department of Chemistry

Technical Progress Report

THE OXIDATION OF THIN SINGLE CRYSTALS OF COPPER

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I. INTRODUCTION

Report No. 64-113-Q1 issued in August 1963 described the techniques and results obtained during the preceding two years in the study of the preparation and oxidation of thin single crystals of copper. The present report covers the period from August 1963 through July 1964.

The previous work showed that the thin (700 Å) crystals prepared by condensation onto NaCl substrates at 330°C could be annealed to produce either (a) dislocation densities of 10^9 cm^{-2} and no stacking faults or (b) wide stacking faults with areas of 5×10^4 cm^2 per cm^3 of crystal and dislocation densities of 10^7 cm^{-2}. Subsequent treatment with oxygen at 525°C and 0.9×10^{-3} torr produced cuprous oxide grains having mainly orientations with the (111) plane of Cu_2O parallel to the (001) of the copper substrate. The smallest grains (0.2μ diameter) were observed in a 2 minute oxidation; diameters of 1.0μ were produced in 15 minutes. Of special interest was the observation of the apparent influence of the stacking faults on the nucleation and growth of the oxide; the nucleation sites often were located on the stacking faults, too often for a random distribution of the nucleation. Moreover, many of the grains grew more rapidly in the direction parallel to the faults. These suggestions of a relation between the physical state of the copper (i.e., the defect structure in this case) and the chemical behavior have stimulated the further study of the preparation of copper films with varying defects and the reaction with oxygen.

A thorough consideration of the influence of physical state on the chemical reactivity of thin Cu crystals would first include a characterization of the crystal with respect to crystallographic orientation, defect structure, surface contours, and surface contamination by adsorption from the residual atmosphere. The influence of variation in these factors on the reaction with oxygen and in particular on the sites and epitaxy of the nucleation and on the growth of the oxide grains would give fundamental information on the nature of gas-solid reactions. Further consideration would be required for the influence of impurities in the copper or of deliberate additions of a second component and for the influence of grain boundaries and grain orientations in thin polycrystalline films.

The 1963 report suggested filling some of the gaps by investigating the influence of other substrates on the Cu film, the relation between stacking faults and surface contour, the influence of stresses due to impurity atoms or applied mechanically and the position and growth of oxide particles. Also suggested was the installation of a gas reaction chamber around the specimen position in a JEM 6A electron microscope whereby the oxidation of the Cu film might be observed continuously from the earliest possible stages.

The present report describes the results to date for these items. It will be noted that extended experience with graphite replication techniques has so improved the quality of the replicas that much more detailed information is available about the film in various stages.

II. RESULTS AND DISCUSSION

A. RESULTS ON PREPARATION AND ANNEALING OF Cu FIIM

1. Studies on NaCl

The role of the NaCl substrate has been examined more closely. The regular procedure for producing films with wide stacking faults has the following steps: (a) cleaving of NaCl(001) in the presence of laboratory air followed by a light polish and water rinse, (b) heating the substrate to 330°C at 10^{-5} torr, (c) condensing of Cu vapor at 400 Å/min to an average thickness of 700 Å, (d) cooling and transferring to a Vycor vacuum line for heating in H_2 for 10 minutes at 1 atm and 630°C, (e) floating the Cu film onto water and mounting sections of the film on 200 mesh copper support grids for examination in the electron microscope. When the film is to be oxidized, the grid-mounted specimens are returned to the Vycor line and heated in H_2 for 10 minutes at 420°C to remove the oxidizing effects of contact with the water and then heated in O_2 at 525°C and 0.9×10^{-3} torr for 2 minutes or longer.

The NaCl surface is prepared for deposition of Cu in steps (a) and (b). The surface produced in step (a) has been previously examined by gold decoration procedures (which show flat regions up to one micron wide) and by graphite replicas (which do not show any resolved features). Now replicas have been prepared following step (b) with the result shown in Fig. 1. Here it is evident that the copper is ordinarily deposited on a surface which has been appreciably roughened by thermal etching, and that the flatness of the cleaned and polished but unheated surface has no significance for the copper as deposited. It may further be noted that the residual pressure of 10^{-5} torr provides a very high rate of bombardment by foreign molecules so that the substrate surface reached by the copper is contaminated with adsorbed molecules as well as being rough.

Replicas were also prepared from NaCl surfaces heated in H_2 to 630°C as in step (d) but without copper (Figs. 2,3 and 4). At this high temperature the surface is greatly roughened. The contour lines in Fig. 2 represent steps of 300 Å or more. Figure 3 shows three mesas standing 3000 Å above the average surface at sites where the volatility of NaCl is below normal. Figure 4 shows a pit which is 1.0 micron in diameter and 2000 Å deep on one side. Whether this pronounced thermal etching is inhibited by the overlay of copper in step (d) of the regular treatment is answered by the replicas shown in Figs. 5-10.

A series of eight copper films were treated by steps (a), (b), (c) and (d), and replicas were prepared of the copper surface still supported on the

NaCl substrate. The copper covering is continuous as shown by micrographs of every substrate-annealed film examined after being removed and mounted on a specimen grid. Figures 5-10 show that the gross roughness due to the thermal etching occurs even under the copper. The total depth of the cliff-like structure in Fig. 5 is estimated at more than a micron; the direction of shadowing happened to be unfavorable for precise estimates of elevation. Notable are the sharp corners showing that the copper follows closely the abrupt changes in contour. Figures 6,7,8 and 9 show deep pits (the smooth regions) which spread progressively until in Fig. 8 the pits are joined and in Fig. 9 isolated islands protrude by 2000 Å or more above the general surface. Figure 10 shows isolated mesas 5000 Å high. The gross roughness observed here is surprising in view of the smoothness previously noted in the micrographs of grid-mounted films.

A less frequent feature appears in Fig. 6. The three light lines and one dark line running diagonally from the edges of the figure represent low terraces; the light lines each are due to the shadowing of a drop in elevation in the direction from top to bottom of the figure, while the dark lines mark increases in elevation in the same direction. The heavy speckling in the background here interferes with estimates of the heights of these low terraces, but even on other replicas with much clearer backgrounds the terrace heights are very low. Of the eight films in this series only two showed any of the low terraces.

For comparison with the preceding series, replicas were prepared from films after step (e), i.e., after the 630°C annealing on the substrate and the subsequent removal on water and mounting on specimen grids. Every such replica showed the features of Fig. 11: the complete absence of the gross roughness appearing in Figs. 5-10 and the frequent terraces running in the (110) directions of the crystal with heights up to about 300 Å. A micrograph taken directly from a substrate-annealed grid-mounted film is shown in Fig. 12 with the stacking fault diffraction patterns previously reported.

The correlation between the high terraces in the replicas and the stacking faults in the direct micrographs has now been established. Substrate-annealed films were mounted on grids and then shadowed with Pt. In the micrograph of Fig. 13 the stacking fault diffraction effects can still be distinguished and some of them lying nearly perpendicular to the shadowing direction (indicated by the shadows of the polystyrene spheres) show the light shadows indicating a drop in elevation. The stacking faults running in this direction but having an increase in elevation in the shadowing direction could not show shadows. The conclusion is that many of the stacking faults in these films have surprisingly high terraces (up to 370 Å) at the film surface.

The examination of the surfaces of thin copper films has also been extended to the unannealed film. Figure 14 is from a replica made of a film after step (c), i.e., without the high temperature anneal and before removal

from the substrate. The scale of the irregularities in the replica is the same as those in the direct micrograph (Fig. 15); comparison of the two figures suggests that the unannealed film has irregular thickness with thicker islands of about 1000 to 1500 Å diameter. The thin regions are often marked by canals on the surface. Figure 16 is a micrograph of a grid-annealed film, for which no corresponding replica is yet available. Figures 15, 16 and 11 are representative of the results previously described for unannealed, grid-annealed and substrate-annealed films as mentioned in the introduction.

2. Studies on KCl

The effect of a change in substrate has been tested by some work using KCl, chosen originally because of its similar structure but different thermal expansion from NaCl and before it was realized that its higher vapor pressure might play a serious role.

The crystals were cleaved and polished in the fashion described for NaCl. Replicas of this surface (Fig. 17) show that the polishing leaves a roughness never observed for NaCl. Subsequent heating to 630°C in H_2 leaves mesas and ledges (Fig. 18 and 19) generally greater than those observed in NaCl. When copper films have first been condensed on the KCl the subsequent heating to 630°C produces a new style of roughness. Many globular bodies of 1500 to 2000 Å diameter appear which are sometimes piled up in ridges of a micron or more in height (Fig. 20). Figure 21 shows the globular bodies lying in what appear to be their original positions with high cliffs and ledges showing in the general background. The sharpness of the contours of these latter features indicates how well the copper film has conformed to the substrate surface. Large pits may also occur as shown in Fig. 22 with a magnification ten times less than the other micrographs.

Again as for NaCl it is observed that the Cu film which has been mounted on a grid after being heated on the substrate shows none of the roughness noted above and has developed the high terraces paralleling the stacking fault directions. A micrograph of a replica from such a mounted film is in Fig. 23. The direct micrographs of films annealed on KCl show no significant differences from those annealed on NaCl.

3. Discussion

The foregoing results combined with previous work lead to the following description of the conditions during the preparation and mounting of substrate-annealed films. The substrate as presented to the condensing Cu vapor is much rougher than a cleaved surface with many asperities of the order of 30 to 50 Å. The 700 Å layer of condensed copper is composed of 1000-1500 Å diameter islands joined by thinner regions but with all of the islands oriented in the

same directions (giving rise to a single crystal diffraction pattern with a few twin spots); some twin boundaries and narrow stacking faults appear in the micrograph of the unannealed film. When the copper on the substrate is heated to 630°C the substrate is greatly roughened by thermal etching; and holes, cliffs and mesas appear with dimensions up to a micron or more, i.e., with heights and depths more than ten times the average thickness of the copper. During this heating the copper must be quite mobile since it finally reproduces very sharply the contours of the grossly roughened substrate without the loose drape which would be expected if the general integrity of the original copper layer were preserved. Only occasionally low terraces (less than 20 Å) can be observed in the smoother regions. When the film is floated off on water and picked up on a 200-mesh grid, the mounted film shows an astonishing smoothness with no trace of the previous gross roughness. The thickness appears to be quite uniform except perhaps at the high (up to 300 Å) terraces which are associated with stacking faults. The stacking faults often have widths of several microns and the total faulted area amounts to 5×10^4 cm^2 per cm^3 of crystal. Dislocations also occur in the substrate-annealed films with a density of 10^7 cm^{-2}. By contrast, films mounted on grids and then heated to the same temperature show no stacking faults and a dislocation density 100 times greater.

The origin of the stacking faults and their associated high terraces in the mounted films is related both to the heating on the substrate and to the subsequent mounting process. If the film on the substrate is heated to only 500°C, no stacking faults appear in the mounted film. On the other hand, if the film with stacking faults is reheated to 630°C, the stacking faults are not removed. (Incidentally the H_2 atmosphere is not significant since the substitution of He or the reduction of the residual pressure to 10^{-4} torr during substrate annealing does not alter the stacking faults.) One may question whether the gross roughness of the Cu film annealed on the substrate is directly related to the stacking fault formation. It is most interesting that this roughness disappears in the mounting process, probably through the action of the high surface tension of the water in spreading and stretching the film. If this be true, then the film is subjected to mechanical working at this stage. One may suppose that stacking faults in fact occur in the copper on the heated substrate and terminate in surface terraces which are low and mostly unobservable. The subsequent application of mechanical stress could easily produce additional slip on the glide plane with a considerable exaggeration of the original terrace. It is also possible that the extensive stacking faults and terraces first arise when the film which was bent around the rough contours of the heated substrate is straightened out on the surface of the water.

