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WETTING AND SPREADING IN THE Cu-Ag SYSTEM

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DISCLAIMER

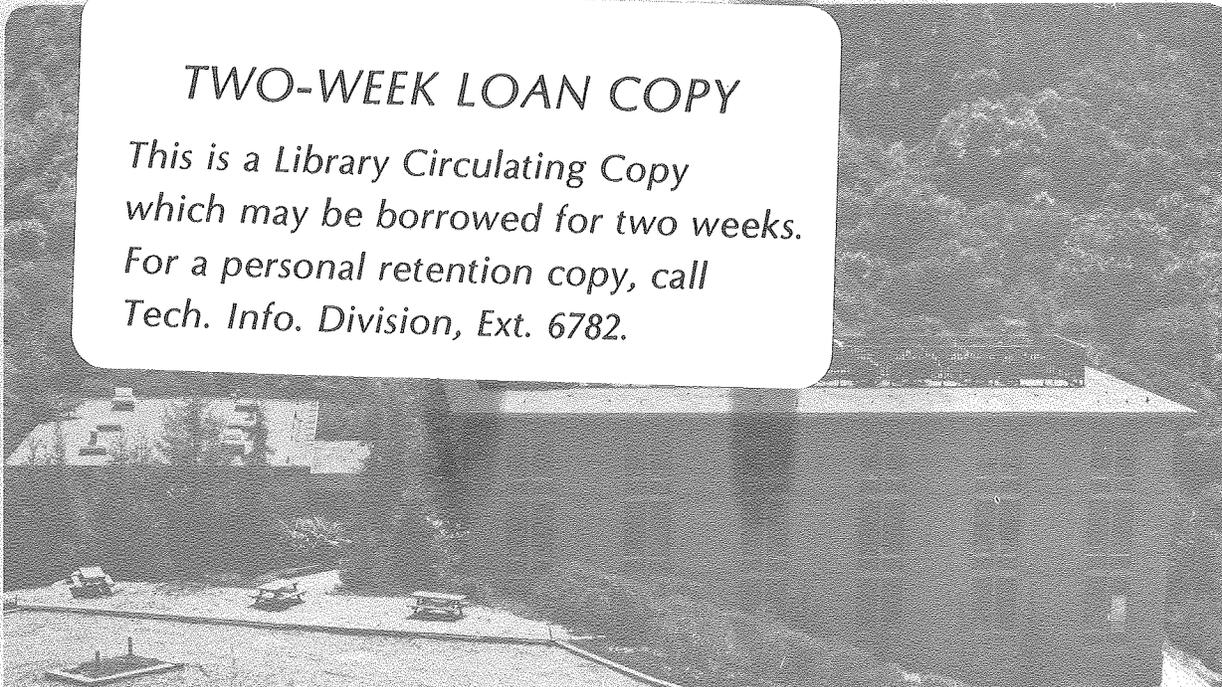# WETTING AND SPREADING IN THE Cu-Ag SYSTEM

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ABSTRACT

Sessile drop experiments were made in the copper-silver system at the
eutectic temperature and 900°C. Wetting, or acute contact angles, were
observed for specimens in chemical thermodynamic equilibrium. Spreading
occured when the substrate was not in chemical equilibrium with the
liquid. The interface does not remain aligned with the free surface of
the substrate only in the presence of reactions.

I. INTRODUCTION

A basic understanding of the interfaces between solids and liquids is important in the development of metal-metal and metal-ceramic seals, of protective coatings on metals, and of composites. It is particularly important to understand the conditions that affect the distribution of phases, one being a liquid, as in liquid phase sintering.

Sessile drop experiments have been widely used to study solid-liquid interfaces. Normally, the systems are considered to be in stable or meta-stable chemical equilibrium, with the final configuration representing the lowest interfacial free energy state for a system. Unfortunately, slight and not easily recognized reactions between the solid and the liquid frequently occur whose effect is not fully taken into consideration. Conditions under which reactions cause spreading have been theoretically evaluated.[1,2]

Many investigators, however, have observed decreasing contact angles during extended reactions. Humenik and Kingery[3] observed an increase in the wettability of ceramics by a liquid metal due to solid-liquid interfacial reactions. Tikkanen, et al.[4] have concluded that the reactions between different phases play a decisive role in wetting. Armstrong, et al.[5] attributed a decreasing contact angle in both the MgO-pure iron and the MgO-iron alloy systems to an interfacial reaction. In a more quantitative study, Chaklader, et al.[6] correlated the decrease in the contact angle to the extent of reaction in the sapphire-copper-oxygen system. Tutorskaya[7] observed a decreasing contact angle with the increased concentration of a reactive species in the liquid phase. Kostikov[8] has proposed that intensive chemical reactions are a necessary condition for

the formation of a zero contact angle, and hence for spreading to occur. Eremenko, et al.[9] suggest that increased wetting of solids by liquid metals due to chemical reactions at the interface is a general rule.

The present study was undertaken to systematically examine several types of nonequilibria that can occur between a solid and a liquid, and to correlate wetting and spreading behavior with the ensuing reactions. The copper-silver (Cu-Ag) system[10] shown in Fig. 1 was chosen for the investigation. Two liquid compositions were used: eutectic (71.9 wt.% Ag) and Cu-liquidus at 900°C (40.9 wt.% Ag). The solids used were Cu, Cu-solidus at 782°C (7.9 wt.% Ag), Cu-solidus at 900°C (7.7 wt.% Ag), Ag-solidus at 782°C (8.8 wt.% Cu), and Ag.

II. BACKGROUND THEORY

Under conditions of stable or metastable chemical thermodynamic equilibrium, wetting occurs when a drop of liquid is placed on a flat solid surface whose specific surface energy (γ_{sv} in N/m^2) is larger than that of the liquid (γ_{lv}) and an interface forms. The specific interfacial energy (γ_{sl}) is equivalent to γ_{sv} reduced by some amount not exceeding γ_{lv}. The degree of reduction ($\gamma_{sv}-\gamma_{sl}$), or the driving force for wetting, in a sessile drop experiment is thus equal to a fraction of γ_{lv} and is expressed by the familiar Young-Dupre equation as $\gamma_{sv}-\gamma_{sl} = \gamma_{lv}\cos\theta$ where θ is the acute contact angle measured inside the drop. When $\gamma_{lv}>\gamma_{sv}$, wetting will then not occur since $\gamma_{sl}>\gamma_{sv}$. The contact angle in this case is obtuse. The sketches based on mechanics showing for both cases the balance of surface and interfacial tensions[*], or more specifically a balance of forces acting on the liquid drop and the resisting force exerted by the liquid are shown in Fig. 2.

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[*] In this paper, energies and tensions for both surfaces and interfaces are considered to be numerically equal and interchangeable.

