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REACTIONS AND SPREADING IN THE Cu-Ag SYSTEM

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(M. S. thesis)

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REACTIONS AND SPREADING IN THE Cu-Ag SYSTEM

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REACTIONS AND SPREADING IN THE Cu-Ag SYSTEM

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ABSTRACT

Sessile drop experiments were conducted using several liquid and solid compositions selected from the copper-silver phase diagram. Reactions between the solid and the liquid are considered to lead to spreading; a number of chemical nonequilibrium conditions were thus established using the various compositions. The copper liquidus drop on the copper solidus at 900°C was in equilibrium assuming that the drop did not melt so as to form two phases. The eutectic liquid on the copper solidus at 780°C was also in equilibrium. The copper liquidus on pure copper at 900°C and the eutectic liquid on pure copper at 780°C were cases of the solid being unsaturated with a component of the liquid. The eutectic liquid on the copper solidus at 900°C was a case of the liquid being unsaturated with a component of the solid. The eutectic liquid on pure copper at 900°C was a case of both the liquid and the solid being unsaturated with a component of the other phase. Only in the case of eutectic liquid on pure copper at 780°C was the spreading solely attributed to a reaction, that being the diffusion of silver into the substrate. The case of the eutectic liquid on copper solidus at 780°C revealed that while the bulk phases were in chemical equilibrium spreading still occurred due to capillary flow along grain boundary grooves. Spreading occurred in the cases of eutectic liquid on pure copper and on copper solidus in the experiments at 900°C due both to reactions and to grain

boundaries. The liquidus drops on both the pure copper and the copper solidus in the experiments at 900°C were bell-shaped due to the disproportionation of the drops into two phases on being heated to experimental temperature with subsequent flow of the liquid to the drop edge.

INTRODUCTION

A basic understanding of the interfaces between solids and liquids is important in the development of metal-metal and metal-ceramic seals, in the liquid phase sintering of materials, and in the development of composites. In these applications it is important to know the conditions leading to different types of interfaces and the factors that affect the distribution of phases, one being a liquid.

Sessile drop experiments have been widely used to study solid-liquid interfaces. Normally, the interfaces are considered in systems that are in chemical equilibrium, with the final configuration resulting in an equilibrium contact angle due to the reduction of the total interfacial energy to a minimum. However, reactions between the solid and the liquid are considered to lower the interfacial energy, hence the contact angle, and in most cases lead to spreading.[1,2]

Many investigators have observed decreasing contact angles due to 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 behavior with the ensuing reactions. The copper-silver system was chosen for the investigation because copper and silver were relatively easy to work with and the various nonequilibria were easily established. The results were compared with a theoretical understanding of solid-liquid interfaces under chemical equilibrium and non-equilibrium conditions.

THEORY

Thermodynamic equilibrium determines the exact configuration of a liquid drop resting on a solid. The solid-liquid-vapor point of a sessile drop (Fig.1) is described by Young's equation,

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \qquad (1)$$

where γ_{sv} is the solid-vapor interfacial tension, γ_{sl} is the solid-liquid interfacial tension, γ_{lv} is the liquid-vapor interfacial tension, and θ is the contact angle measured through the liquid. Young's equation has been derived by several methods, all of which assume chemical equilibrium.[10-12] When $\gamma_{sv} > \gamma_{sl}$, then $\theta < 90°$, and the liquid wets the solid. When $\gamma_{sl} > \gamma_{sv}$, then $\theta > 90°$, and the liquid does not wet the solid. The liquid spreads over the solid when $\theta = 0°$. If the system is not at mechanical equilibrium, the contact angle will adjust so that equilibrium is reached.

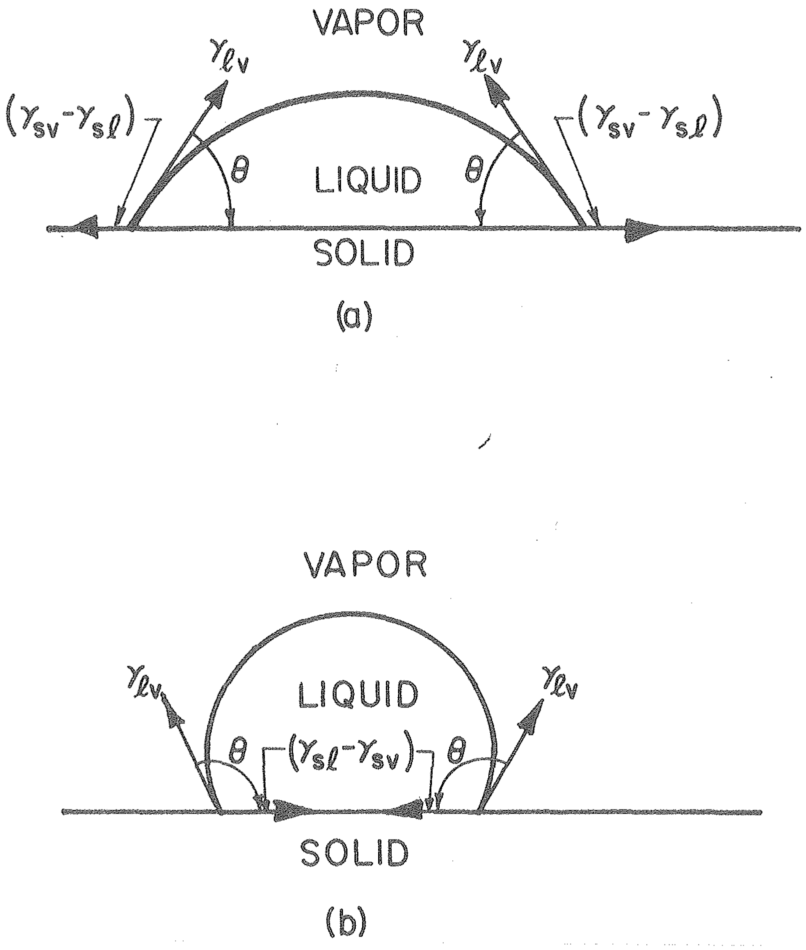

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Fig. 1. Schematic of a sessile drop
(a) $\theta < 90°$, the liquid wets the solid.
(b) $\theta > 90°$, the liquid does not wet the solid.

Reactions occur at the interfaces when the various phases are not in chemical equilibrium, and Aksay, Hoge, and Pask[13] have developed a theoretical model describing the behavior of a liquid on a solid under such conditions. Nonequilibrium conditions between the solid and liquid were considered, and the solid-vapor and the liquid-vapor interfaces were either assumed to be in equilibrium or the kinetics of the reactions were assumed to be relatively slow. Care must be taken in experiments with materials of high vapor pressure so that this assumption is valid.

Although reactions involve the transport of mass from one phase to another to change bulk compositions, initially only the interface is involved. The initial decrease in the free energy of the system is attributed to a decrease (Δg_{sl}) in the free energy at the interface.[14] (Δg_{sl}) is equal to the free energy change of the reaction divided by the area over which the reaction occurs. The interfacial tension is related to the interfacial free energy according to

$$\gamma_{sl} = g_{sl} - \sum_i \mu_i^{sl} \Gamma_i \qquad (2)$$

where g_{sl} is the solid-liquid interfacial free energy, μ_i^{sl} is the chemical potential of component i at the solid-liquid interface, and Γ_i is the excess concentration of component i at the interface. The last term in Eq.(2) will only be important in cases of adsorption, where no mass is transferred between phases. Thus, the interfacial tension will also be reduced by (Δg_{sl}) due to the reaction.[15]

For reactions proceeding by diffusion, the reacting component in one phase will start diffusing into the unreacted phase. A concentration gradient is established from the interface into the bulk of the unsaturated phase, and the concentration at the interface approaches equilibrium. The driving force for the reaction at the interface will decrease, and the free energy change per unit time will also decrease. According to theory,[16] g_{sl} goes through a minimum and then increases until an equilibrium value for the static interface is reached. The interfacial tension correspondingly changes. After an initial decrease it will increase until a value for the reacted phases is reached (Fig. 2).

Three types of nonequilibrium are considered in the theoretical model. They are: (i) when the solid is not saturated with a component of the liquid; (ii) when the liquid is not saturated with a component of the solid; and (iii) when neither phase is saturated with respect to the other.