Further work on the role of the action of the water and of the previous roughness of the film will follow two lines. In the first a mechanical support will be provided for the film during the removal from the substrate in order that a grid-mounted film with the rough contours may be examined in the electron microscope for stacking faults. Supports proposed are condensed

graphite (not later removed) or a special wax to be removed after mounting by leaching with the condensing vapor of a low surface-tension organic liquid. The other approach involves the use of more refractory substrates such as LiF or MgO so that the gross roughness never occurs at the temperatures previously used. This should lead to more precise information on the factors responsible for the stacking faults and determine whether films can be produced with stacking faults but without high terraces. Then it may be possible to discover whether the previously reported effect of stacking faults on nucleation and growth of the oxide is in fact an effect of terraces on the surface.

B. RESULTS ON OXIDATION OF Cu FILMS

Some of the interesting previous results on oxidation of substrate-annealed Cu films at 525°C and 0.9×10^{-3} torr of oxygen are recalled in Figs. 24 and 25. The first is a direct micrograph of a film oxidized for 2 minutes and illustrates the tendency for oxide nucleation to occur over stacking faults and in some cases for the growth to be extended parallel to the faults. The micrograph of a replica in Fig. 25 shows that the oxide grains extend above or below the surface with a convexity or concavity greater than the original thickness of the Cu film and suggests that details of the growth process might be discovered in a systematic examination of films oxidized for different times.

1. Study of Various Oxidation Times

A series of eleven substrate-annealed films were oxidized at times ranging from 2.2 to 15 minutes. The average number of oxide grains was established at 4 or 5×10^{7} cm^{-2} at the end of 3 minutes and remained the same for the longer times. On the other hand the average diameter of the grains increased from 0.4 micron at 3 minutes to 1.0 micron at 5 minutes and 1.4 microns at 10 and 15 minutes. It is evident the oxide nuclei are formed nearly simultaneously and remain constant in number while increasing in size during the oxidation period observed here. While there is a general impression of approximate uniformity in size at a given oxidation time, some size discrepancies did appear among the three characteristic grain shapes, i.e., triangular, square and elongated. In particular, the long dimension of the elongated grains was greater than those of the other two shapes but rarely by more than a factor of two. It would be possible to estimate the total oxide formed per cm^2 of film as a function of time, but a much more extensive series of films would be required; and the principal interest for the present is still in the behavior of individual grains of oxide.

Replicas were prepared from both sides of the foregoing films. The high terraces described in the preceding section appear on both sides of the films with heights ranging from 90 to 270 Å with most of them in the smaller range between 150 and 200 Å. The replicas also show the elevation of the oxide grains above (or below) the Cu film by distances greater than the thickness of the

film and indicates an extensive migration of copper during the reaction with oxygen.

A number of the oxidized films were dipped for 5 seconds in 50% HCl solution, which dissolves the oxide but not the copper. Micrographs from four such films with oxidation times of 3, 5, 10 and 15 minutes, respectively, are shown in Figs. 26, 27, 28 and 29. The first shows small clean holes of 0.2μ diameter; these correspond to the smallest oxide grains observed to date and the holes indicate the expected result that the copper down through the thickness of the film is completely oxidized by the time the lateral growth of the oxide has exceeded the thickness of the film. Large holes appear with longer oxidation times and the shapes are quite similar to those observed in the replicas. Not all the holes in the 10 and 15 minute films are clear but there is some chance of contamination in the microscope and it is not certain that the holes in question are partially blocked by unoxidized copper.

2. Slow Cooling of Oxidized Films

The question has arisen whether the shape and size of the oxide grains may be determined in part by the cooling from 525°C to room temperature. Accordingly the treatment was altered for several films so that the temperature drop occurred during 50 minutes rather than 3 or 4 minutes. During this time the oxygen pressure was held at about 2×10^{-5} torr or about 1/50 of that used for oxidation. Figure 30 shows a micrograph of such a slow cooled film which had been oxidized for 5 minutes; Fig. 31 represents the corresponding replica; and Fig. 32 shows the oxidized film cooled at the normal rate. (Figures 30 and 32 show a reversal between light and dark regions due to accidental variations in the precise orientations of the films relative to the electron beam; the light appearance of oxide grains in Fig. 30 and the dark appearance of the grains in Fig. 32 does not signify any difference in the films.) The slow cooling does not affect the size of the grains, i.e., no further oxidation is evident during cooling at reduced oxygen pressure. The boundaries around the oxide grains have become more diffuse and the elevations observed in the replicas are lower. Moreover, the copper begins to show the texture of thicker regions connected by thinner bands previously noted in unannealed films which had been heated to 330°C. These results suggest movement of copper during the long cooling period although the stacking fault patterns have not disappeared.

3. Oxidation of Mechanically Stressed Films

An attempt to apply mechanical stress to the copper prior to oxidation was made by bending the grid supporting the film in a direction (a) parallel to (001) or (b) parallel to (110). The first direction lies at 45° to the stacking faults while the second is parallel or normal to stacking faults.

The bent films were oxidized under the usual conditions for 3 minutes and then examined in the electron microscope. Other than the cracks in the films no distinctions appeared between these and the films which had been oxidized without deliberate bending. The size and general distribution of the oxide grains appeared to be unaffected by the bending of the film. This simple experiment is not an adequate test of the effect of mechanical stress in the film on its oxidation properties, but no further work on this point has been done.

C. RESULTS ON OXIDATION OF FILMS CONTAINING Te

The work on Te-doped films described in the August 1963 report has been brought to a conclusion with observations on the oxidation of paired films of pure and doped copper. The nominal compositions of Te covered five values in the range from 0.26 to 1.00 atomic percent and were determined by the relative weights of Te and Cu evaporated in the sandwich technique previously described. There is a real possibility that the weight ratio in the condensed films is not the same as the weight ratio of the evaporated material, but the attempt to analyze the condensed material by neutron activation methods did not yield reliable results because of the low total weight of the films. Moreover, the compositions mentioned above are considerably in excess of that for Te-saturated copper in a bulk phase; but the thin films as prepared gave no diffraction evidence for the existence of a second phase.

In spite of these uncertainties the oxidation experiments show an interesting result. In every case the oxide grains produced on grid-annealed doped films (oxidized for 20 minutes at 525°C and 0.9×10^{-3} torr) are smaller than those produced on pure copper oxidized simultaneously. For each concentration of Te the doped and pure films are immediately distinguishable by the size of the oxide grains. Figures 33 and 34 are micrographs of pure and doped (0.44% Te) films oxidized in the same run; while the number of grains is about the same, the diameters of those on the doped film average less than a quarter of those on the pure film. The same discrepancy appears in the pair of replicas shown in Figs. 35 and 36. Data from a series of twelve doped films run in pairs with pure Cu films suggest a correlation between average oxide grain size and the nominal tellurium composition of the film (Fig. 39). For pure copper the grains average 1.0 micron in diameter and the doped films show grains averaging 0.12 microns for Te concentrations of 0.66% to 1.0%; this implies a total oxide growth 60 times greater on the pure copper (assuming that the oxide spreads in only two dimensions). Lower Te concentrations produce lesser discrepancies in grain size but the effect is always unmistakable and in the same direction.

This result is particularly interesting since other work (Reference 19 in August 1963 report) on bulk copper showed an increase in oxidation rate with addition of Te. The difficulty of determining the Te concentration in the thin films suggests the use of a different material affording more precise information on the extent of the contamination of the copper.

It is now proposed to contaminate copper films with H_2S gas so that the total exposure to the impurity can be readily estimated and controlled by changing the pressure of the gas and the period of exposure. With the assumption of a constant although not precisely known sticking coefficient for H_2S on copper, definite variations in the H_2S contamination can be produced and the corresponding variations in oxide nucleation sites and growth can be observed.

D. PRELIMINARY WORK ON OXIDATION OF Cu IN THE MICROSCOPE

It was proposed in August 1963 that a gas reaction chamber be installed in the JEM 6A electron microscope whereby a copper film might be treated with H_2 and then with O_2 at various temperatures up to 630°C and at various pressures down to 10^{-4} torr while the film was under continuous observation on the microscope screen. This should provide a view of the earliest stages of oxide nucleation and allow the history of individual oxide grains to be followed.

The Japanese Electron Optical Laboratory, manufacturer of the microscope, offered a special stage with gas flow and high temperature but never accepted a purchase order. After nine months they concluded that their stage needed further major development and would not make it available in 1964.

In the meantime a gas reaction chamber for the JEM microscope has been designed and constructed here at the university. The tilting heated stage supplied with the microscope has been modified (Fig. 39). The lavite furnace body has been fitted with a molybdenum liner, whose bore holds the specimen supporting tube and a retainer tube. These molybdenum parts are shown in Fig. 38. The gas is carried by an Inconel tube to a channel in the liner which is matched by slots in the specimen tubes. The gas has access to both sides of the copper film on its supporting grid, and the gas is vented into the microscope chamber through diaphragms both above and below the specimen. This scheme should reduce contamination of the specimen by the residual atmosphere of the microscope. The auxiliary vacuum line and gas-handling line have been constructed and connected to the microscope together with the necessary instruments and controls for measuring the pressure around the specimen stage and in the gas supply line, for heating the stage and for measuring its temperature. General views of the modified microscope and of the auxiliary rack are shown in Figs. 40 and 41.

Preliminary tests have been made on the temperature control and measurements. The specimen stage has been operated up to 800°C. The moving film camera supplied with the microscope is constructed so that the film is contained within the vacuum chamber of the microscope and receives the electron image directly rather than recording the optical image from a fluorescent screen; the operation of this camera has required adjustments and has been tested in recording successive stages in the thermal annealing of thin Cu films. At present the vacuum system of the microscope is undergoing testing and improvement.

III. FURTHER WORK

Further work on copper films will be directed along the following lines:

(a) Study of stacking faults in films given mechanical support during removal from the substrate and in films condensed on more thermally resistant substrates such as LiF and MgO.

(b) Annealing and oxidation reactions carried out on specimens in place in the microscope.

(c) Preparation and treatment of copper films in an ultrahigh vacuum unit to reduce contamination by the residual atmosphere.

(d) Examination of films exposed to H_2S and observation of the effects on oxidation.

(e) Preparation and oxidation of films having dislocation densities near 10^6 cm^{-2}.

(f) Oxidation of polycrystalline films to observe effects of grain boundaries.

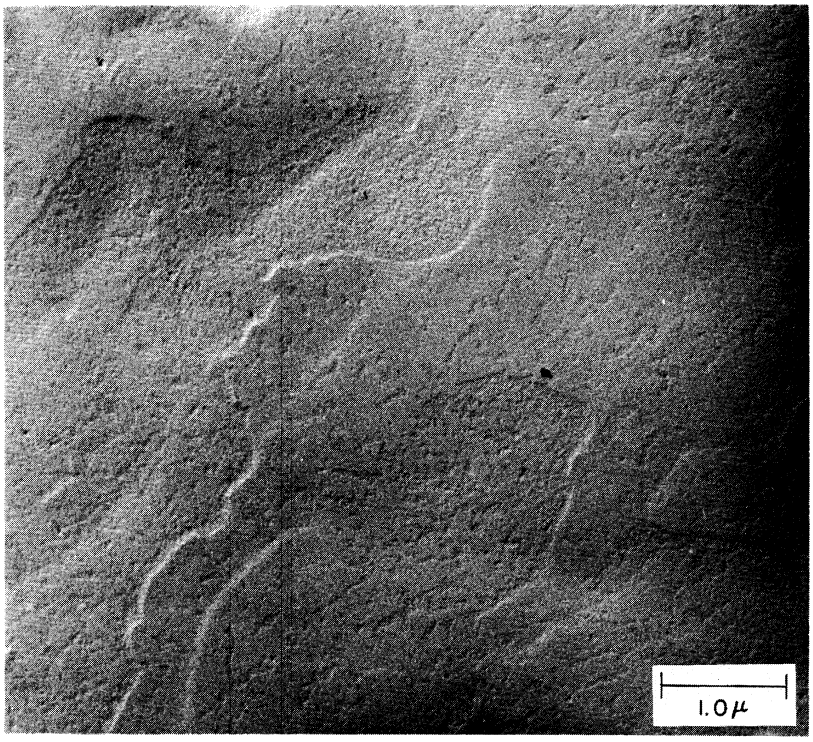

Fig. 1. Replica of polished NaCl after heating to 330°C.