If a reaction occurs at the interface because the solid is undersaturated relative to a component in the liquid, the specific free energy of the reaction at the periphery -- dG_R per unit area -- contributes to the driving force for wetting. The driving force can be expressed as $\gamma_{sv} - (\gamma_{sl} + dG_R) \geqq \gamma_{lv} \cos\theta$. The magnitude of dG_R at a given instant is dependent on the rate of the reaction which is transient and thus dynamic in nature. With increase of the driving force for wetting, the contact angle decreases; and if the overall force exceeds the surface tension of the liquid, spreading occurs, i.e. the liquid surface and interfacial area continue to be extended as long as a supply of liquid is available. This effect can occur whether γ_{sv} is larger or smaller than γ_{lv}, i.e. whether the contact angle is acute or obtuse under chemical equilibrium conditions. If the reaction occurs only because the liquid is undersaturated relative to a component in the solid, the driving force for wetting of the solid is not increased and spreading thus does not occur. The magnitude of the contact angle, however, will be affected since the surface energy of the liquid will change with changes in its composition. The thermodynamic analysis of various cases has been reported.[1]

Another phenomenon that has been proposed as a contributing factor to wetting is the capillarity of grain boundaries due to surface etching or grooving. This suggestion was based on observations by Parker and Smoluchowski[11] of liquid metal movement along grain boundaries beyond the periphery of the liquid drop. Thermal grooving is the result of the formation of equilibrium dihedral angles along grain boundaries which can be observed in cross-section. The dihedral angles ($s_1/v/s_2$) can be quantified as $\gamma_{gb} = \gamma_{s_1 v} \cos\phi_1 + \gamma_{s_2 v} \cos\phi_2$ where $\phi_1 + \phi_2 = \phi$, the dihedral angle;

s_1 and s_2 refer to grains of same composition but of different orientation. In contact with liquid the dihedral angles $(s_1/l/s_2)$ can be smaller and deeper if $\gamma_{sl} < \gamma_{sv}$ and γ_{gb} is unchanged.

III. EXPERIMENTAL PROCEDURE

A. Materials

The starting metals were oxygen-free high conductivity (OFHC) Cu of 99.99% purity obtained from Alascan Brass and Copper Company and Ag shot of 99.99% purity obtained from Apache Chemical Company. The Cu and Ag substrates were approximately 1 mm thick and were cut into 12 x 12 mm squares from cold-rolled metals. The alloy substrates were prepared from the same metals.

Charges of about 50 grams of each alloy were weighed, placed in a graphite crucible, and covered with a graphite lid. The graphite crucible reduced the oxygen partial pressure so that neither silver nor copper oxidized during alloy preparation. The graphite lid minimized the vaporization of the alloys. The alloys were melted in a tantalum resistance heating furnace* under gettered helium.

Each charge was first heated to 1200°C and held for 30 minutes, cooled to and held at 1100°C for one hour, quenched to 775°C ($\pm$ 1°) in a few seconds and held for 24 or 100 hours, and quenched to room temperature. Holding the charges at 775°C ensured equilibrium in the solid substrates and grain growth. Alloys equilibrated at 775°C for 24 hours were cold-rolled to about 2 mm thickness, and substrates of 12 x 12 mm were cut from the rolled ingots. Alloys equilibrated for 100 hours were used in the as-cast form for most of the wetting studies.

All substrates were polished on a set of diamond wheels and finally given a high polish on a lap wheel with 0.3 micron alumina. The substrates

*Richard D. Brew and Co., Inc., Concord, N.H.; Model 4665-4.

were ultrasonically cleaned in acetone, ethyl alcohol, and distilled water.

The liquid drop compositions were prepared from the same starting materials. Approximately 30 gram charges were melted under gettered helium in the BREW furnace at 1200°C for half an hour and quenched to room temperature. The "Drops" were cut using a diamond saw from as-cast ingots in the form of disks with 1.0 mm thickness and 5.0 mm diameter, and from cold-rolled pieces in the form of cubes of 1.5 x 3 x 3 mm size. The cut specimens were ultrasonically cleaned in acetone, ethyl alcohol, and distilled water.

B. Experimental Equipment

All experiments were run in a furnace consisting of a graphite tube resistance heating element.[12] The presence of carbon establishes a level of P_{O_2} below the dissociation pressure for both copper and silver oxide. The furnace was inside a large vacuum chamber that had a vacuum capability of 1×10^{-4} Pa. The temperature in the furnace was measured with two calibrated Pt-Pt 10% Rh thermocouples with an accuracy of $\pm$ 2°C. The contact angles were measured through a porthole in the vacuum chamber by a telegoniometer. A camera was attached to the telegoniometer through which pictures of the substrates and drops were taken. A leak valve on the vacuum chamber allowed gettered helium to be introduced into the furnace.

C. Experimental Run

For each experiment a substrate and a drop were placed on the alumina D-tube and situated in the center of the furnace. Before heating to the experimental temperature, the vacuum chamber was pumped to less than 10 torr, flushed with helium, and then pumped with a cold-trapped diffusion

pump to less than 1 x 10^{-4} Pa.   The chamber was then filled with helium slightly below atmospheric pressure.

For the experiments at ∿782°C the temperature was increased in 1 hour to 775°C and then slowly (1°/min) until the eutectic drop melted. As soon as the melting started the furnace temperature was held constant. For experiments at 900°C, the temperature was increased from 775°C to 900°C in 10 minutes. All samples were held at the test temperature for 5 minutes and furnace-cooled.

D. Sample Examination

The surface of the substrates, particularly at the drop edge, were examined with a metallographic microscope. The substrates were cut with a diamond saw perpendicular to the substrate-drop interface. The sectioned substrate was mounted in bakelite. The cross-sections were polished on a set of diamond wheels on a lap wheel with 0.3 micron alumina and finally with 0.05 micron alumina. A mixture of 1 part H_2O_2 (3%), 1 part NH_4OH (58%) and 1 part distilled water was used to etch the samples. Etching time varied with the sample but was about 15 seconds. The interfaces were examined with a metallograph and with a scanning electron microscope. X-ray line scans were made with an EDAX unit on the scanning electron microscope.

IV. RESULTS AND DISCUSSION

A. Eutectic Liquid on Cu-Solidus and Cu

Slightly above the eutectic temperature, ∿782°C, an eutectic liquid drop on a Cu substrate spread rapidly. On Cu-solidus specimens the liquid formed acute contact angles of 2 to 19° depending on the thermal and mechanical treatment of the solidus, which will be discussed later. The

of the substrate is thus a result of both the liquid around the periphery and the substrate attempting to reach equilibrium compositions within the system.

C. Eutectic Liquid on Ag-Solidus and Ag

At ∿782°C, the eutectic liquid on Ag-solidus showed an acute contact angle of 40-50° (Fig. 9) which corresponded to a reduction of the surface energy of the solid by the liquid by an amount equivalent to 0.77 to 0.64 of the surface energy of the liquid. The figure also shows that the interface is flat and continuous with the surface of the substrate indicating no reaction. On Ag, spreading occurred rapidly because of solution of Cu from the eutectic liquid by the Ag substrate.

D. Grain Boundary Effect on Wetting and Spreading

Sessile drop experiments ideally should be performed on single crystal substrates to avoid complications introduced by grain boundaries. Single crystals of Cu-solidus and Ag-solidus compositions, however, are extremely difficult, if not impossible, to grow. It thus becomes necessary to interpret experiments with polycrystalline substrates properly.

Micrographs of Cu and Cu-solidus substrate surfaces adjacent to the edges of the eutectic liquid drops at ∿782°C are shown in Fig. 10. On Cu, spreading has occurred across the grains with the grain boundaries playing no significant role indicating that the spread of liquid due to the reaction was faster than any contribution due to capillary flow that may occur along grain boundaries; a greater grain boundary effect was observed at 900°C. This behavior was the same on Ag. On the Cu-solidus specimen, the liquid moved ahead of the main drop along grain boundaries; this effect was more pronounced at 900°C. On Ag-solidus, however, this movement along grain

boundaries was not apparent.