In type (i) nonequilibrium the component in the liquid not saturated in the solid diffuses across the interface and into the bulk. Different configurations result, depending on the kinetics of the reaction (Fig. 3). If the diffusing rate of the reacting component is such that the reaction zone in the solid moves ahead of the liquid, the liquid will be in contact with solid saturated with the component (Path ab'c'd Fig. 3). Both γ_{sl} and γ_{sv} will be reduced by approximately the same amount (Δg_{sl}), and according to Eq.(1), the contact angle will vary only slightly. The final angle will depend on the equilibrium interfacial tensions of the reacted phases. If the diffusing rate of the reacting component is such that the liquid is always in contact with unsaturated solid, path abcd will result. γ_{sl} decreases while γ_{sv} remains unchanged, and hence the contact angle will decrease. Spreading occurs (a contact angle of 0°) if the reduction in γ_{sl} is large enough. Otherwise, the

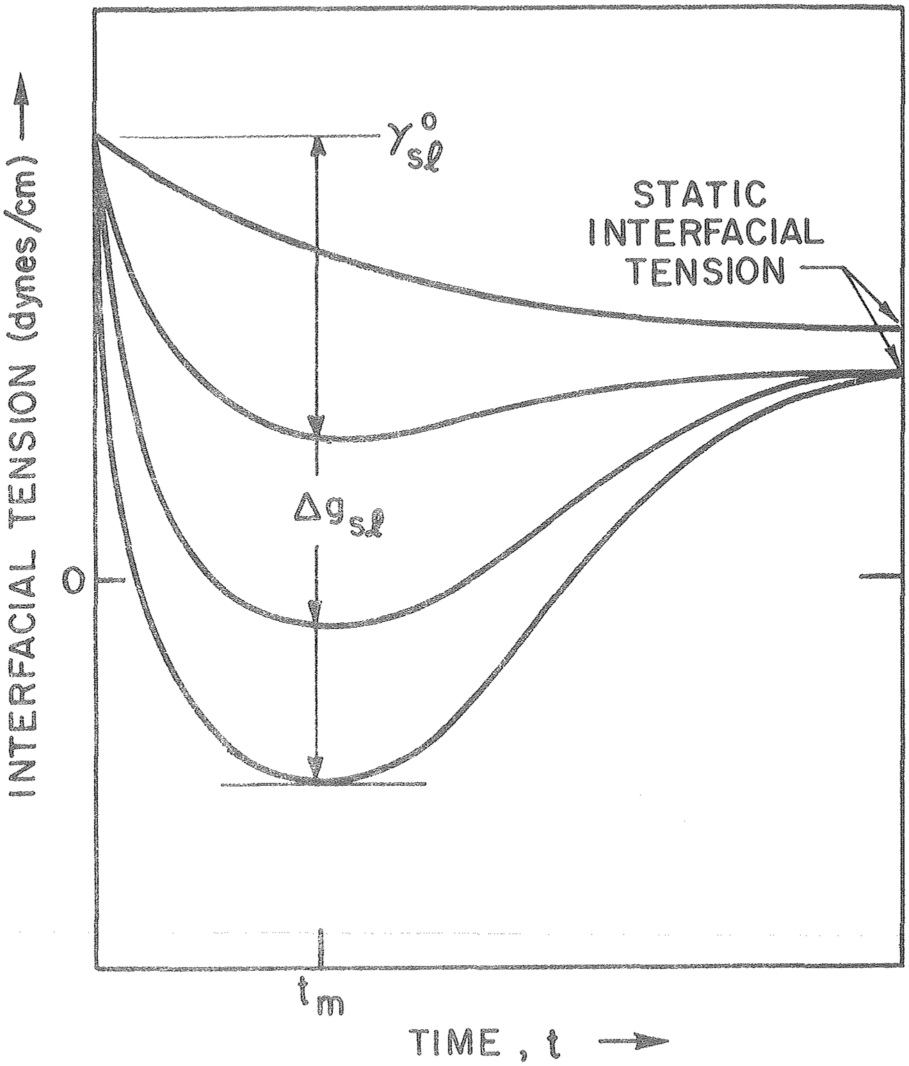

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Fig. 2. Variation of the interfacial tension with time for a reaction at the interface. The top line is for adsorption with no reaction occurring.

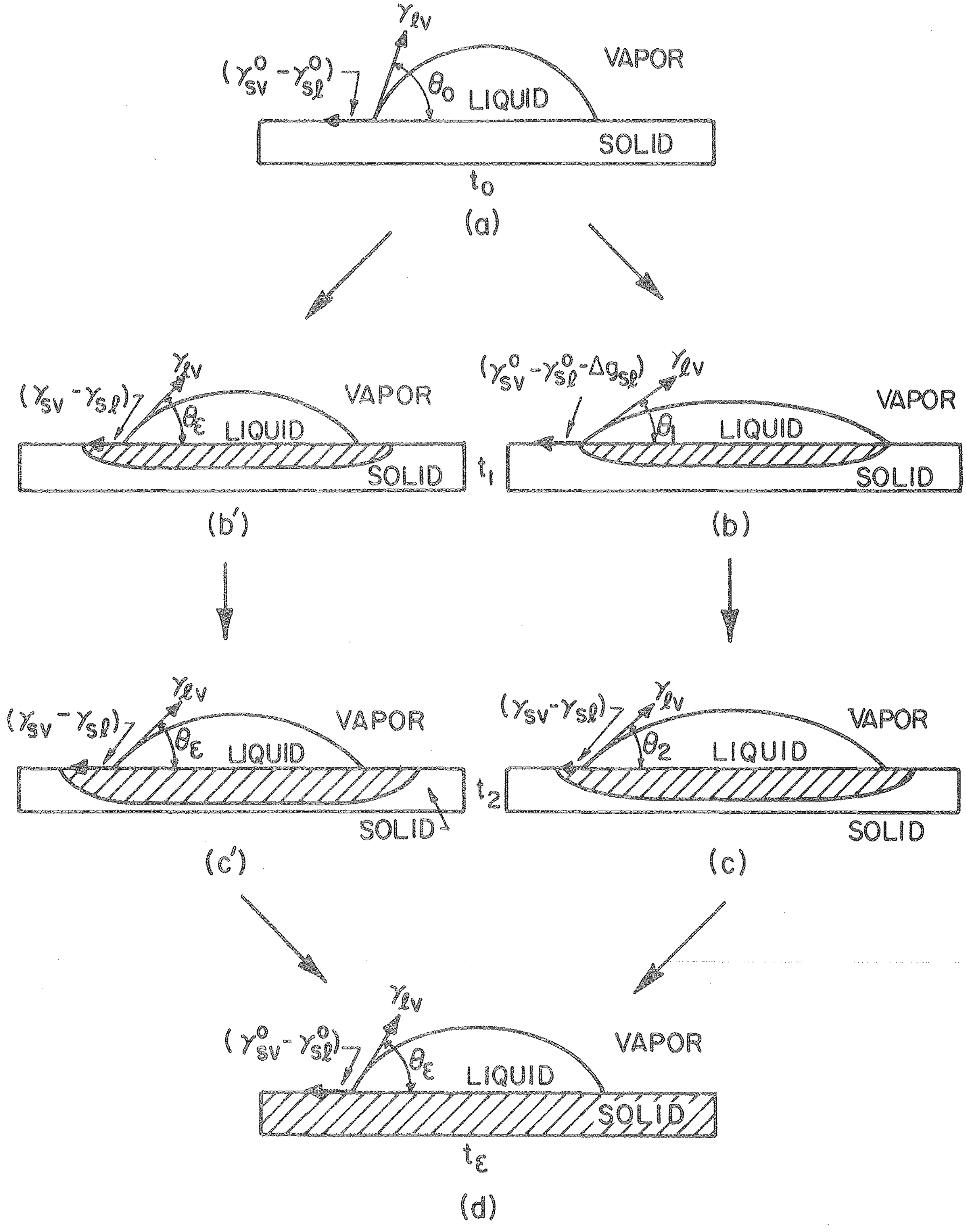

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Fig. 3. Various configurations resulting when the solid is unsaturated with a component of the liquid. Path ab'c'd results when the reaction zone moves ahead of the liquid. Path abcd results when the liquid initially moves ahead of the reaction zone.

contact angle goes through a minimum corresponding to the minimum in the interfacial tension as shown in Fig. 2. At the minimum point in the contact angle the reacting component in the solid can move ahead of the liquid (Fig. 3c) and the liquid will eventually be in contact with completely reacted solid (Fig. 3d). The equilibrium contact angle occurs when the equilibrium interfacial tensions of the reacted phases are reached.

In type (ii) nonequilibrium, two types of reactions may occur. The first type occurs when the reacting component of the solid diffuses into the liquid, and the substrate remains essentially flat (Fig. 4). The contact angle will decrease as reaction initiates, and if the free energy of reaction is large enough, spreading will occur. If spreading does not occur, the contact angle will go through a minimum as in case (i) path abcd. The liquid at the drop periphery becomes saturated. A second type of reaction occurs if the unsaturated component of the liquid is a major component in the solid. Then the liquid will dissolve the substrate, and the dissolved species will diffuse throughout the liquid. The substrate will not remain flat, and the configuration will be similar to Fig. 4 except that the substrate will be concave beneath the drop. Young's equation cannot be applied. However, the liquid will still "spread" if the free energy change of the reaction is large enough and if the depression in the substrate is not too deep. If "spreading" does not occur, the "contact angle" goes through a minimum before equilibrium is reached.