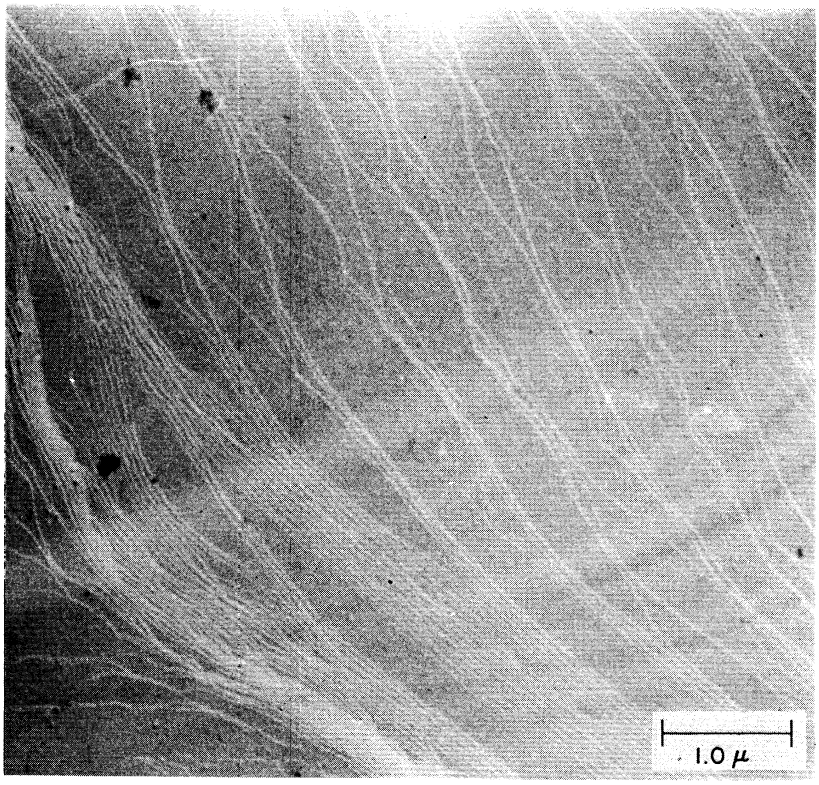

Fig. 2. Replica of NaCl after heating to 630°C for 10 min.

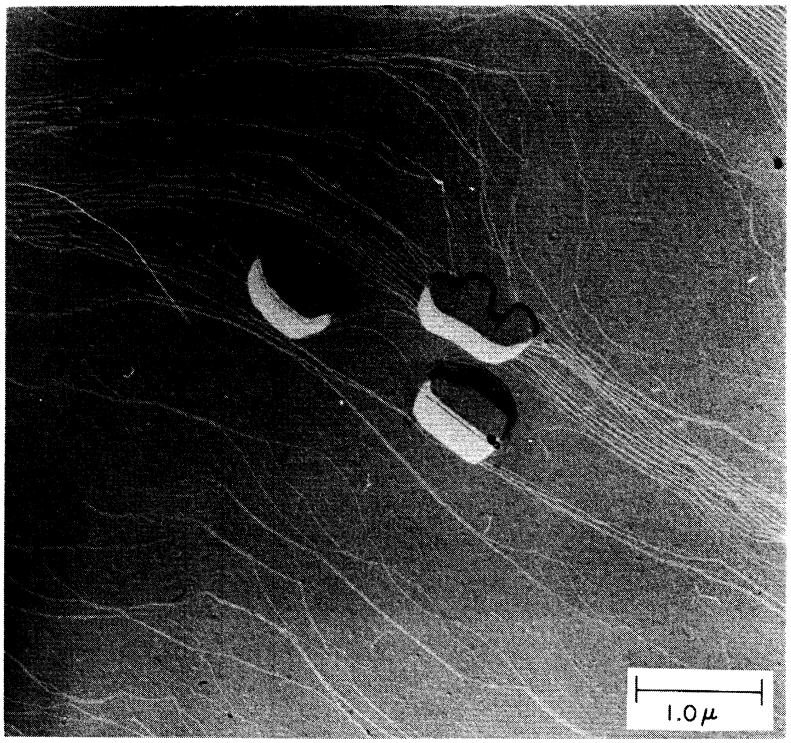

Fig. 3. Replica of NaCl after heating to 630°C for 10 min.

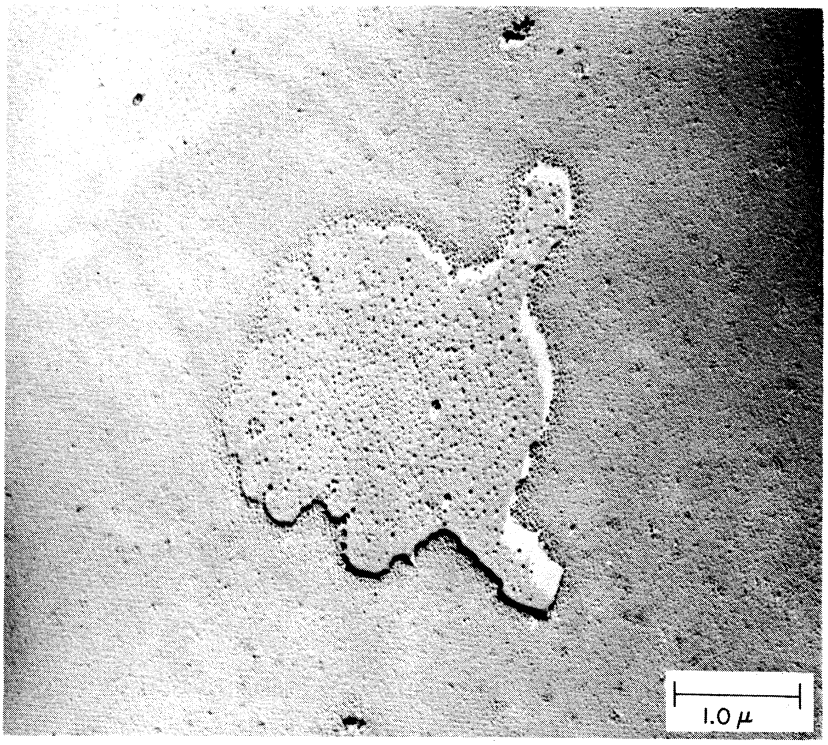

Fig. 4. Replica of NaCl after heating to 630°C for 10 min.

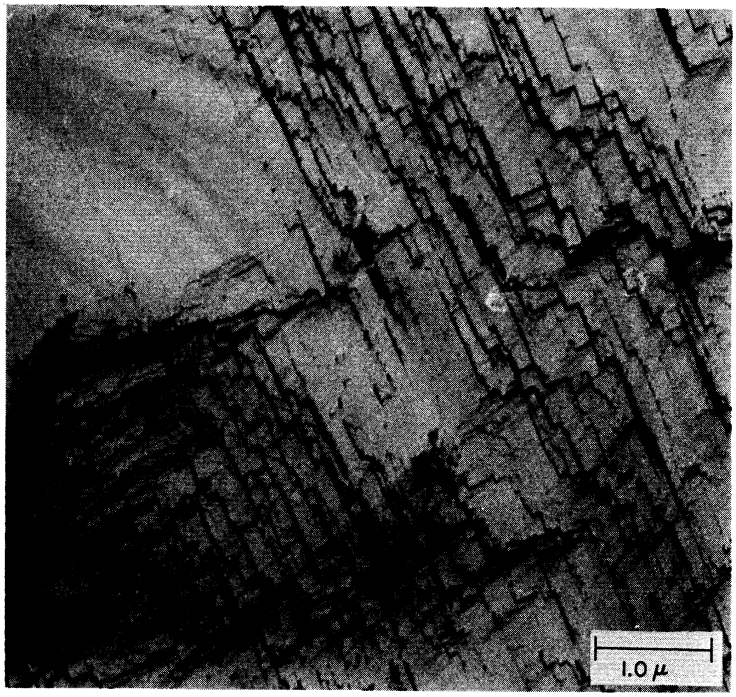

Fig. 5. Replica of Cu film on NaCl after heating to 630°C for 10 min.

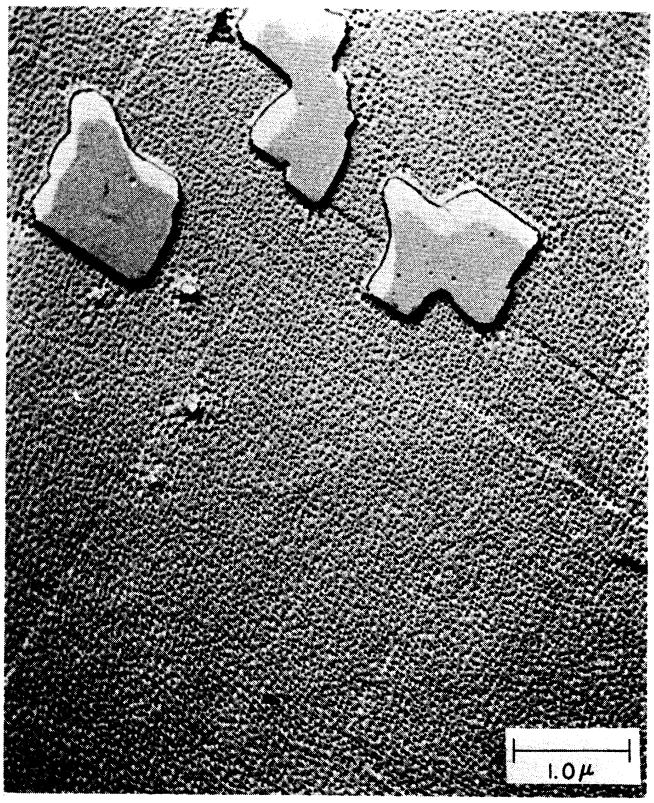

Fig. 6. Replica of Cu film on NaCl after heating to 630°C for 10 min.

Fig. 7. Replica of Cu film on NaCl after heating to 630°C for 10 min.

Fig. 8. Replica of Cu film on NaCl after heating to 630°C for 10 min.

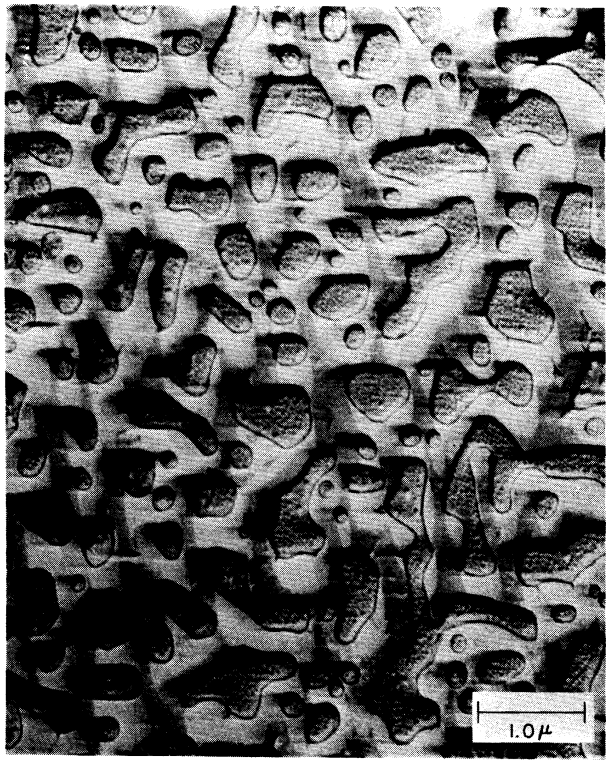

Fig. 9. Replica of Cu film on NaCl after heating to 630°C for 10 min.