Grain boundary grooving providing a means for capillary flow, which has been proposed as an explanation for movement of liquid along grain boundaries, does not appear to be consistent on comparing the experimental observations with Cu-solidus and Ag-solidus. Another factor is changes in composition along the grain boundaries of the solid solutions resulting from some expulsion of Ag from the grains of the Cu-solidus and Cu from the grains of Ag-solidus due to crossing two-phase fields on cooling from and heating to the test temperatures (Fig. 1). Microstructure studies of the Ag-Cu system[13] indicate that in hypereutectic alloys the primary Cu-rich phase is not continuous with the Cu phase in the eutectic structure, and in hypoeutectic alloys the primary Ag-rich phase is continuous with the Ag phase in the eutectic structure. It can then be concluded that if complete homogeneity is not attained in the Cu-solidus substrates, the grain boundaries would have a continuous nonequilibrium Ag-enriched structure relative to the bulk; in the case of the Ag-solidus substrates, the enrichment of the grain boundaries with Cu would not be continuous. These structures would be consistent with the observations of liquid moving along grain boundaries of the Cu-solidus but not of the Ag-solidus, the exsolved material being unsaturated and thus reactive with a component of the liquid.

Efforts were made to prepare 780°C Cu-solidus substrate specimens with large grains and complete homogeneity by various heat treatments. These treatments resulted in the reported range of contact angles formed with the eutectic liquid on Cu-solidus. The largest contact angle of 19° was obtained with the most homogeneous substrate which had grains about

1 cm in size and which showed the least movement of liquid along grain boundaries. The existence of a tendency for movement or spreading along unsaturated grain boundaries undoubtedly contributes to the smaller contact angles.

Another factor which appears to affect the experimental contact angle is mechanical treatment of the Cu-solidus. Cold-rolled specimens consistently showed smaller contact angles ($\sim 2°$) than as-cast specimens ($\sim 12°$), with the liquid and conditions of the experiments kept constant. A suggested reason for this difference is the difference in grain size since the cold-rolled specimens showed a smaller grain size, i.e. about 20 μm.

V. CONCLUSIONS

The sessile drop experiments in the Ag-Cu system support the generalization that the use of solids and liquids in chemical equilibrium in metal systems results in wetting or the formation of an acute contact angle but no spreading, i.e. the surface energy of the solid is greater than that of the liquid but the driving force for wetting does not exceed the surface energy of the liquid. Specifically, the driving force for wetting of the Cu-solidus by the eutectic liquid is greater than that of the Ag-solidus. With a constant liquid surface energy in parallel experiments and an assumption that the interfacial energies are essentially the same, it can be postulated that the surface energy of Cu-solidus is greater than that of Ag-solidus. The only reported values[14] at 950°C are for Cu, 1.775 N/m^2 and for Ag, 1.1 N/m^2; and for the eutectic composition at 1000°C, 0.93 N/m^2. Another experimental observation for these cases is that no mass distribution occurs, as indicated in Fig. 2, i.e., the interfaces remain flat and are

continuous with the surfaces of the substrates.

When the sessile drop phases are not in chemical equilibrium, solution reactions occur. If the substrate is undersaturated relative to a component in the liquid, the specific free energy of the reaction contribution to the driving force for wetting in most cases is large enough to cause spreading. If only the liquid is undersaturated relative to a component in the substrate, no increase occurs in the driving force for wetting, i.e. spreading forces exerted by the solid on the liquid. In both cases, however, a mass redistribution occurs and the interface does not remain flat and continuous with the substrate surface. For example, the eutectic liquid on Cu-solidus at 900°C causes a lenticular depression by dissolving sufficient substrate to reach the equilibrium Cu-liquidus composition (Fig. 5).

Development of nonhomogeneity in the Cu-solidus with grain boundaries attaining continuous nonequilibrium compositions results in some movement or spreading of liquid along the grain boundaries ahead of the liquid drop and in a contribution to the driving force for wetting. This appearance can be misinterpreted as primarily capillary movement of liquid along thermally grooved grain boundaries.

This study indicates the importance of controlling the conditions of the sessile drop experiment and of careful preparation of specimens. Cross-sections should be made and analyzed to determine the details of any reactions that may have been occurring during the experiment. That is, careful characterization must be applied to the specimen assemblies, especially in the possible presence of inhomogeneities, in order to fully understand and avoid misinterpretations of "simple" sessile drop experiments.

VII. ACKNOWLEDGMENTS

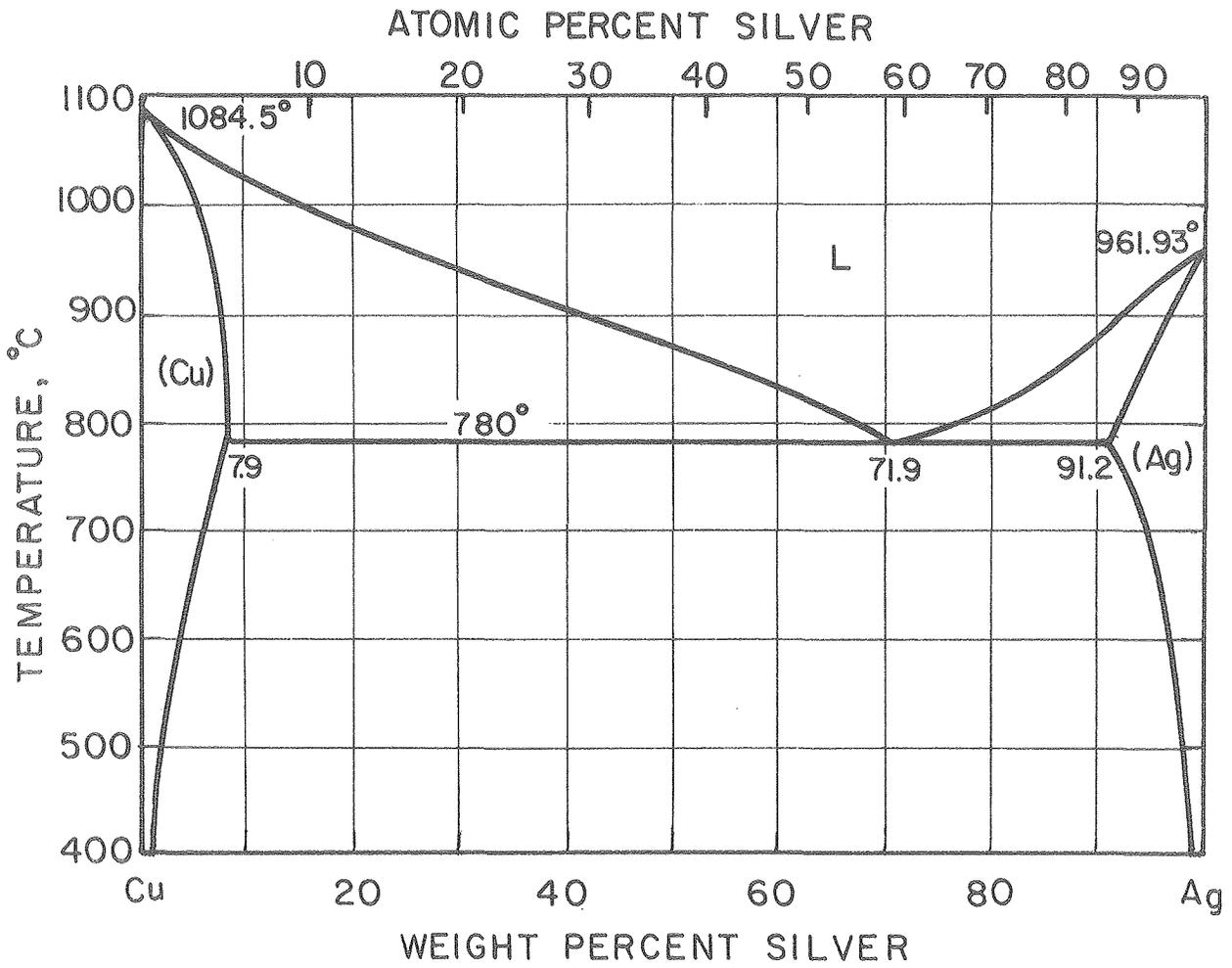# REFERENCES

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FIGURE CAPTIONS

Fig. 1.   Cu-Ag equilibrium phase diagram.