Type (iii) nonequilibrium will be a combination of types (i) and (ii). The tendency for spreading will increase because the free energy

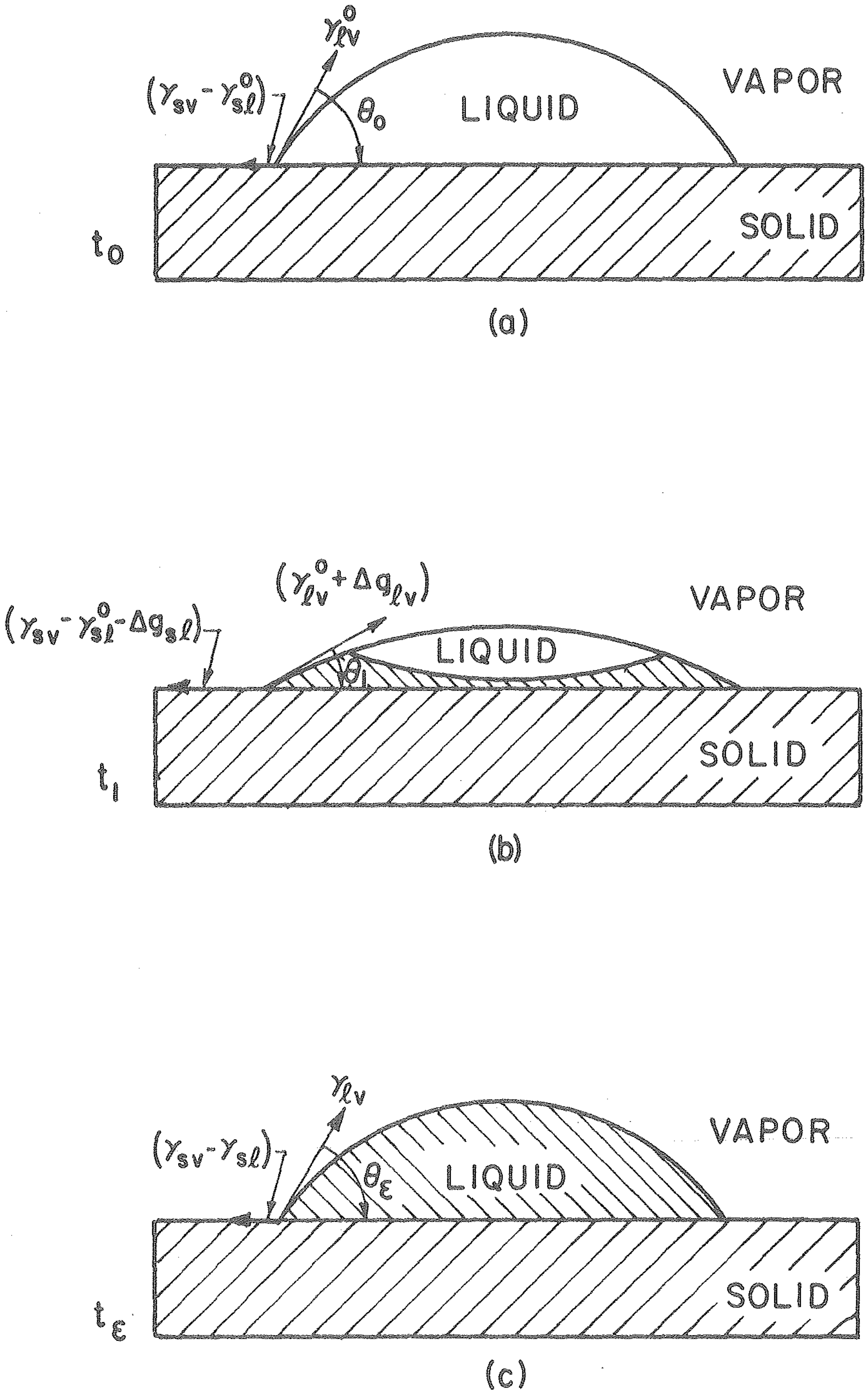

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Fig. 4. Configuration resulting when the liquid is unsaturated with a component of the solid and the component diffuses into the liquid. The substrate remains essentially flat.

of reaction will be larger than in either case (i) or in case (ii).

The penetration of liquids along grain boundaries is related to spreading. When liquid is in equilibrium with a solid, equilibrium dihedral angles develop at grain boundaries according to

$$\cos \frac{\phi}{2} = \frac{\gamma_{GB}}{2\gamma_{sl}}$$

where ϕ is the dihedral angle, γ_{sl} is the solid-liquid interfacial energy, and γ_{GB} is the grain boundary energy (Fig. 5). Under nonequilibrium conditions, assuming that ϕ is not initially zero, it will be reduced to zero and grain boundary penetration occurs if the reduction of γ_{sl} is large enough due to reaction and the grains are not externally held in place.

EXPERIMENTAL PROCEDURE

A. EXPERIMENTAL DESIGN

The various experimental cases can be easily understood with the aid of the copper-silver phase diagram (Fig. 6). Working on the copper side of the diagram at 900°C, the equilibrium sessile drop experiment was set up with a substrate of the solidus composition and a drop of the liquidus composition. Type (i) nonequilibrium was established with a substrate of pure copper and a drop of the liquidus. Type (ii) nonequilibrium was set up with a substrate of the solidus composition and a drop of the eutectic liquid. Type (iii) nonequilibrium was achieved with a pure copper substrate and a drop of the eutectic. The two phase nature of the liquidus drops formed in going from 780°C to 900°C created difficulties in the experiments, as will be explained later. To avoid this problem a second equilibrium case with eutectic liquid on the

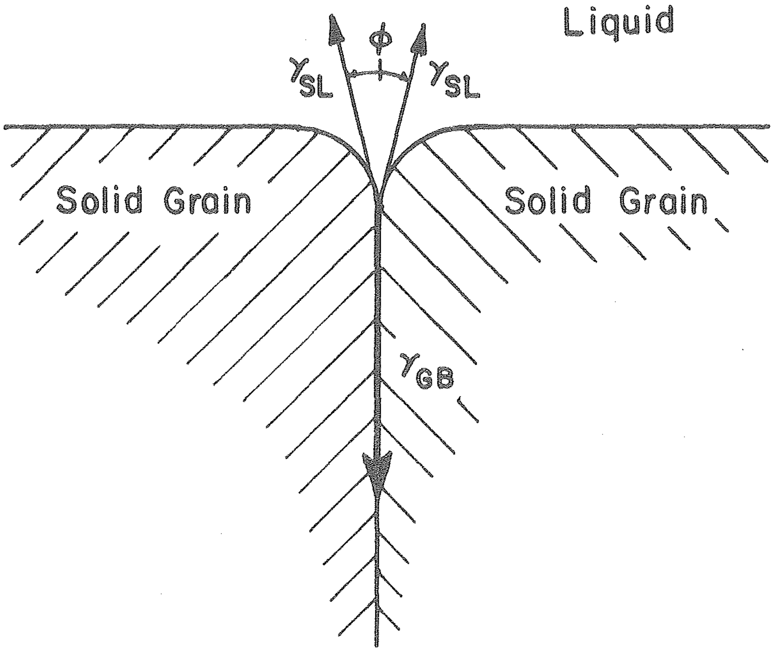

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Fig. 5. Schematic of equilibrium dihedral angles.