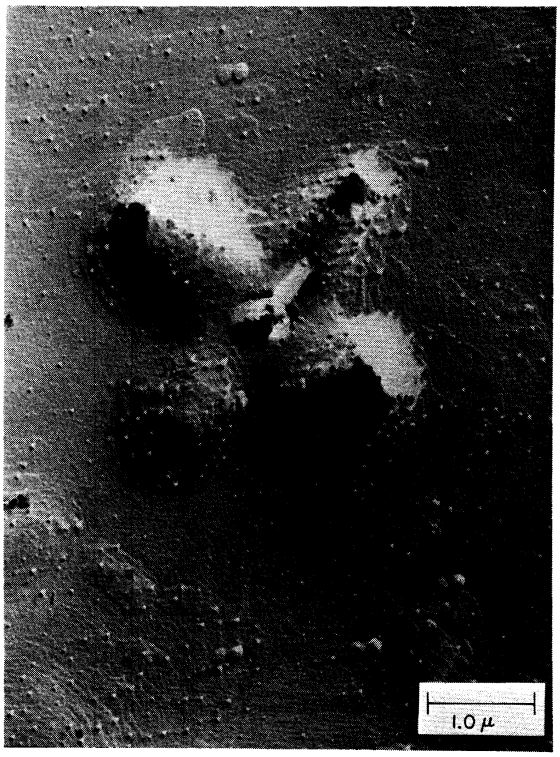

Fig. 10. Replica of Cu film on NaCl after heating to 630°C for 10 min.

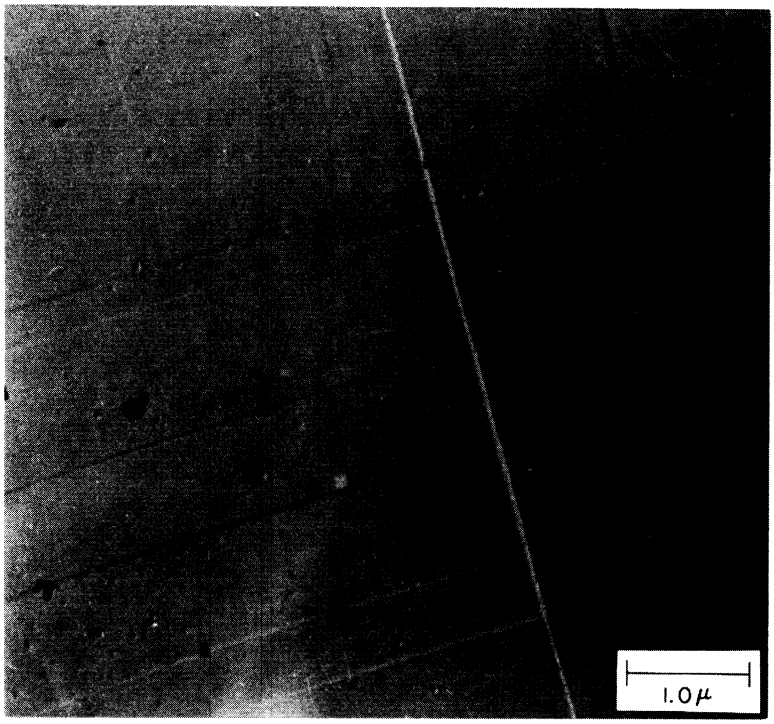

Fig. 11. Replica of Cu film mounted on grid after heating to 630°C on NaCl.

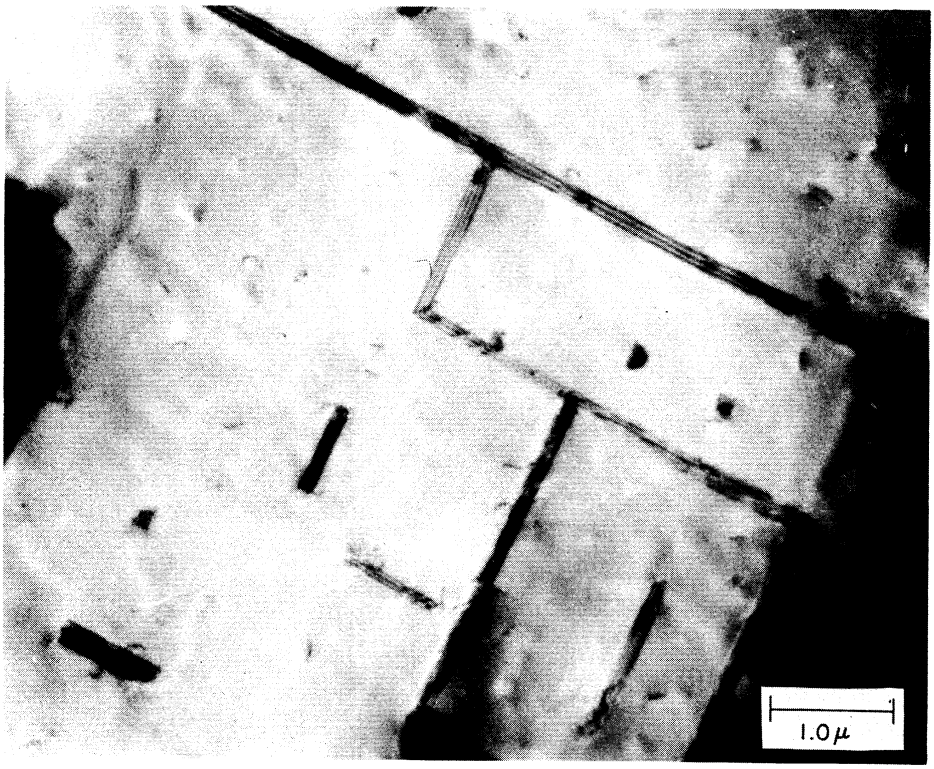

Fig. 12. Micrograph of Cu film treated as for Fig. 11.

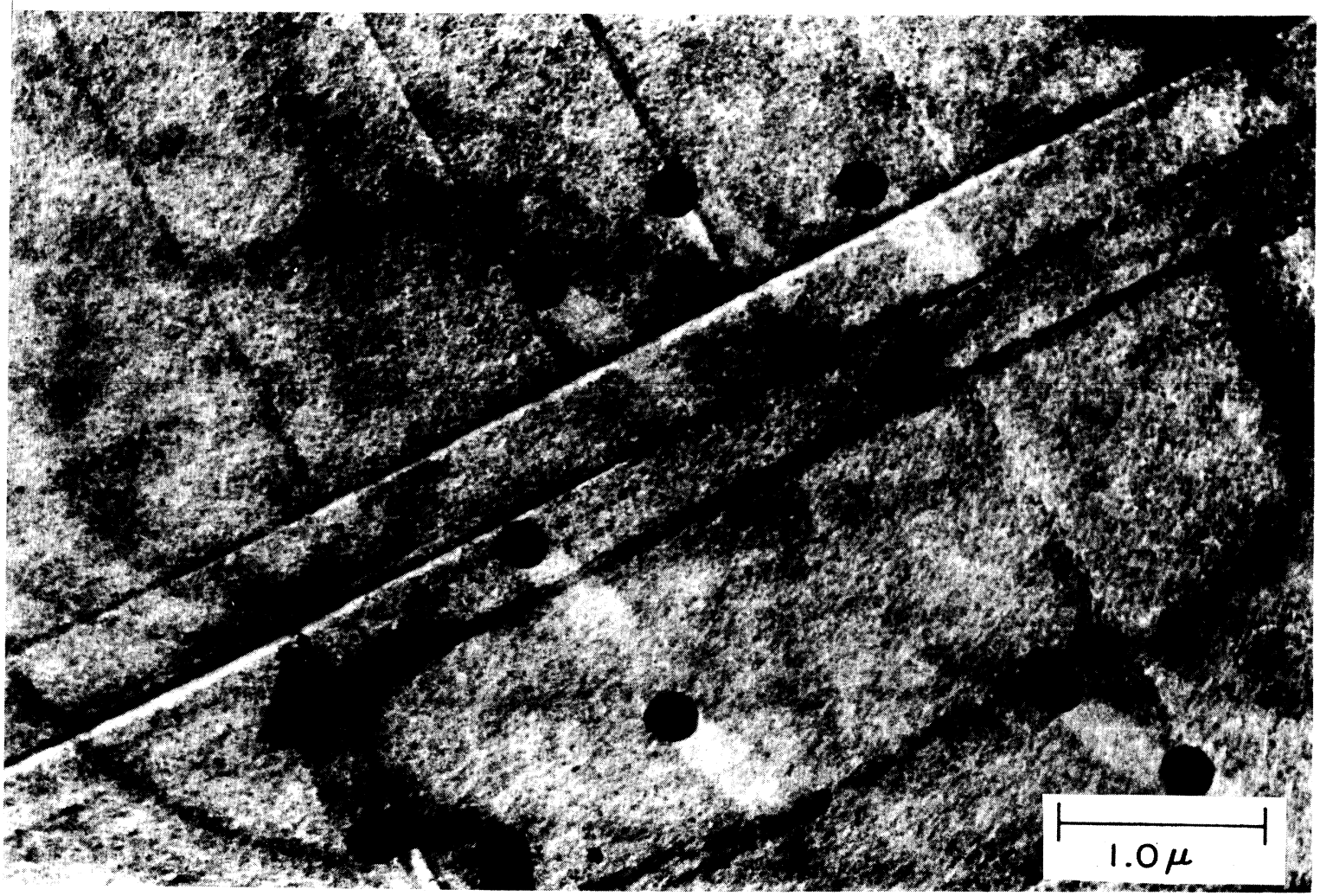

Fig. 13. Micrograph of Cu film pre-shadowed with Pt after heating to 630°C on NaCl and mounting on grid.

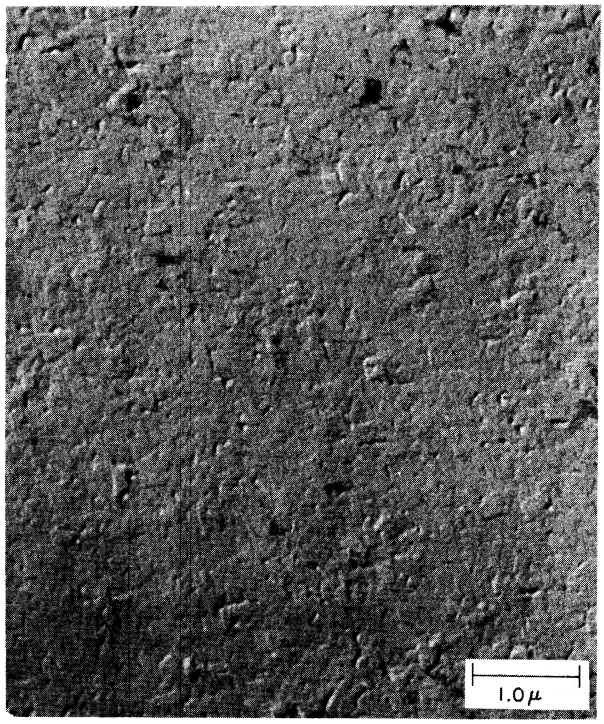

Fig. 14. Replica of Cu film on NaCl not annealed at 630°C.