Fig. 2.   Schematic of sessile drop interfacial forces.

Fig. 3.   Eutectic liquid at ~782°C on a) Cu and on b) Cu-solidus.

Fig. 4.   EDAX traces across interfaces of Fig. 3 at higher magnifications
          (eutectic to the right).

Fig. 5.   Eutectic liquid at 900°C on a) Cu and b) Cu-solidus.

Fig. 6.   EDAX traces across interfaces of Fig. 5 at higher magnifications
          (eutectic to right).

Fig. 7.   Cu-liquidus for 900°C held on Cu-solidus at ~782°C for 10 seconds.

Fig. 8.   Cu-liquidus on Cu-solidus at 900°C.

Fig. 9.   Eutectic liquid at ~782°C on Ag-solidus.

Fig. 10. Micrographs of surfaces adjacent to eutectic liquid drops at ~782°C
          on substrates a) Cu and b) Cu-solidus. The drop in both photos is
          in lower left.
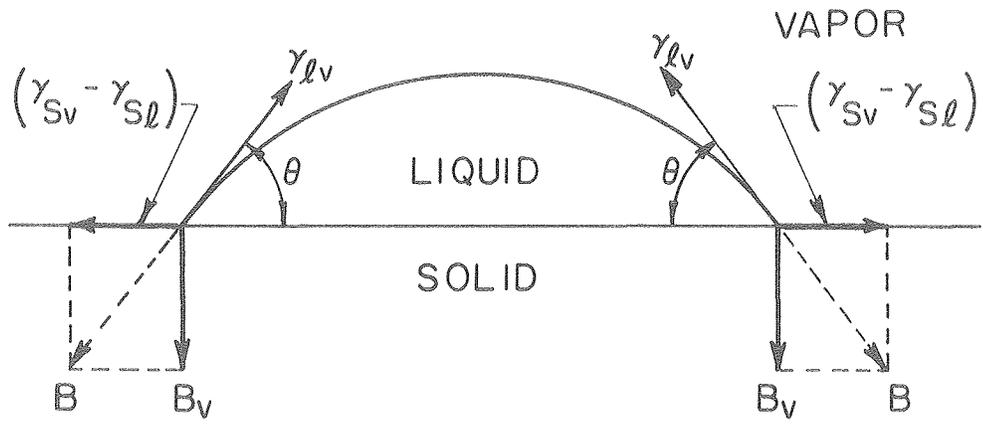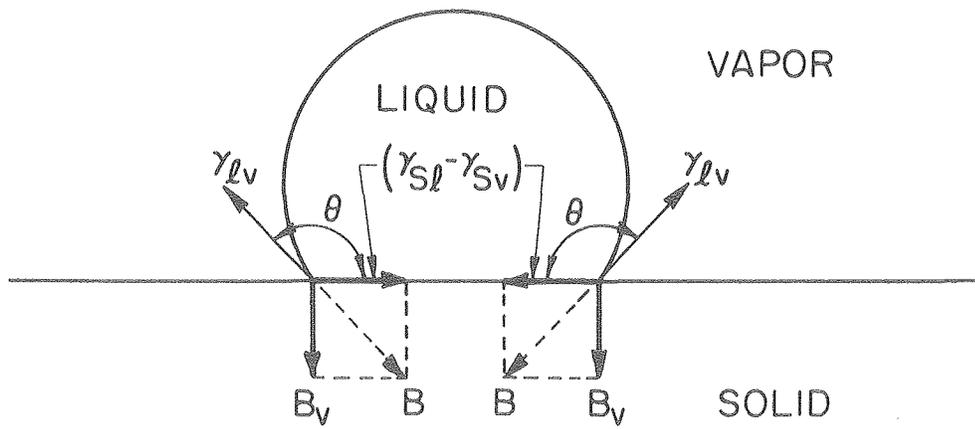
ATOMIC PERCENT SILVER

Fig. 1

XBL 7811-6108

(a)

(b)