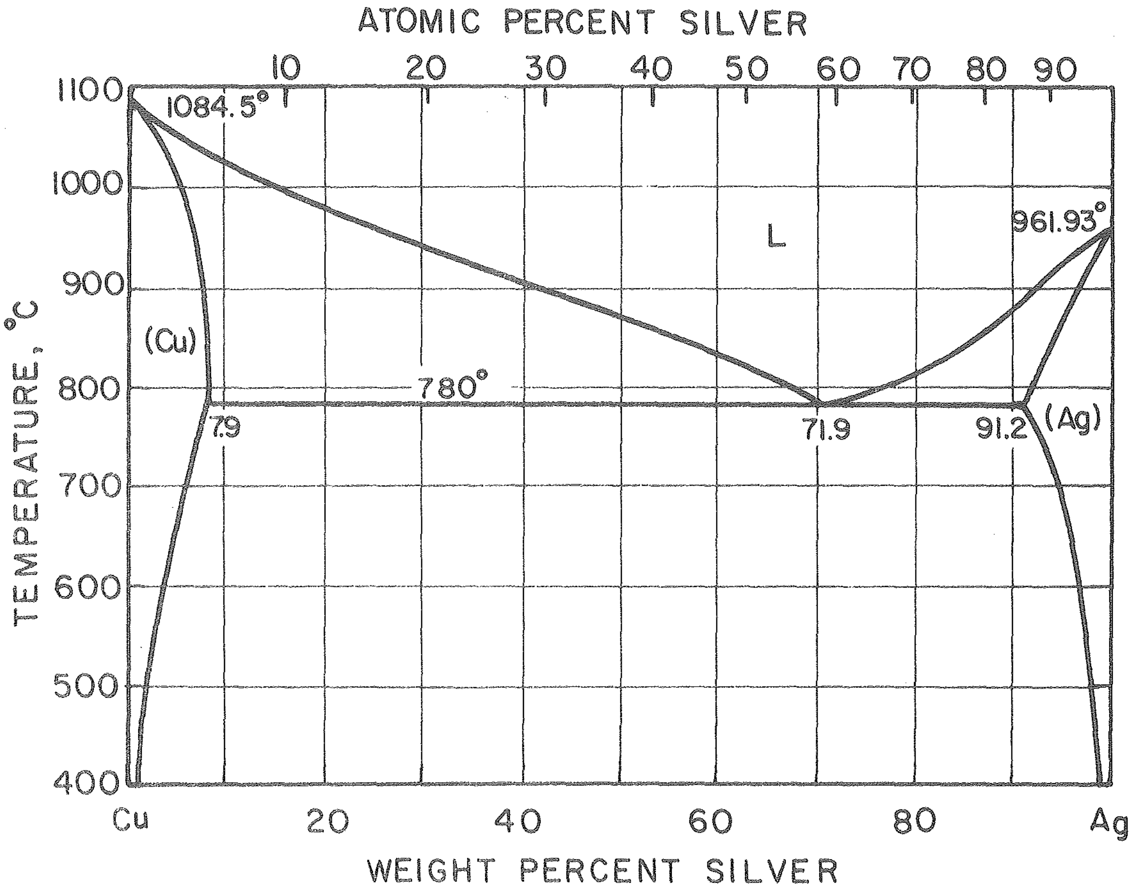

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Fig. 6. The copper-silver phase diagram.

solidus composition at 780°C and a second type (i) case with eutectic liquid on pure copper at 780°C were set up.

The right side of the phase diagram, or for that matter any simple eutectic phase diagram with limited solid solubility of either end member could also be used to establish the various experimental cases.

Only type (iii) nonequilibrium was considered in connection with grain boundary penetration. Type (iii) was the most extreme case. If no grain boundary penetration occurred in this case it would not occur in any of the other cases.

Table I contains a summary of the types of nonequilibrium and the experimental conditions which established the various cases.

B. MATERIALS

Polycrystalline substrates of pure copper and of compositions corresponding to the solidus at 900°C (7.7 wt% silver), the solidus at 780°C (7.8 wt% silver), and just to the right of the solidus at 780°C (8.3 wt% silver) were prepared. The pure copper substrates, approximately 1/2 inch by 1/2 inch by 1/16 inch, were cut from a cold rolled OFHC copper sheet of 99.99% purity obtained from LBL. The alloy substrates were prepared from silver shot of 99.99% purity obtained from Apache Chemical Company and from copper shot of 99.999% purity obtained from the Atomergic Chemical Company. 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 BREW furnace under gettered helium. Each charge was first heated to

	DESCRIPTION	EXPERIMENTAL CONDITIONS AT 900°C	EXPERIMENTAL CONDITIONS AT 780°C
EQUILIBRIUM	SOLID AND LIQUID SATURATED WITH RESPECT TO EACH OTHER	SOLID- SOLIDUS COMPOSITION LIQUID- LIQUIDUS COMPOSITION	SOLID- SOLIDUS COMPOSITION LIQUID- EUTECTIC COMPOSITION
TYPE (i) NONEQUILIBRIUM	SOLID NOT SATURATED WITH A COMPONENT OF THE LIQUID	SOLID- PURE COPPER LIQUID- LIQUIDUS COMPOSITION	SOLID- PURE COPPER LIQUID- EUTECTIC COMPOSITION
TYPE (ii) NONEQUILIBRIUM	LIQUID NOT SATURATED WITH A COMPONENT OF THE SOLID	SOLID- SOLIDUS COMPOSITION LIQUID- EUTECTIC COMPOSITION	NONE
TYPE (iii) NONEQUILIBRIUM	NEITHER PHASE SATURATED WITH RESPECT TO THE OTHER	SOLID- PURE COPPER LIQUID- EUTECTIC COMPOSITION	NONE

Table I. Summary and description of experimental conditions.

1500°C for five minutes, held at 1200°C for one hour, held at 780°C for twenty hours, and finally quenched to room temperature. Holding the charges at 780°C for twenty hours ensured equilibrium in the solid substrates. The resulting ingots, approximately 3/8 of an inch thick and 1 inch by 1-1/2 inch, were cold rolled to 1/16 of an inch. Substrates of approximately 1/2 inch by 1/2 inch were cut from the rolled ingots. All substrates were polished on a set of diamond wheels and finally given a high polish on a lap wheel at 0.3 micron alumina. The substrates were ultrasonically cleaned in acetone, ethyl alcohol, and finally distilled water.

Attempts were made to prepare single crystals of pure copper, of the solidus composition at 900°C (7.7 wt% silver), and of the solidus composition at 780°C (7.8 wt% silver) at LBL by the Bridgemann technique. The starting material was silver shot of 99.9999% purity obtained from the Apache Chemical Company and copper polycrystalline rod of 99.9999% purity obtained from LBL.

Substrates approximately 1/8 inch thick and 1 inch in diameter were cut from the LBL specimens. Single crystals of pure copper were obtained, but examination of the copper solidus substrates revealed a second silver rich phase. During growth the crystals were slowly cooled through the copper solidus-silver solidus two phase region, allowing the second phase to precipitate. With the present crystal growing equipment it was not possible to avoid the slow cooling, so an additional step was taken in an attempt to homogenize the solidus specimens. They were held at 800°C under gettered helium in the BREW furnace for twenty hours. Upon cooling the substrates were found to be polycrystalline, and so were not used.

Work is continuing in growing the crystals, with the most promising method involving the alteration of the crystal growing furnace so that the whole apparatus is kept at 780°C. After the crystals are grown, they will then be quenched through the two phase region, and the second phase should not precipitate.

The liquid drops were of the copper liquidus composition at 900°C (40.9 wt% silver) and of the eutectic composition (71.9 wt% silver). The same silver and copper shot used in the preparation of the polycrystalline substrates was used. Approximately 30 gram charges of each alloy were weighed, placed in the graphite crucible, and covered. The charges were melted under gettered helium in the BREW furnace, held at 1200°C for half an hour, and quenched to room temperature. The resulting ingots, approximately 3/8 of an inch thick and 3/4 inch by one inch, were cold rolled to 1/16 of an inch. The drops were cut from the rolled ingots and were approximately 1/16 inch by 1/8 inch by 1/8 inch. The base and corners were filed to give the final shape shown in Fig. 7. The shape of the drop was chosen so that on melting the liquid would always be in contact with solid that had not previously been covered by liquid. Solid drops were ultrasonically cleaned in acetone, ethyl alcohol, and finally distilled water.

C. EXPERIMENTAL EQUIPMENT

All experiments were run in a one inch diameter eight inch long Kanthal wound tube furnace (Fig. 8). The furnace was inside a large vacuum chamber that had a vacuum capability of 1×10^{-6} torr. The inside of the furnace was fitted with a tantalum sheet which reduced the oxygen partial pressure so that CoO, CO_2O, and AgO were reduced to pure metals