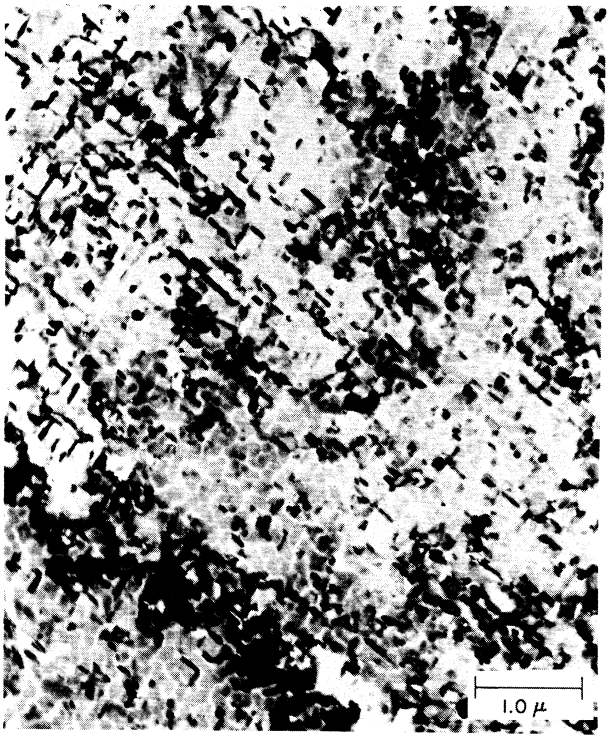

Fig. 15. Micrograph of Cu film on NaCl not annealed at 630°C.

Fig. 16. Micrograph of Cu film heated to 630°C for 10 min after mounting on grid.

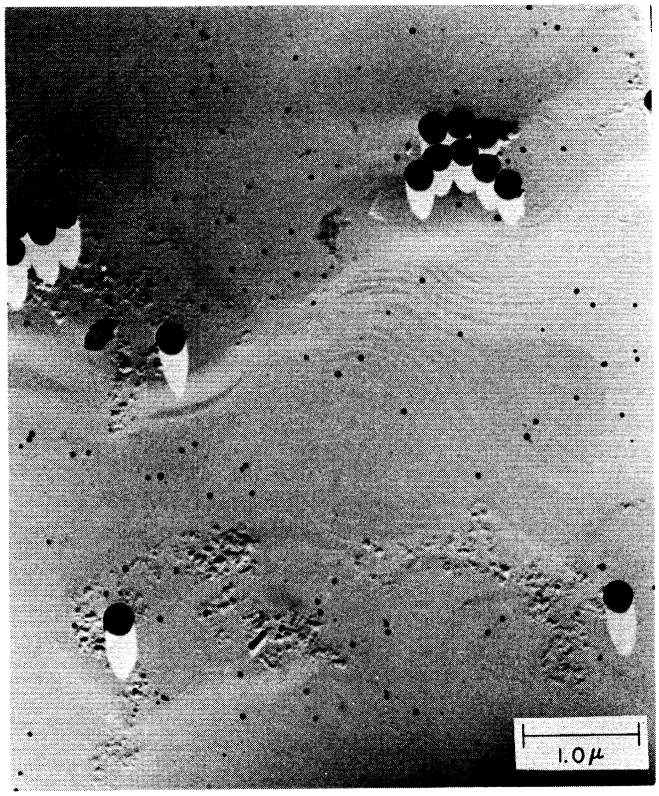

Fig. 17. Replica of polished KCl.

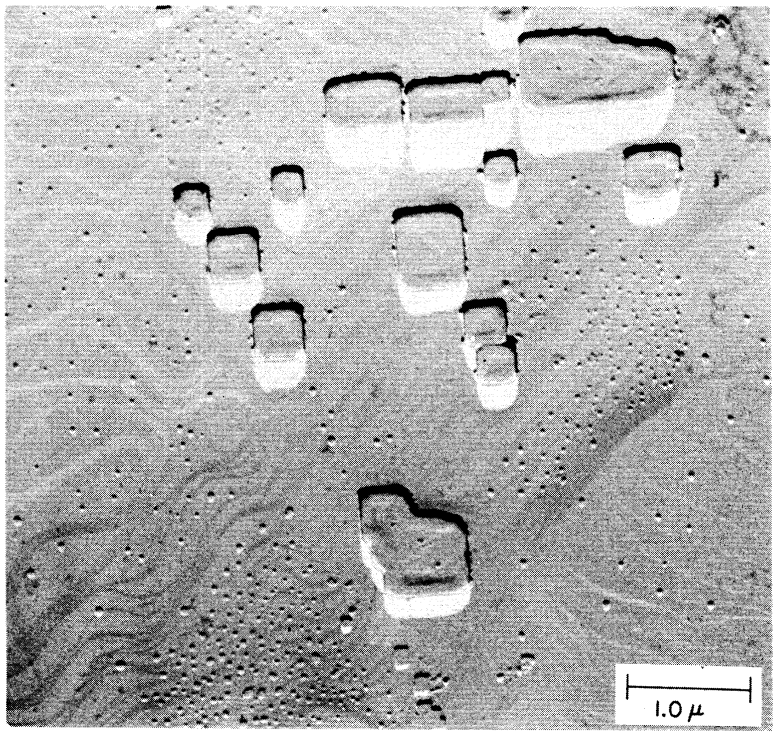

Fig. 18. Replica of KCl after heating to 630°C for 10 min.

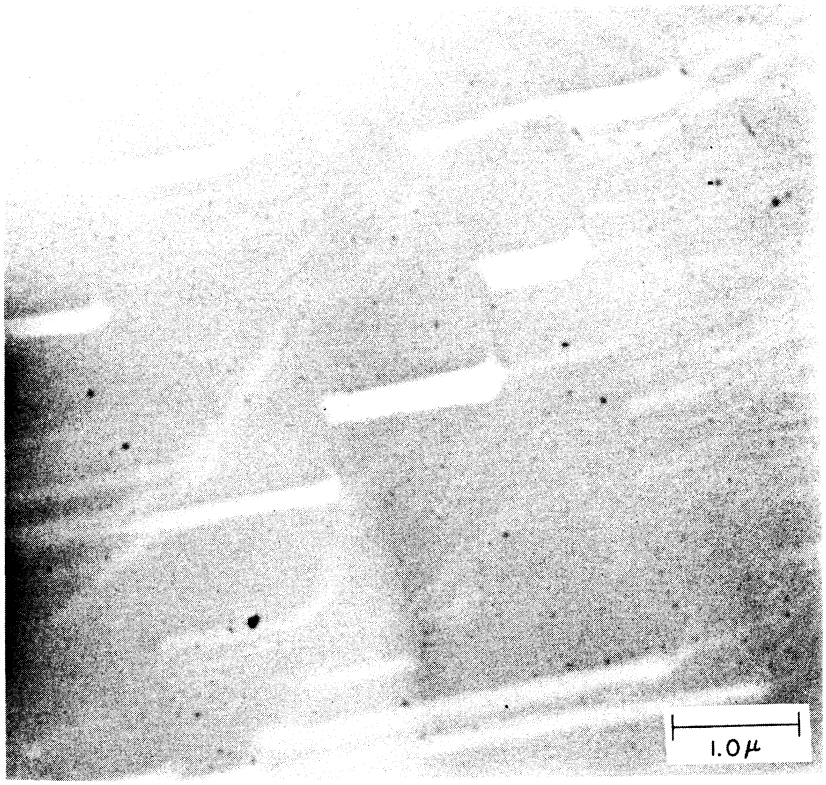

Fig. 19. Replica of KCl after heating to 630°C for 10 min.

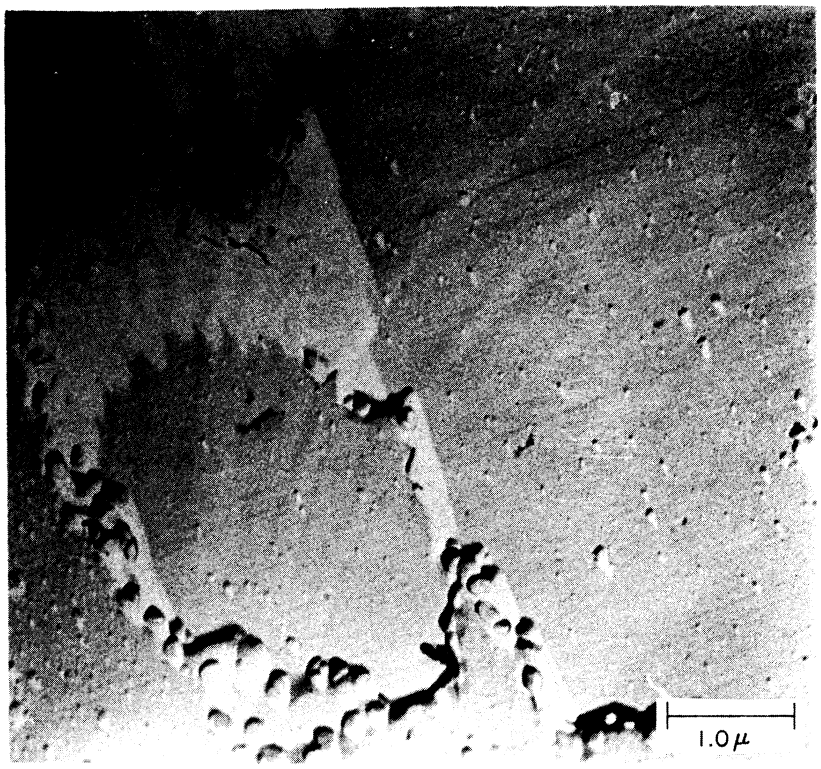

Fig. 20. Replica of Cu film on KCl after heating to 630°C for 10 min.

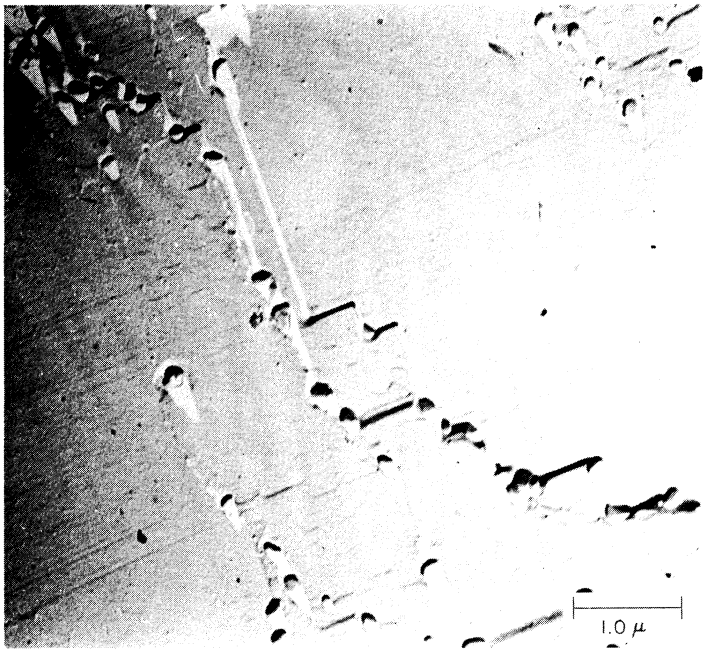

Fig. 21. Replica of Cu film on KCl after heating to 630°C for 10 min.