XBL 738-1699

Fig. 2

A

1 mm

B

L mm

XBB807 8509

Fig. 3

Fig. 4

A

1mm

B

1mm

XBB807 8510

Fig. 5

Ag

A

10 μm

Ag
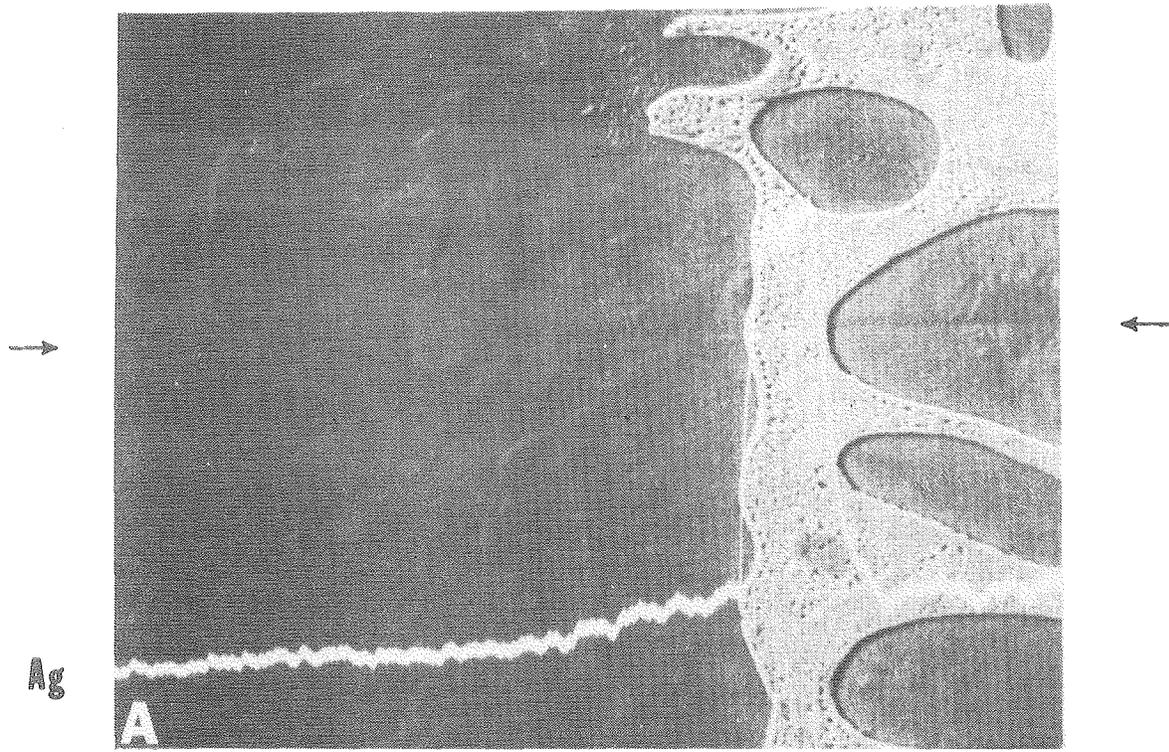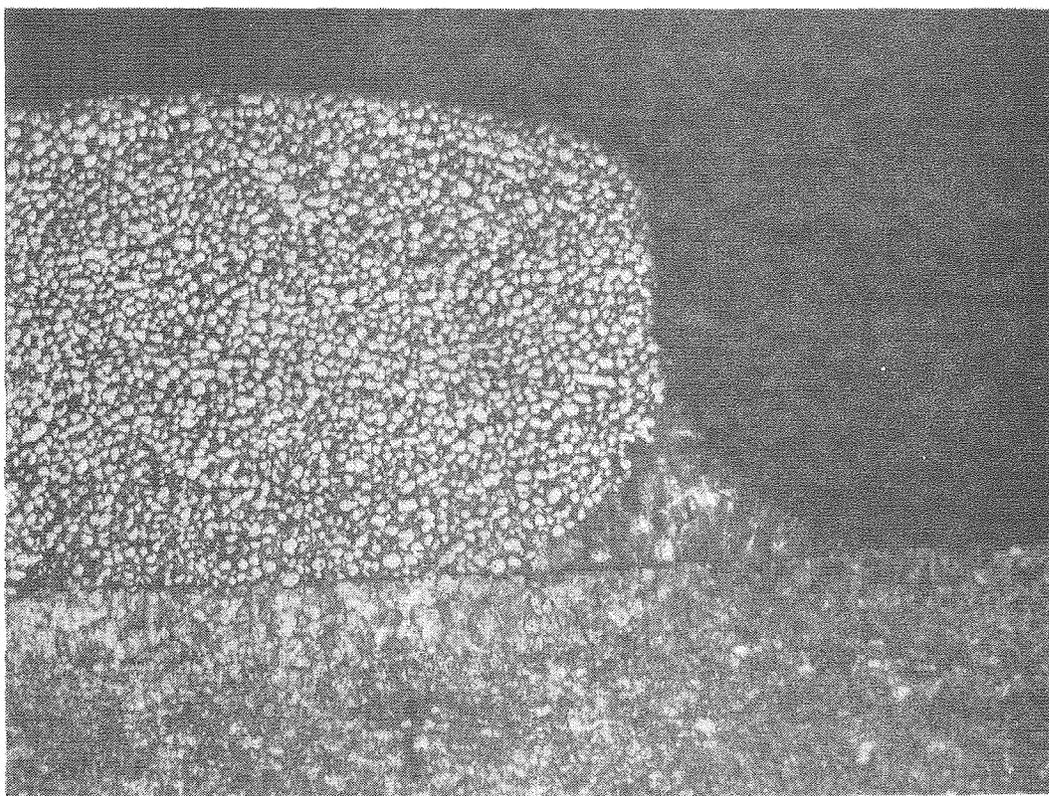