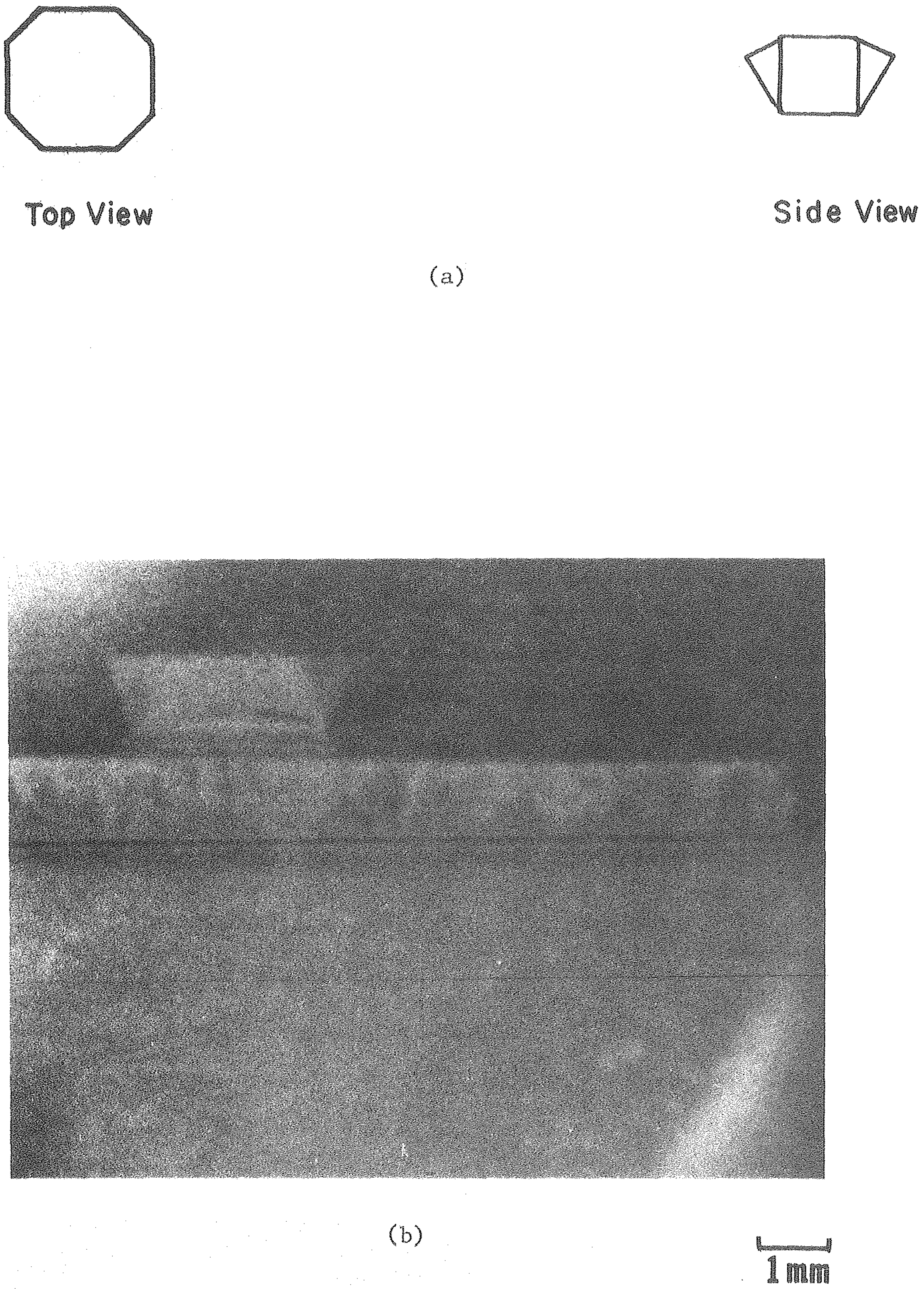

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Fig. 7. (a) Schematic of drops prior to melting.
(b) A drop on a substrate in the furnace at 780°C.

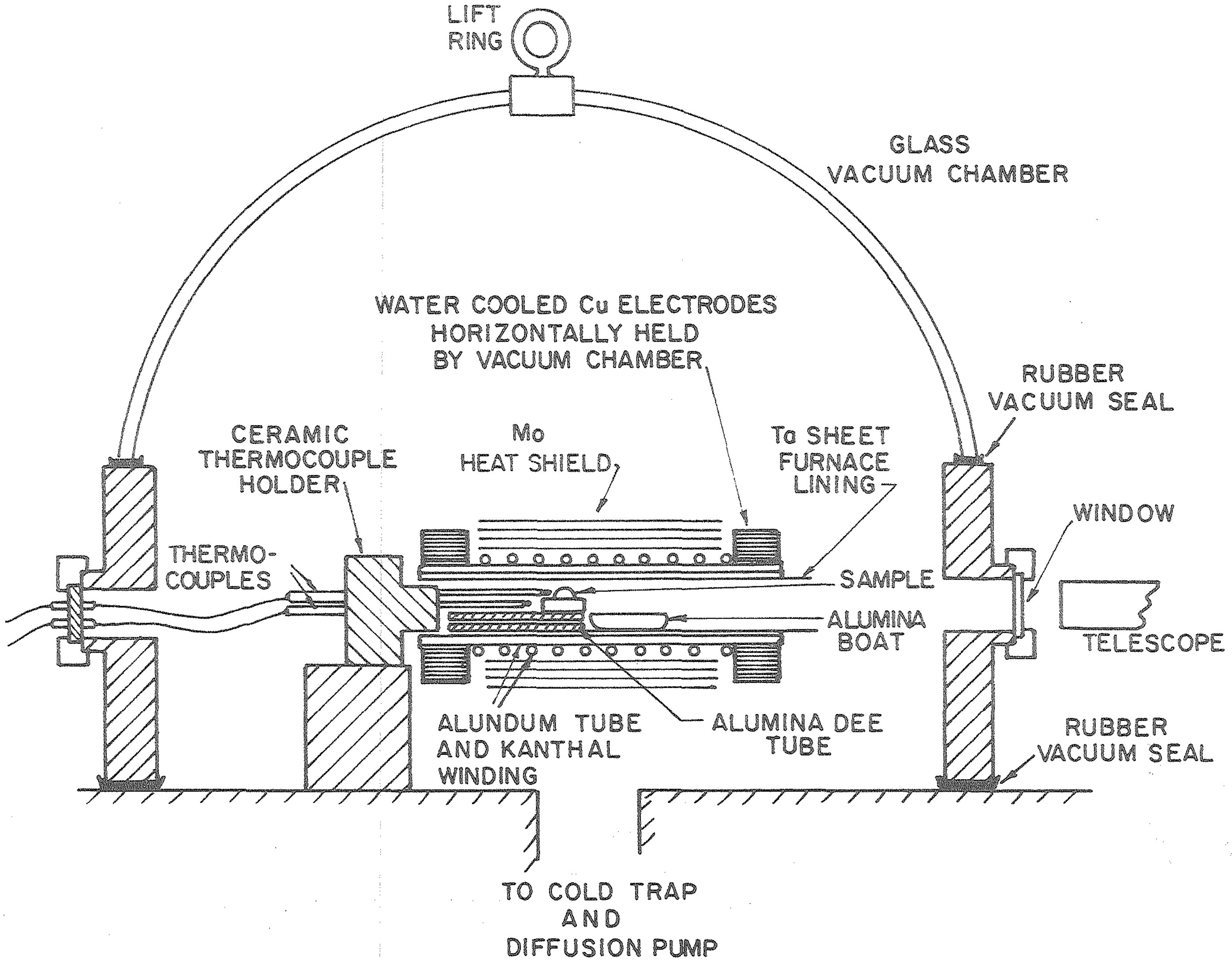

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Fig. 8. Schematic of the sessile drop furnace.

when the furnace was at experimental temperature. The furnace had a capability of 1000°C, and the hot zone was about four inches long. One end of the furnace was fitted with a thermocouple holder so that thermocouples could be placed next to the samples. The other end of the furnace was open and the experiments were observed through a porthole in the vacuum chamber by means of a telegoniometer. Contact angles were measured by movable cross hairs, with the estimated accuracy being ±2°. A camera was attached to the telegoniometer and pictures of the substrates and drops were taken.

A leak valve on the vacuum chamber allowed helium to be introduced into the furnace. The helium was Grade A, obtained from LBL, and was gettered with drierite (W. A. Hammond Drierite Company) and with 87.5 wt% zirconium - 12.5 wt% titanium turnings kept at 800°C.

D. EXPERIMENTAL RUN

For each experiment a substrate and a drop were placed on an alumina dee-tube and situated about an inch from the center of the furnace (Fig. 8). A one inch long boat containing material of the liquidus composition at 900°C was placed in the center of the furnace. When the substrate was 770°C, the center of the furnace was about 30°C hotter. The material in the alumina boat was necessary to establish the equilibrium vapor pressure of copper and silver. If the vaporization material was not in the furnace, a large amount of the drop was lost during an experiment. In several initial experiments under high vacuum without vaporization material the liquid phase of the liquidus drop (on heating through 780°C only part of the liquidus drops melted) vaporized so rapidly that only the solid in the drop remained. Two thermocouples were placed within 1/2 inch of the drop, and the temperature was monitored continually by a chart recorder and by a digital read out.

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 1.5×10^{-6} torr. The system was finally backfilled with gettered helium. Back filling also helped to reduce the vaporization loss. The substrate and drop were heated to 770°C in about 15 minutes and held for 1-1/2 hours so that the equilibrium vapor pressures were reached.