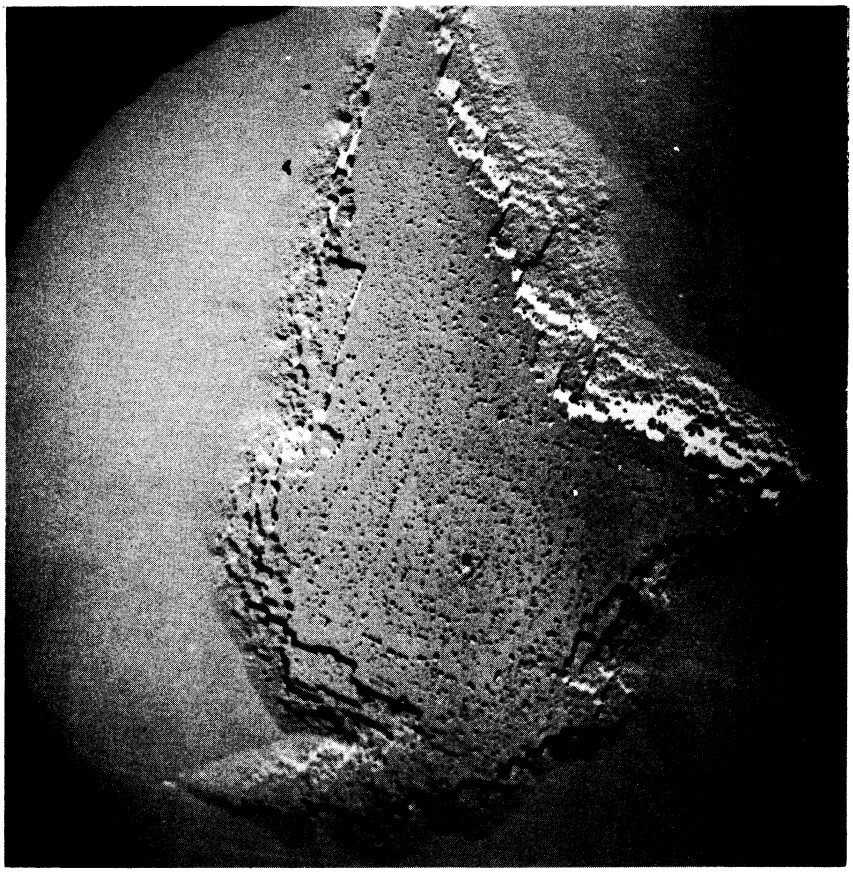

Fig. 22. Replica of Cu film on KCl after heating to 630°C for 10 min. (3000x magnification).

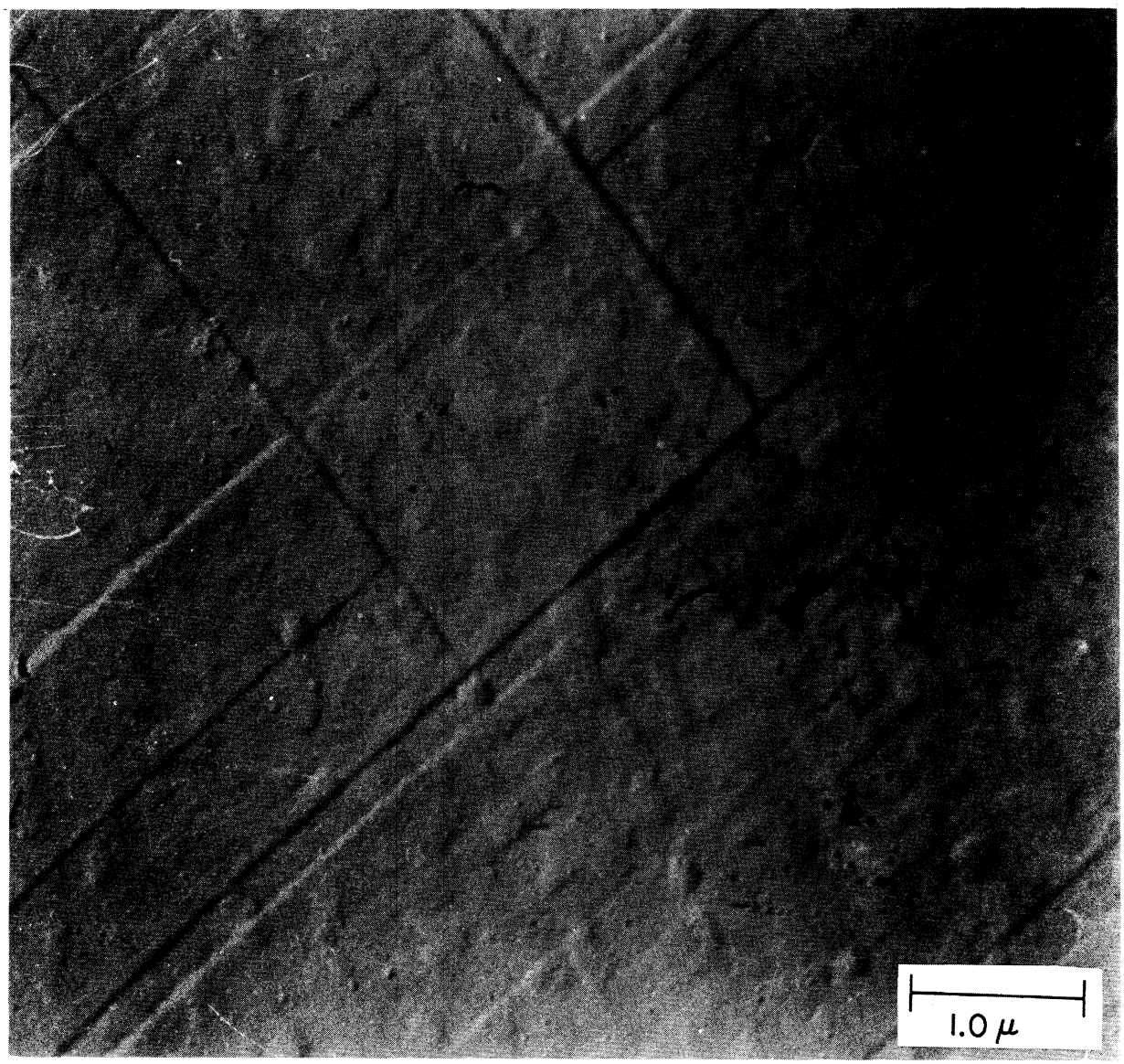

Fig. 23. Replica of Cu film mounted on grid after heating to 630°C on KCl.

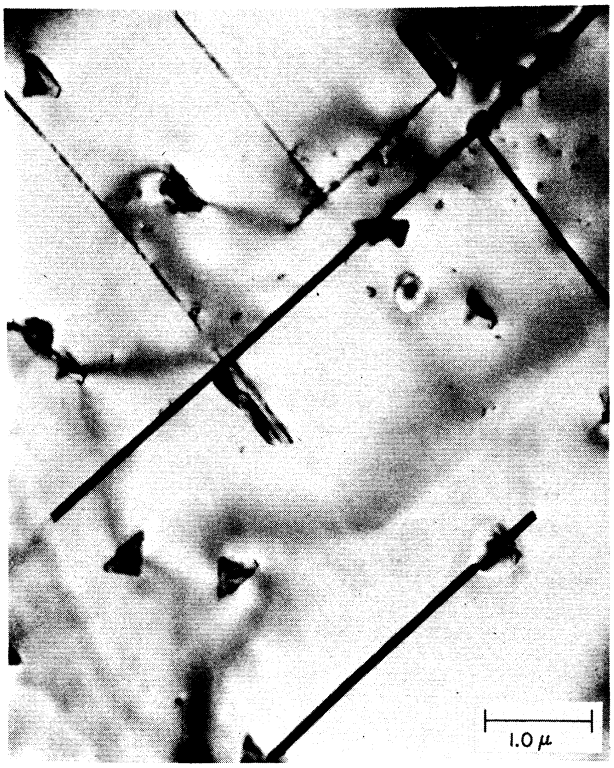

Fig. 24. Micrograph of substrate-annealed Cu oxidized in O_2, 0.9 x 10^{-3} torr, 525°C, 2 min.

Fig. 25. Replica of substrate-annealed Cu oxidized in O_2, 0.9 x 10^{-3} torr, 525°C, 15 min.

Fig. 26. Micrograph of oxidized Cu film treated with HCl solution, 3 min oxidation.

Fig. 27. Micrograph of oxidized Cu film treated with HCl solution, 5 min oxidation.

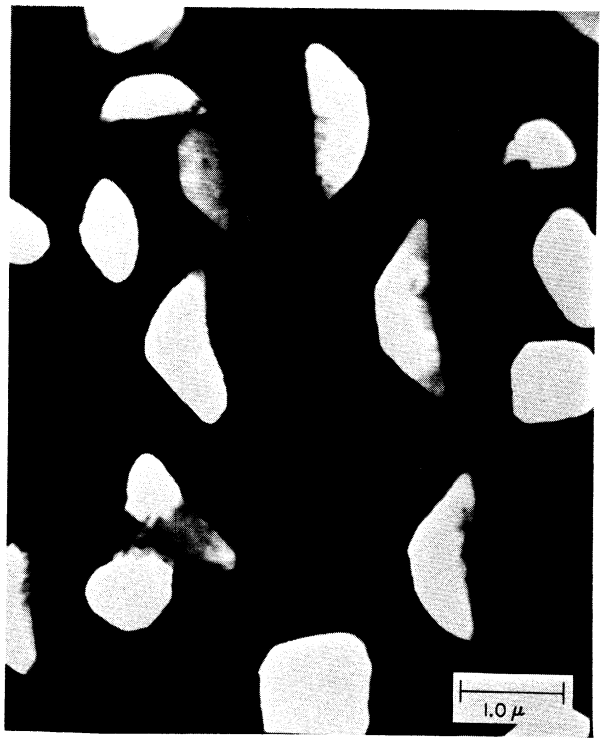

Fig. 28. Micrograph of oxidized Cu film treated with HCl solution, 10 min oxidation.

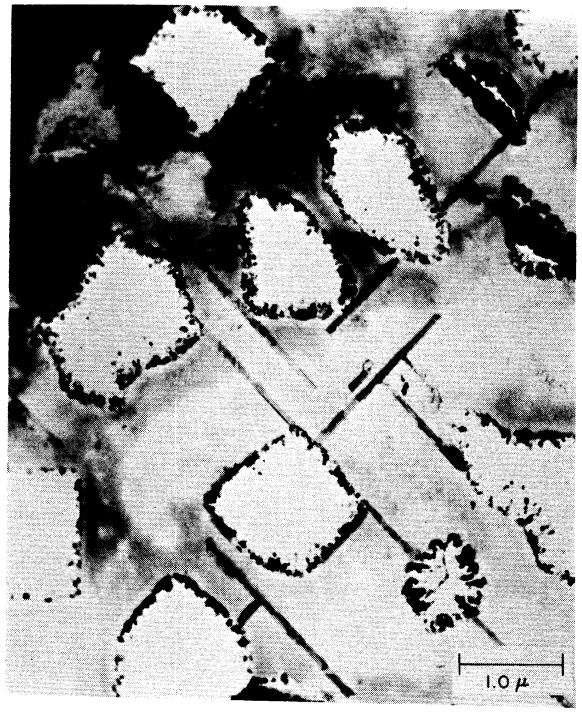

Fig. 29. Micrograph of oxidized Cu film treated with HCl solution, 15 min oxidation.