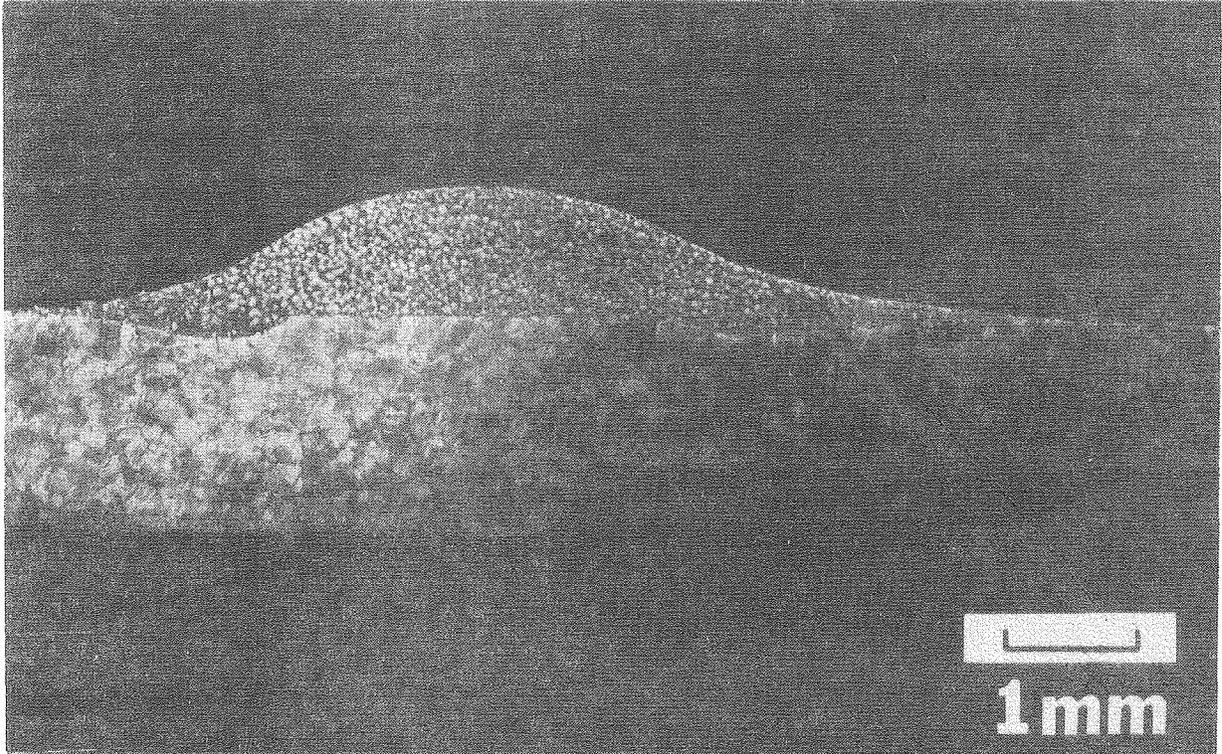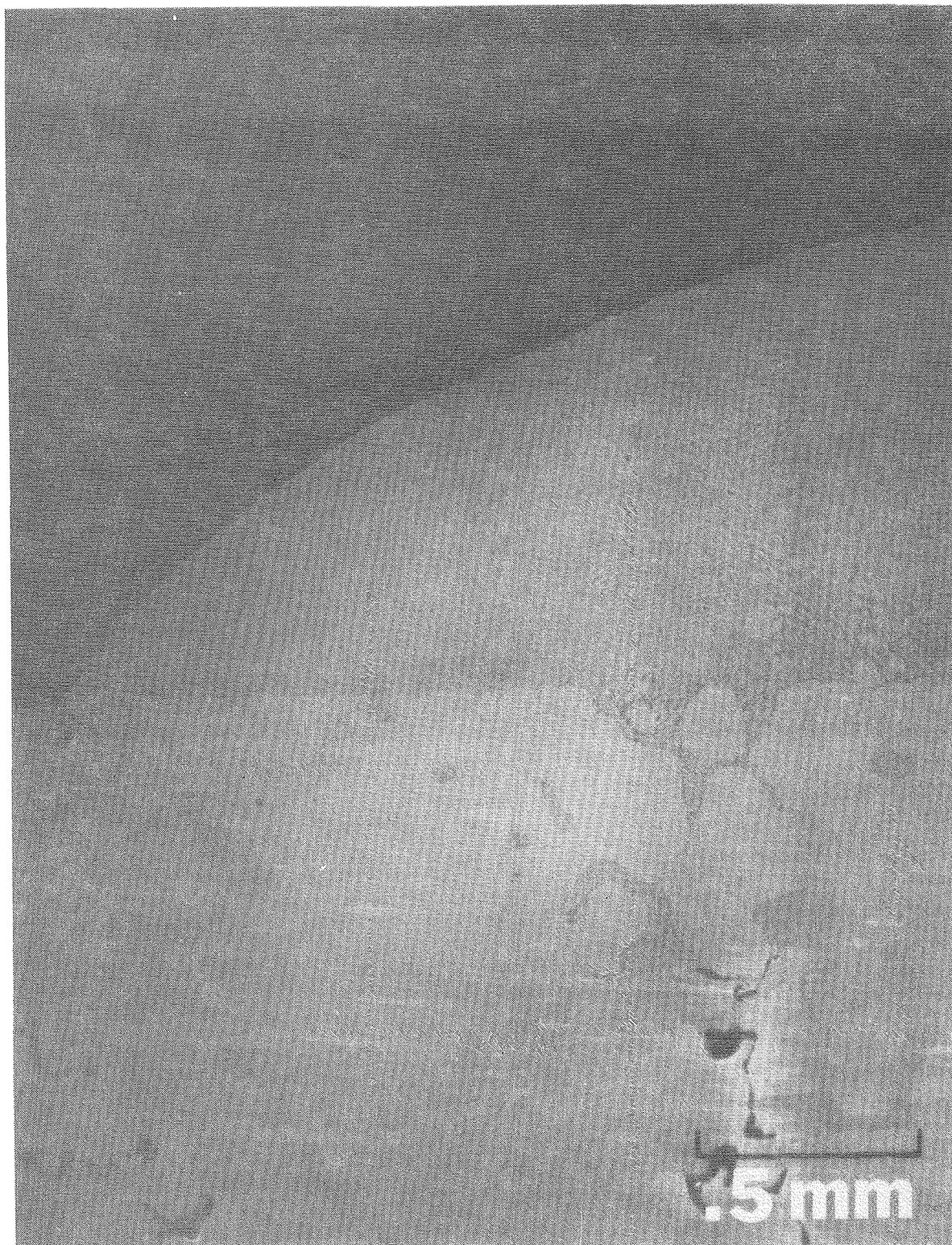
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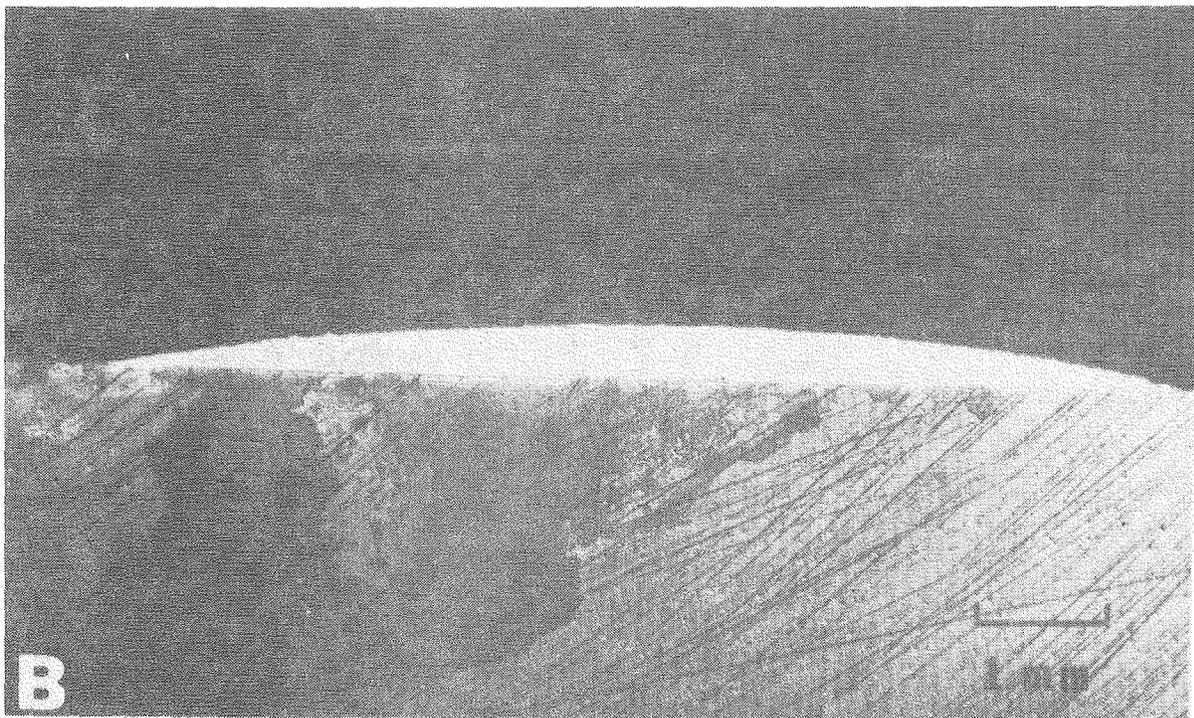