For experiments at 780°C the temperature was increased at about 20°C per hour, and the drop monitored closely. As soon as melting started, the furnace temperature was held constant. Fluctuations in the furnace controller resulted in about a one degree fluctuation in the furnace temperature. For experiments at 900°C, the temperature was increased rapidly, and about 10 minutes elapsed in going from 770°C to 900°C. All samples were held at experimental temperature for about 10 minutes.

E. SAMPLE EXAMINATION

The surface of the substrates, particularly at the drop edge, were examined after experiments with a metallograph. The substrates were cut with a diamond saw on a plane perpendicular to the substrate-drop interface, and a 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 on a lap wheel 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, which measure the concentration of an element on a line across a sample, were done with an EDAX unit on a scanning electron microscope.

RESULTS AND DISCUSSION

The results for the various experimental cases are summarized in Table II. Each case will be discussed in detail.

A. EUTECTIC LIQUID ON COPPER SOLIDUS AND ON PURE COPPER AT 900°C

The eutectic liquid spread immediately upon melting on both the pure copper and the copper solidus in the experiments at 900°C. Cross-sections of the solid-liquid interface revealed solution of the substrate occurring in both cases (Fig. 9). At 900°C the eutectic liquid was unsaturated with respect to copper, which was the major component in either substrate. To reach saturation, the liquid dissolved the substrate. According to the phase diagram the final equilibrium liquid consisted of either 47 wt% of copper solidus or 42 wt% of pure copper (the remainder was the eutectic composition), dissolved from the respective substrate. In the case with pure copper, silver also diffused into the substrate, so the actual amount dissolved was less.

The solution of the substrates occurred preferentially along grain boundaries, but in the case with pure copper substrates optical examination and x-ray line scans gave no evidence of grain boundary penetration (Fig. 10). In the case with solidus substrates penetration appeared to occur (Fig. 9B). Since such penetration was not observed in the pure copper substrates, which are more extreme cases than the copper solidus substrates, penetration by the liquid was ruled out. Careful examination of the solidus substrate after experiments revealed a silver rich phase

	SPREADING	SPREADING ALONG GRAIN BOUNDARIES	DIFFUSION INTO SUBSTRATE	SOLUTION OF SUBSTRATE
LIQUIDUS ON SOLIDUS AT 900°C	BELL SHAPED DROP, SPREADING	YES	NO	YES, BUT ONLY AT DROP EDGE
LIQUIDUS ON PURE COPPER AT 900°C	BELL SHAPED DROP, SPREADING	YES	YES	YES, MAINLY AT DROP EDGE BUT ALSO AT DROP CENTER
EUTECTIC ON SOLIDUS AT 900°C	YES	YES	NO	YES
EUTECTIC ON PURE COPPER AT 900°C	YES	YES	YES	YES
EUTECTIC ON SOLIDUS AT 780°C	YES	YES	NO	NO
EUTECTIC ON PURE COPPER AT 780°C	YES	NO	YES	NO

Table II. Summary of experimental results.

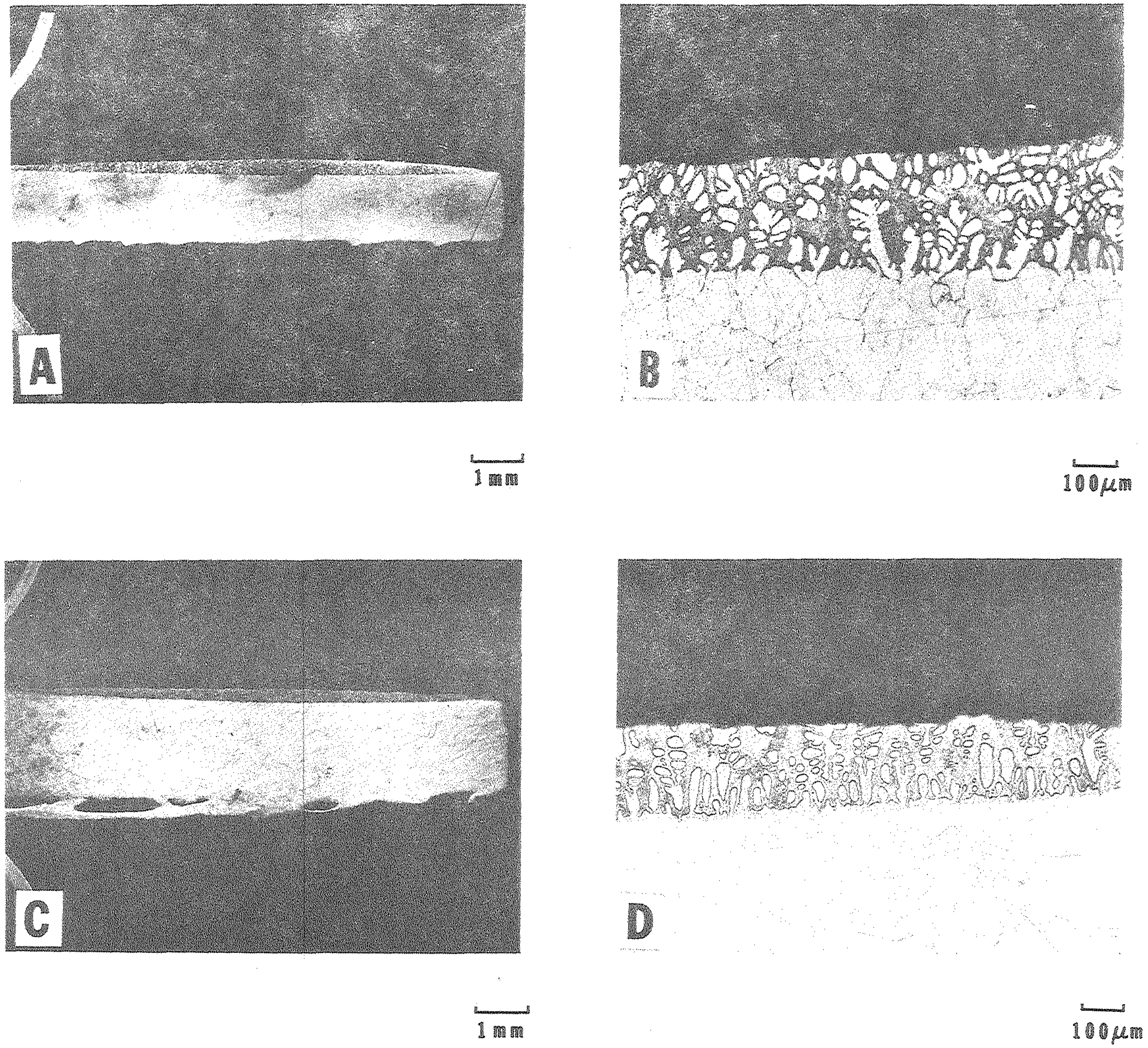

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Fig. 9. A,B. Photomicrographs of cross-sections of eutectic liquid on copper solidus, 900°C.
C,D. Photomicrographs of cross-sections of eutectic liquid on pure copper, 900°C.