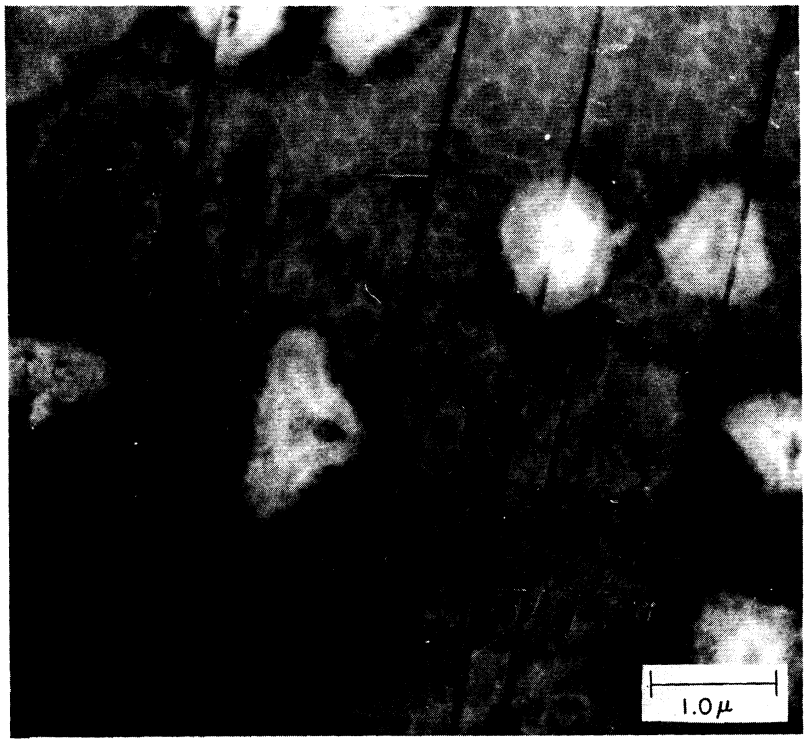

Fig. 30. Micrograph of Cu film oxidized for 5 min and cooled at 10°/min.

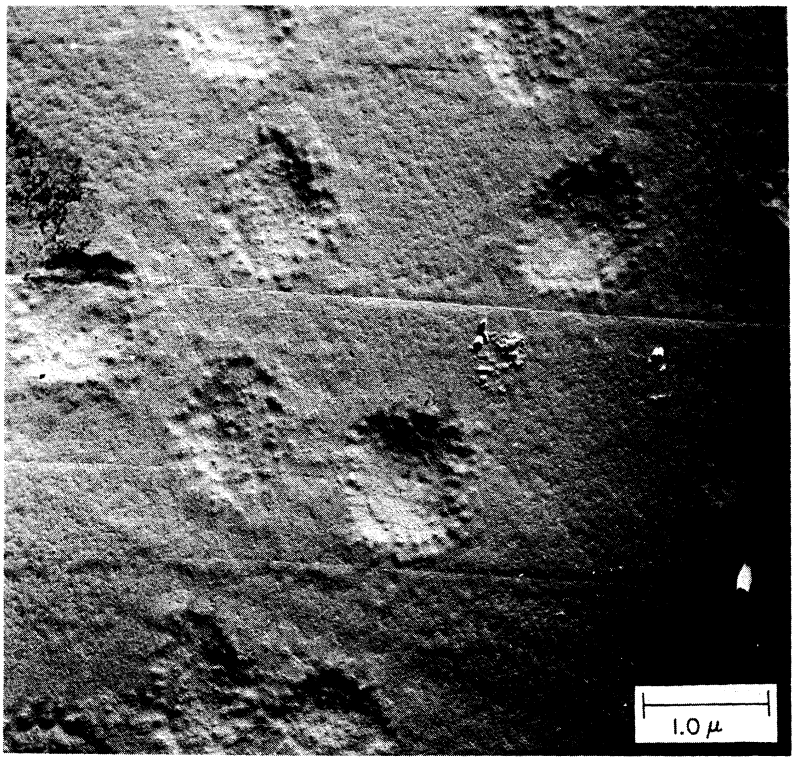

Fig. 31. Replica of Cu film treated as for Fig. 30.

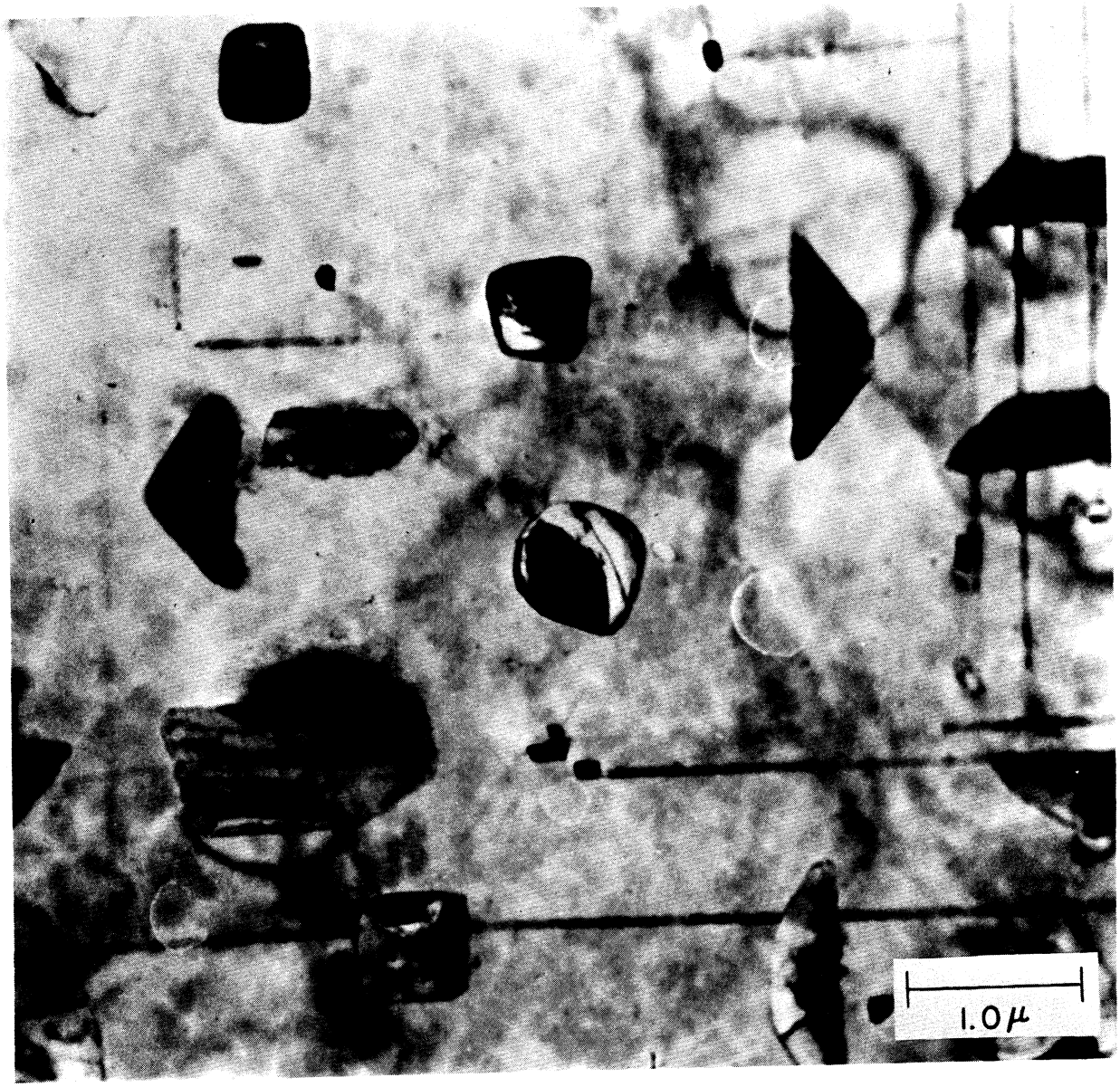

Fig. 32. Micrograph of Cu film oxidized for 5 min and cooled at 150°/min.

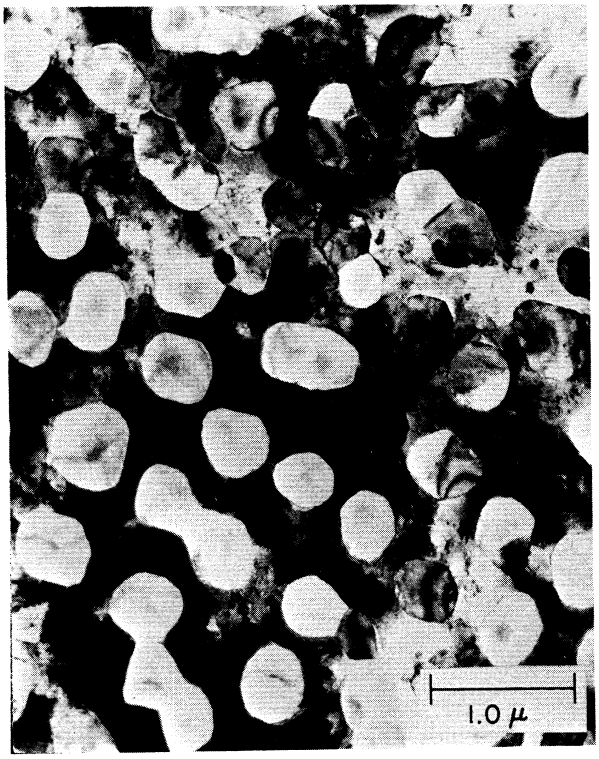

Fig. 33. Micrograph of pure Cu film oxidized for 20 min.

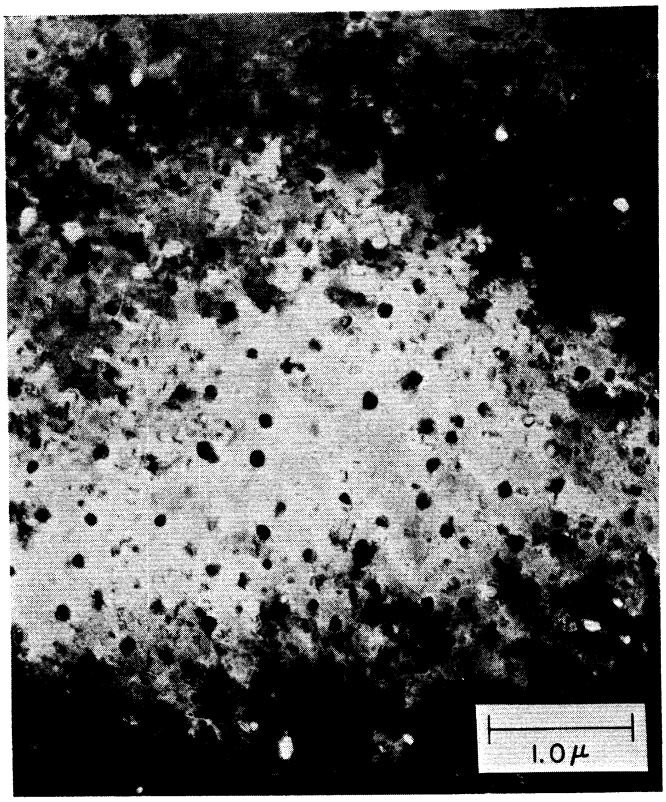

Fig. 34. Micrograph of Cu + 0.44% Te, oxidized for 20 min.