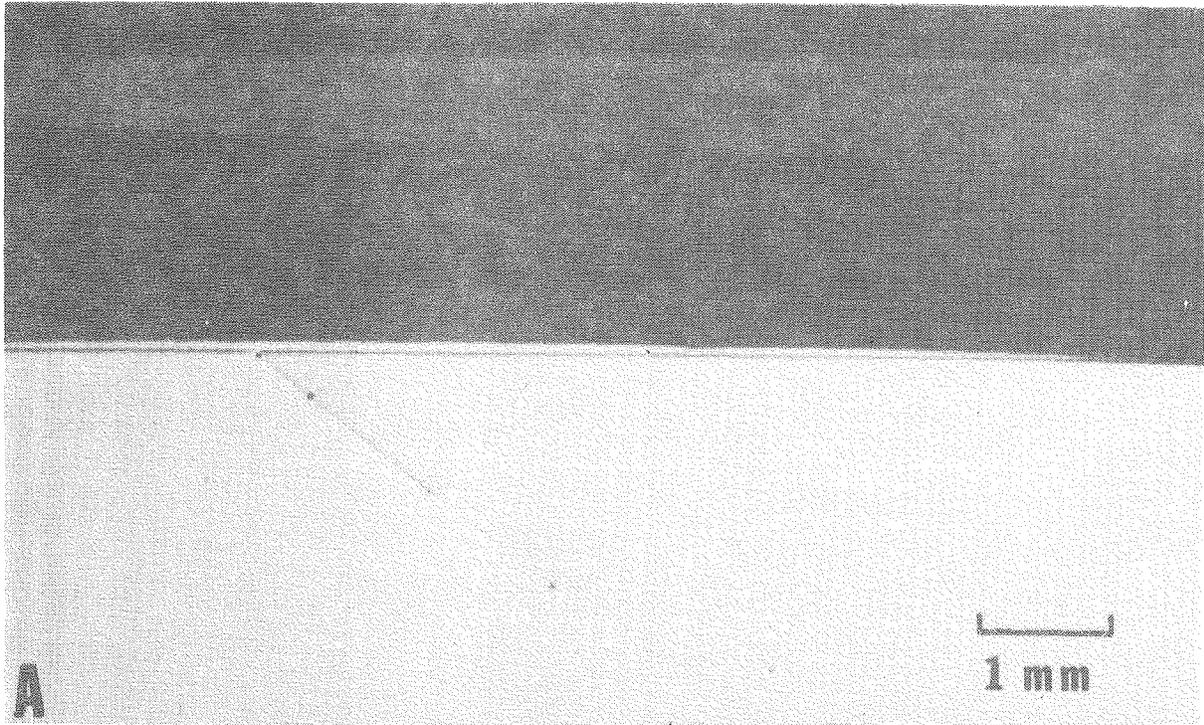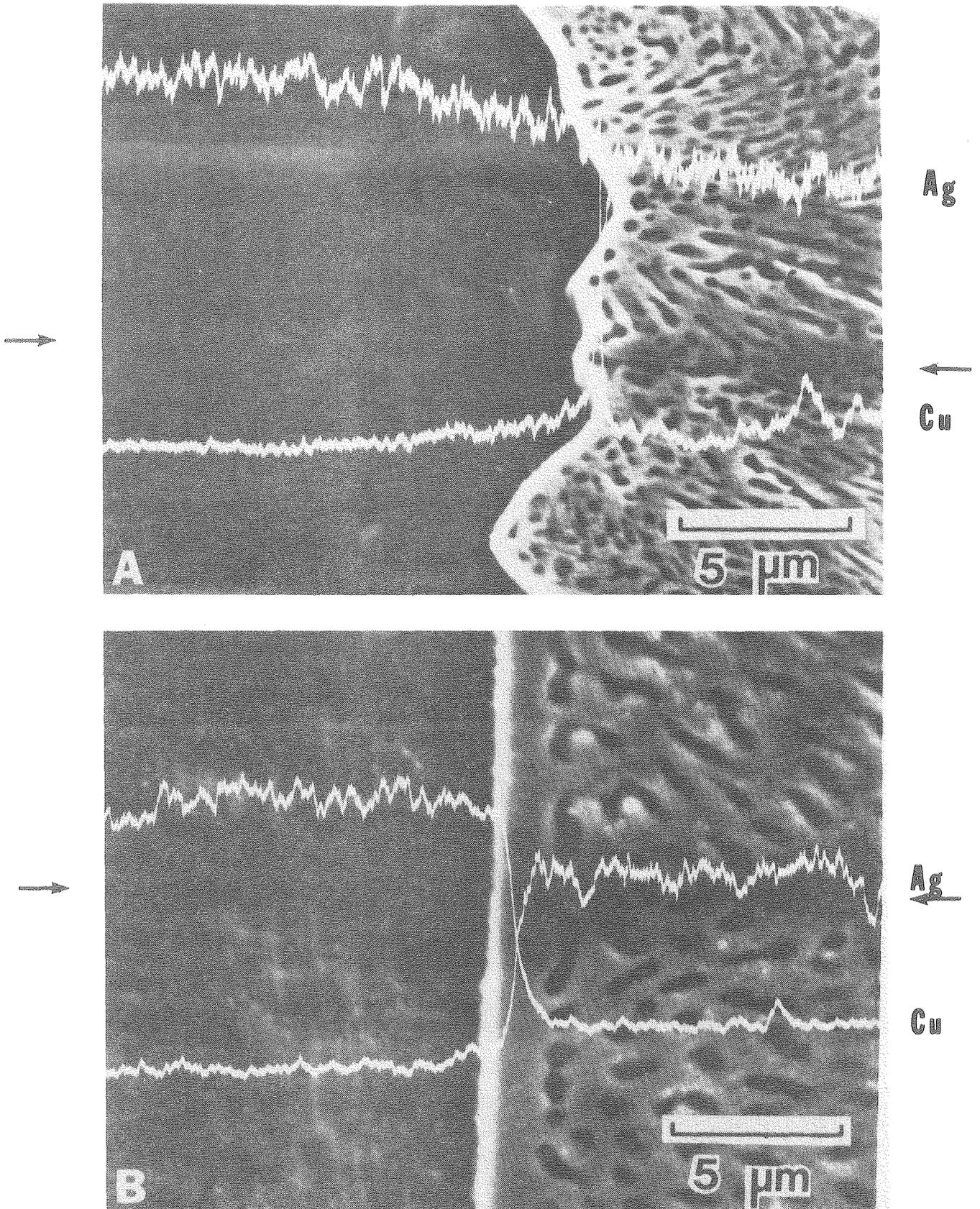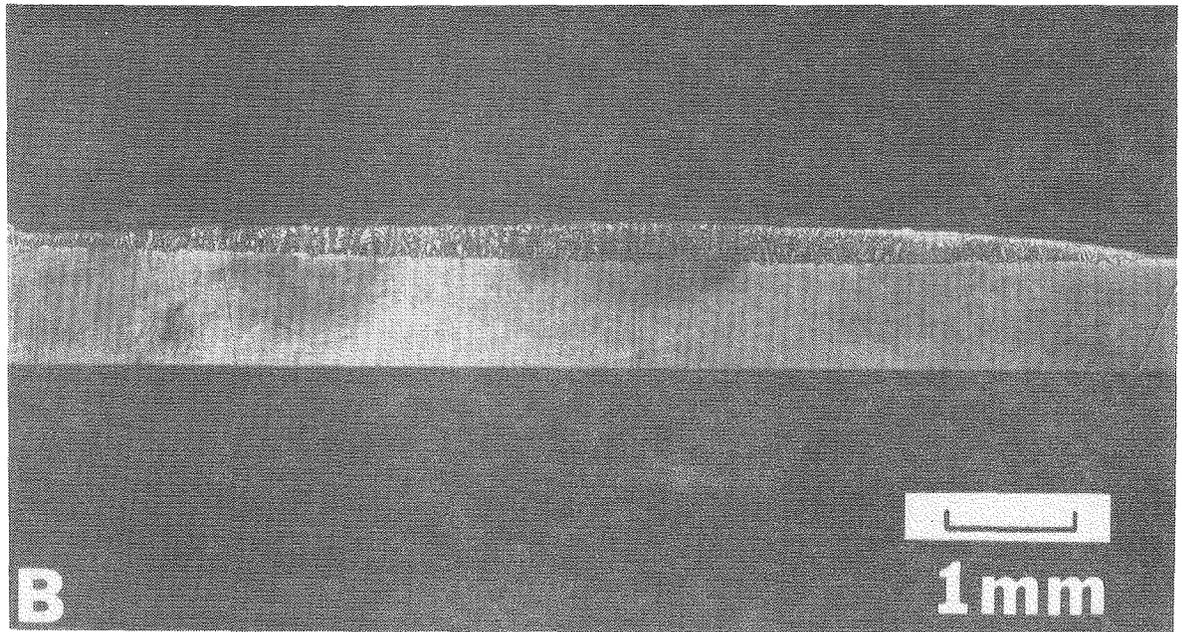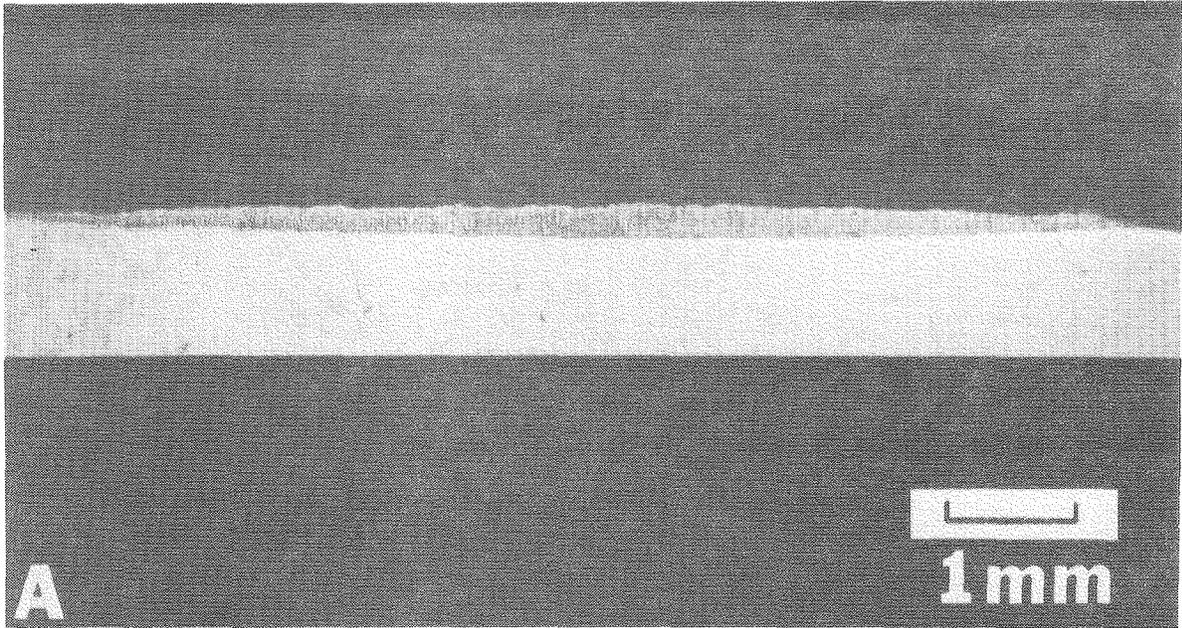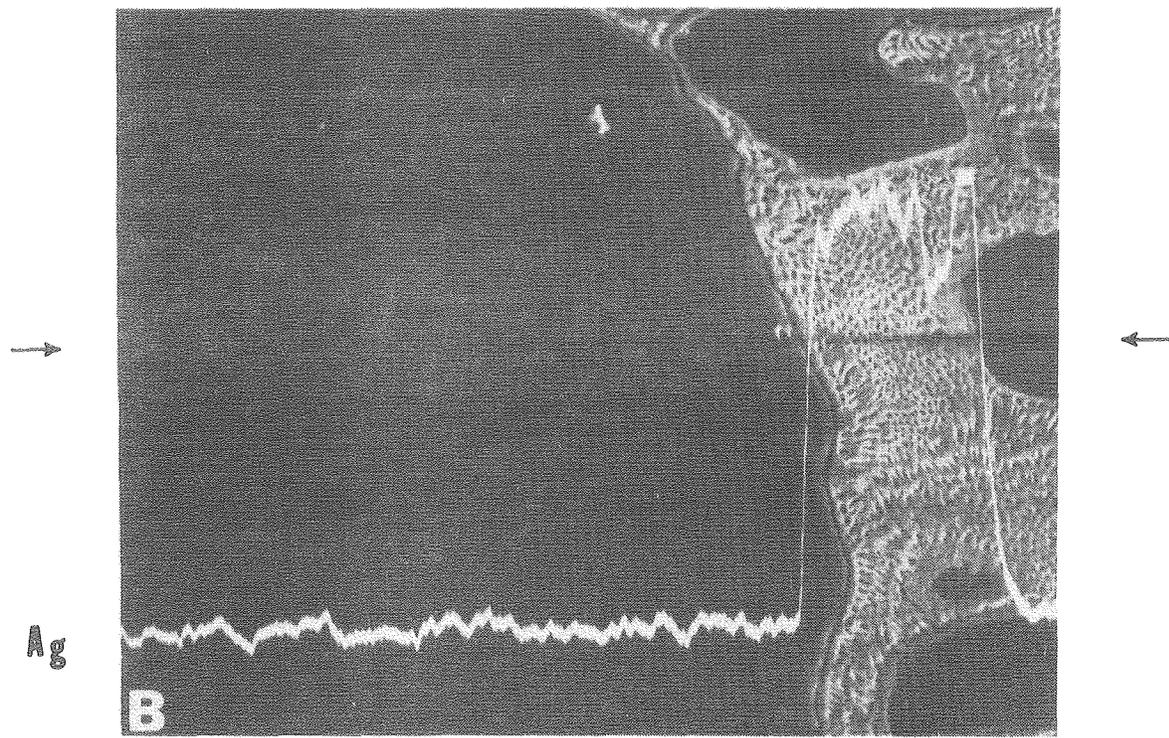
10 μm