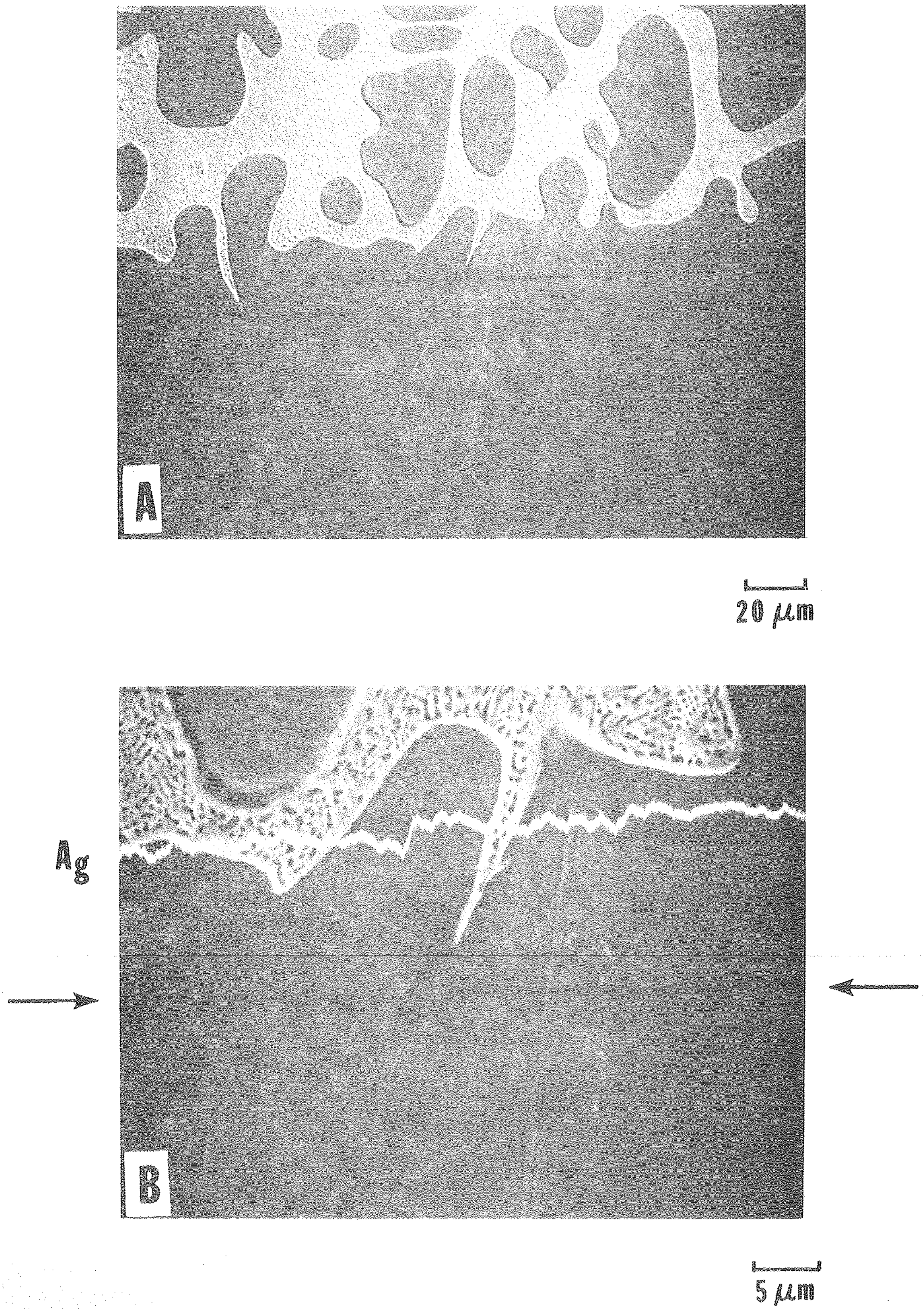

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Fig. 10. Micrographs of eutectic on pure copper, 900°C.
(A) Cross-section of the interface.
(B) X-ray line scan across a grain boundary at the interface. The scan was taken in between the arrows. The concentration of silver is along the vertical axis.

at surface and bulk grain boundaries throughout the sample. Prior to experiments no second phase was observed, and no weight gain occurred during experiments indicating that silver was not being absorbed from the vapor. The second phase was then considered to be due to the heating of the substrates slightly over 900°C into the two phase region and to the slow cooling of the substrates through the copper solidus-silver solidus two phase region. There is also the possibility, however, that diffusion of silver from the liquid into the pure copper substrate played a role in preventing the penetration of liquid into the grain boundaries.

Silver diffusion into the pure copper substrate was shown by x-ray line scans (Fig. 11A). EDAX analysis of the interface indicated that the copper contained about 5 atomic % silver, being roughly the solidus composition at 900°C. No diffusion was detected in the case with the solidus substrates, and none was expected since the substrate was already saturated with silver (Fig. 11B).

Examination of both substrate surfaces at the edge of spreading indicated that the liquid did not spread evenly across the grains (Fig. 12), as would be expected if the liquid spread solely due to reactions. Spreading occurred preferentially along grain boundaries, but the appearance of the spreading along the grain boundaries differed for the two substrates. Capillary forces along grain boundary grooves were the probable reason for the preferential spreading. The appearance was different due to silver diffusion in the case with pure copper substrates. As the liquid moved along the grain boundary groove it lost silver due to diffusion, the composition of the liquid moved into the two phase solidus-

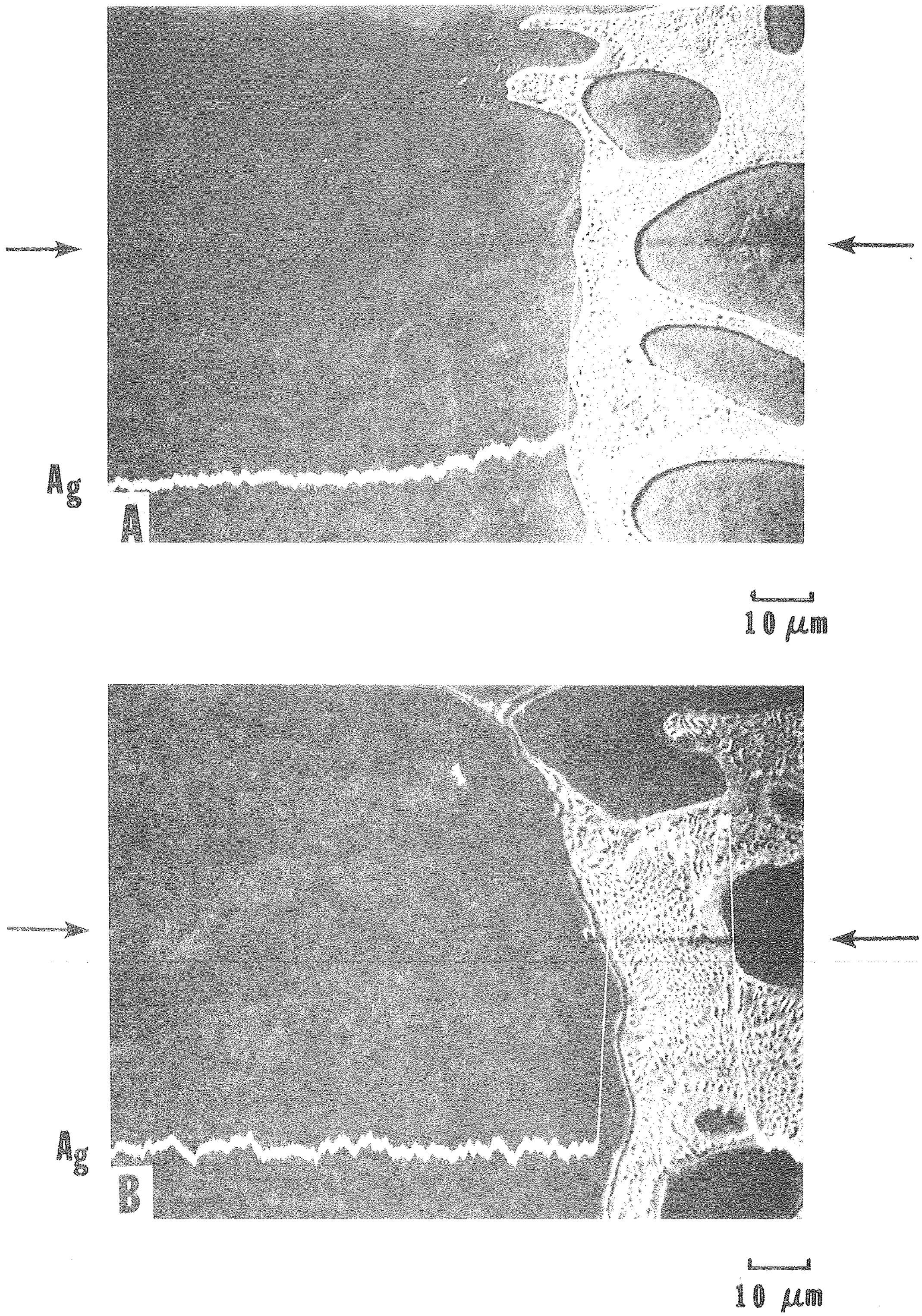

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Fig. 11. X-ray line scans across cross-sections of the solid-liquid interface. The scans were taken on the lines in between the arrows. The concentration of silver is on the vertical axis.
(A) Eutectic liquid on pure copper, 900°C.
(B) Eutectic liquid on copper solidus, 900°C.