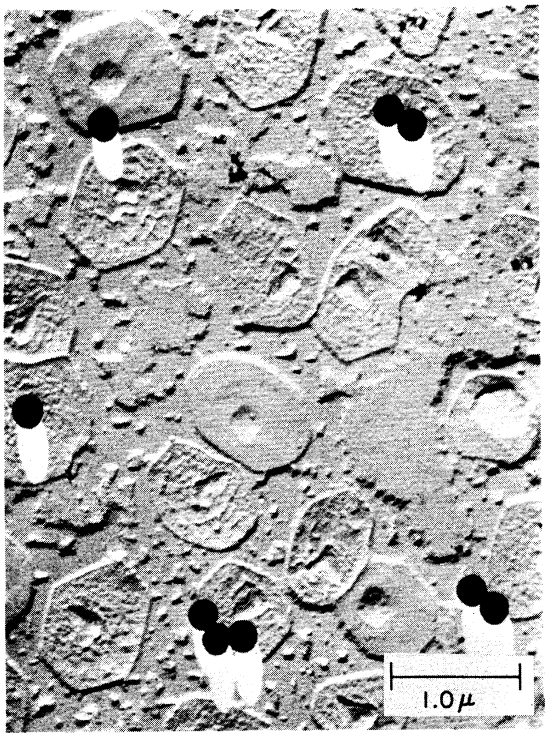

Fig. 35. Replica of pure Cu film oxidized for 20 min.

Fig. 36. Replica of Cu + 0.44% Te oxidized for 20 min.

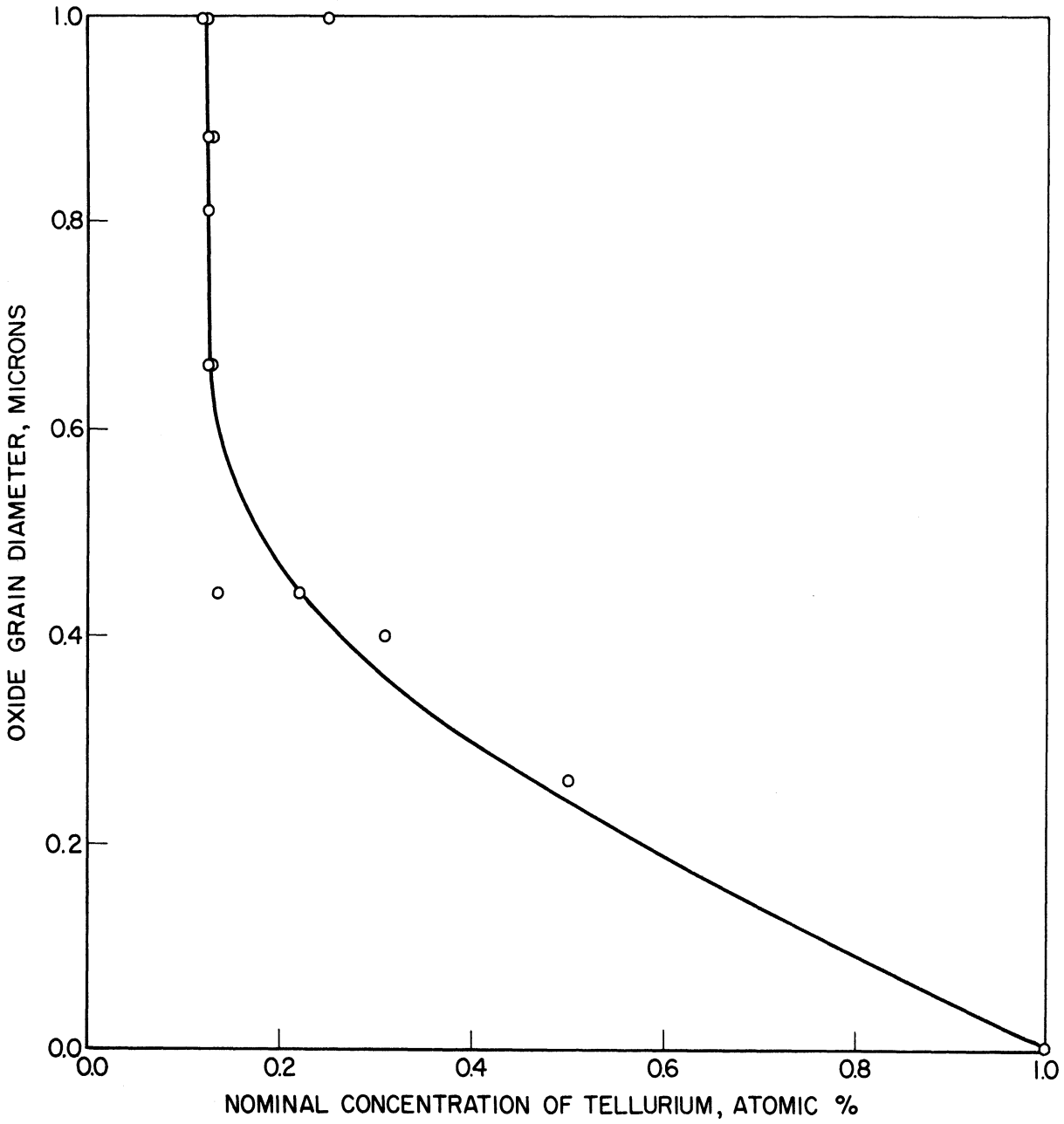

Fig. 37. Relation between nominal concentration of tellurium in copper and the oxide grain size after 20 min oxidation.

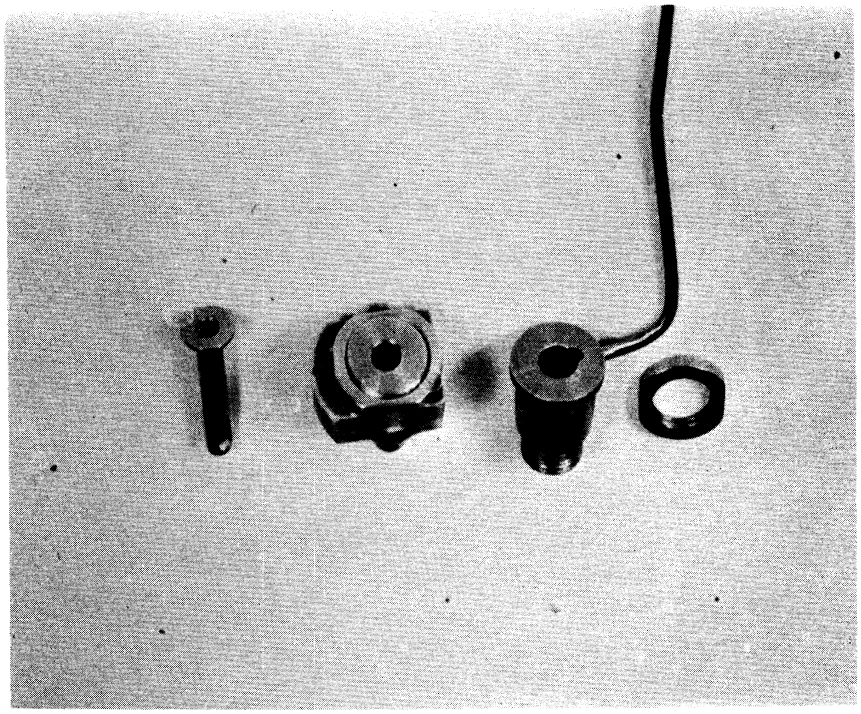

Fig. 38. Parts of gas reaction chamber.

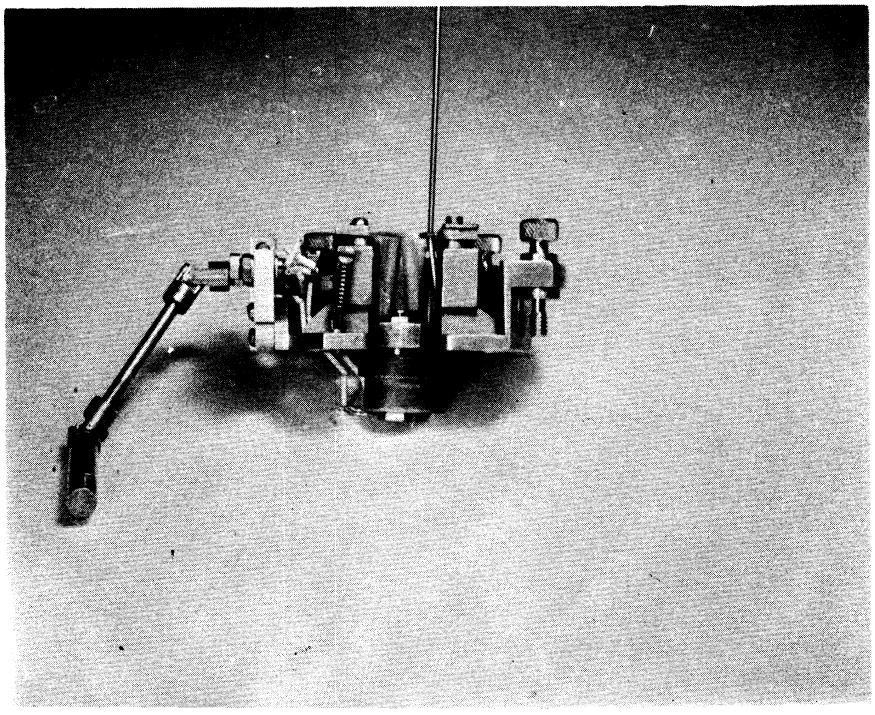

Fig. 39. Heated specimen stage for JEM 6A electron microscope, fitted with gas reaction chamber.

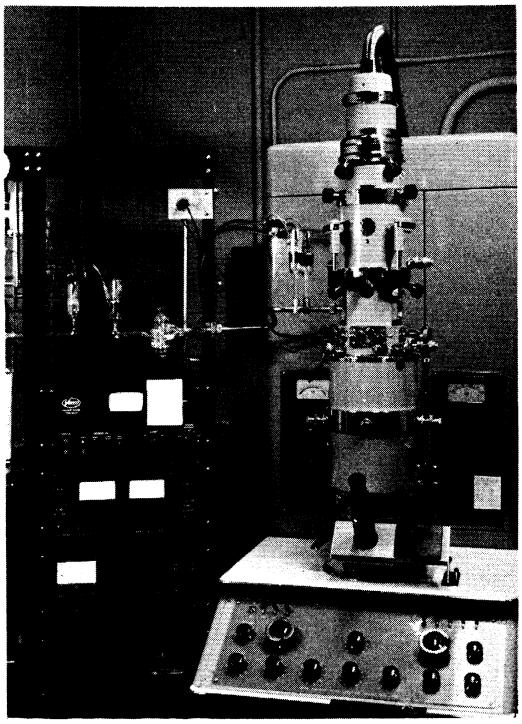

Fig. 40. View of JEM 6A electron microscope with attachments for gas reaction.

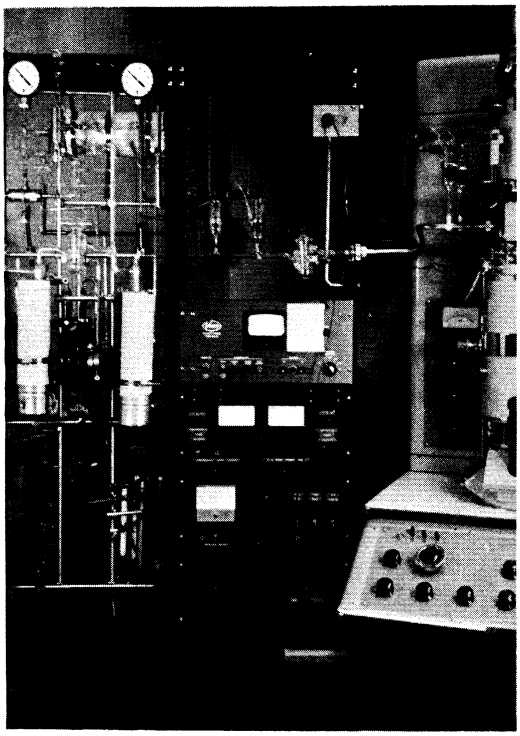

Fig. 41. Auxiliary equipment (supply line for purified H_2 and O_2, vacuum gauges, control and measuring equipment for heated stage).