XBB807 8506

Fig. 6
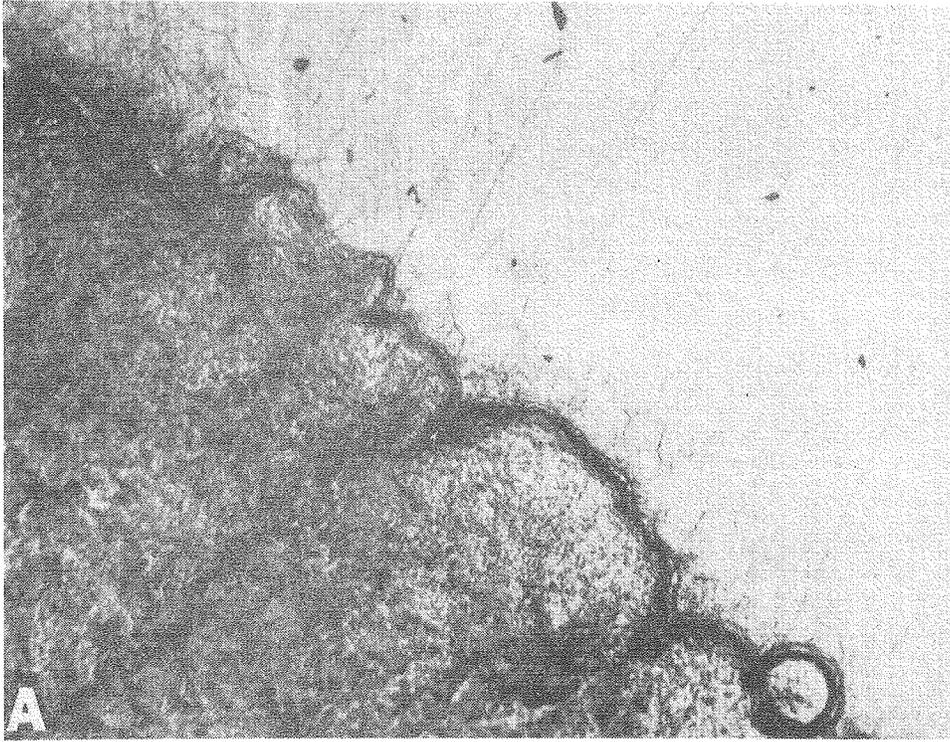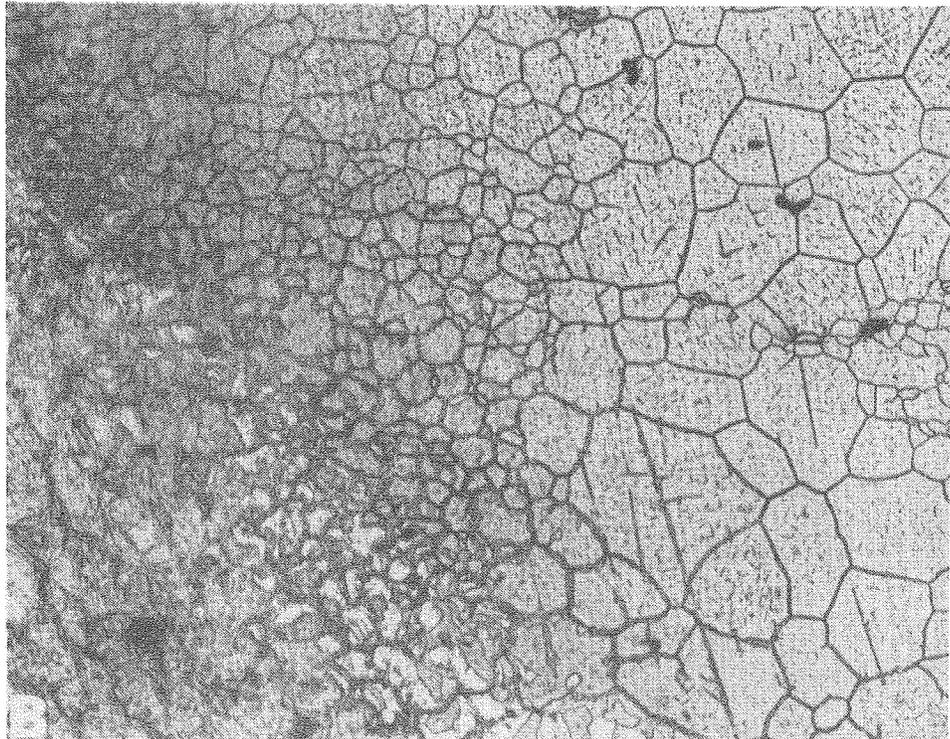
.5 mm

XBB807 8507

Fig. 7

XBB812-1662

Fig. 8

XBB807 8511

Fig. 9

100 μm

100 μm

Fig. 10

XBB807 8504