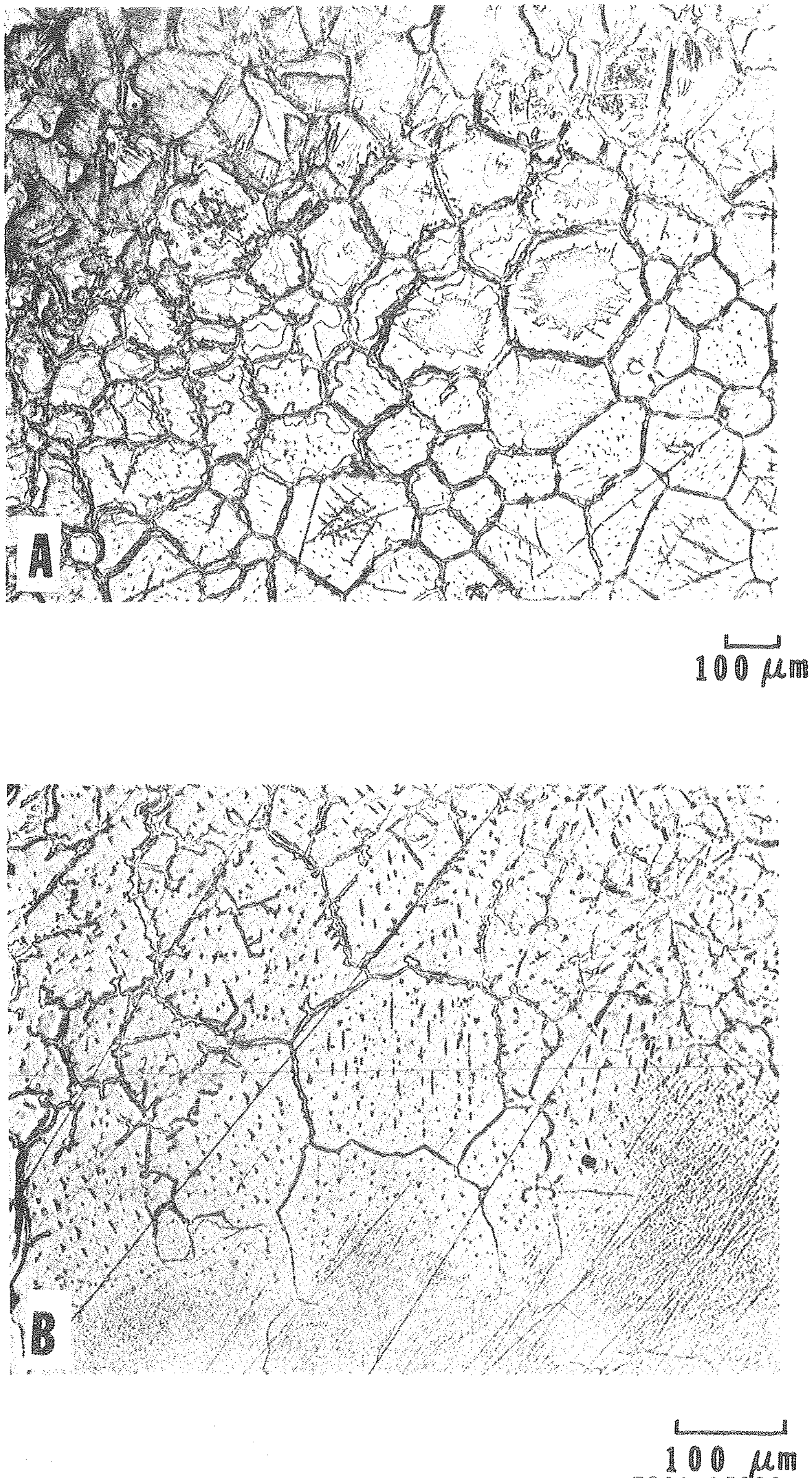

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Fig. 12. Micrographs of the surface of the substrates at the edge of spreading. The spreading direction was from top to bottom.
(A) Eutectic liquid on copper solidus, 900°C.
(B) Eutectic liquid on pure copper, 900°C.

liquidus region, and the flow decreased due to the solidus precipitates. Since the copper solidus substrate was unsaturated with silver, no diffusion and no decrease in the flow of the liquid occurred.

No definite conclusions can be made with respect to the theory previously mentioned because of the spreading complications introduced by the presence of grain boundaries. The effect of reactions on spreading will not be fully resolved until single crystal substrates are obtained.

B. COPPER LIQUIDUS ON PURE COPPER AND ON COPPER SOLIDUS AT 900°C

The copper liquidus drop was expected to be a single phase liquid at 900°C and to form a true contact angle on the copper solidus because according to the phase diagram the solid and liquid were in equilibrium. On melting, however, the liquid assumed a bell-shape (Fig. 13C and D). Contact angles were meaningless. A similar bell-shaped drop was seen in the case of liquidus on pure copper (Fig. 13A and B). Cross-sections of the substrate-drop revealed that the interface for both cases was not planar (Fig. 13B and D). The pure copper substrate was preferentially dissolved at the edge of the drop, with some solution also occurring at the drop center. The copper solidus substrate was also preferentially dissolved at the drop edge, but little or no solution occurred at the drop center.

A liquidus drop was placed on a solidus substrate and just heated to 780°C to determine if the way the drop melted caused the preferential solution. As soon as melting occurred, the furnace was cooled, freezing the drop. A cross-section (Fig. 14) revealed the cause of the nonuniform solution. Prior to melting the liquidus composition consisted of a copper

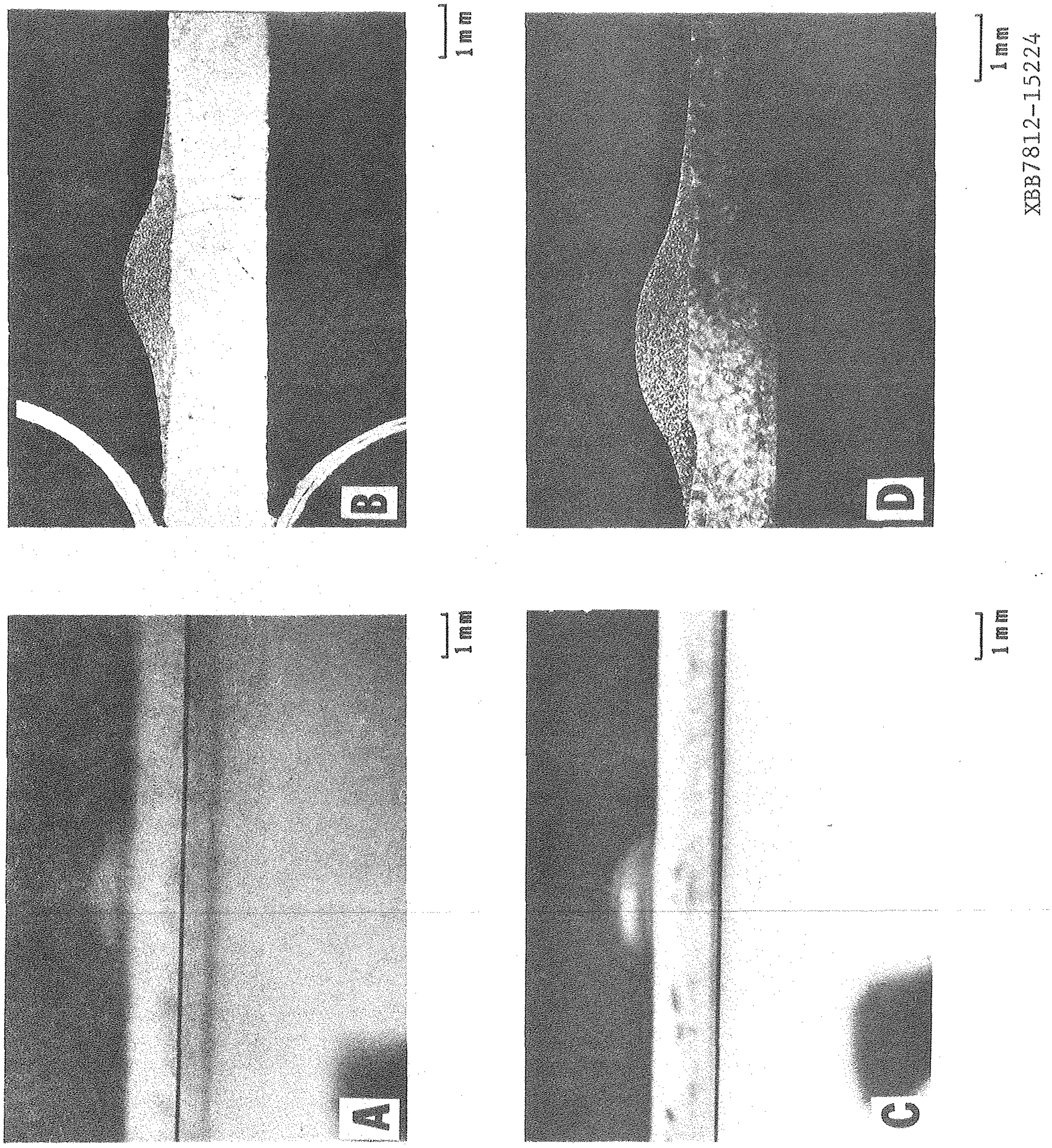

Fig. 13. The bell-shaped liquidus drops.

(A) Liquidus on pure copper in the furnace at 900°C.

(B) Micrograph of a cross-section of the liquidus on pure copper.

(C) Liquidus on copper solidus in the furnace at 900°C.

(D) Micrograph of a cross-section of the liquidus on copper solidus.

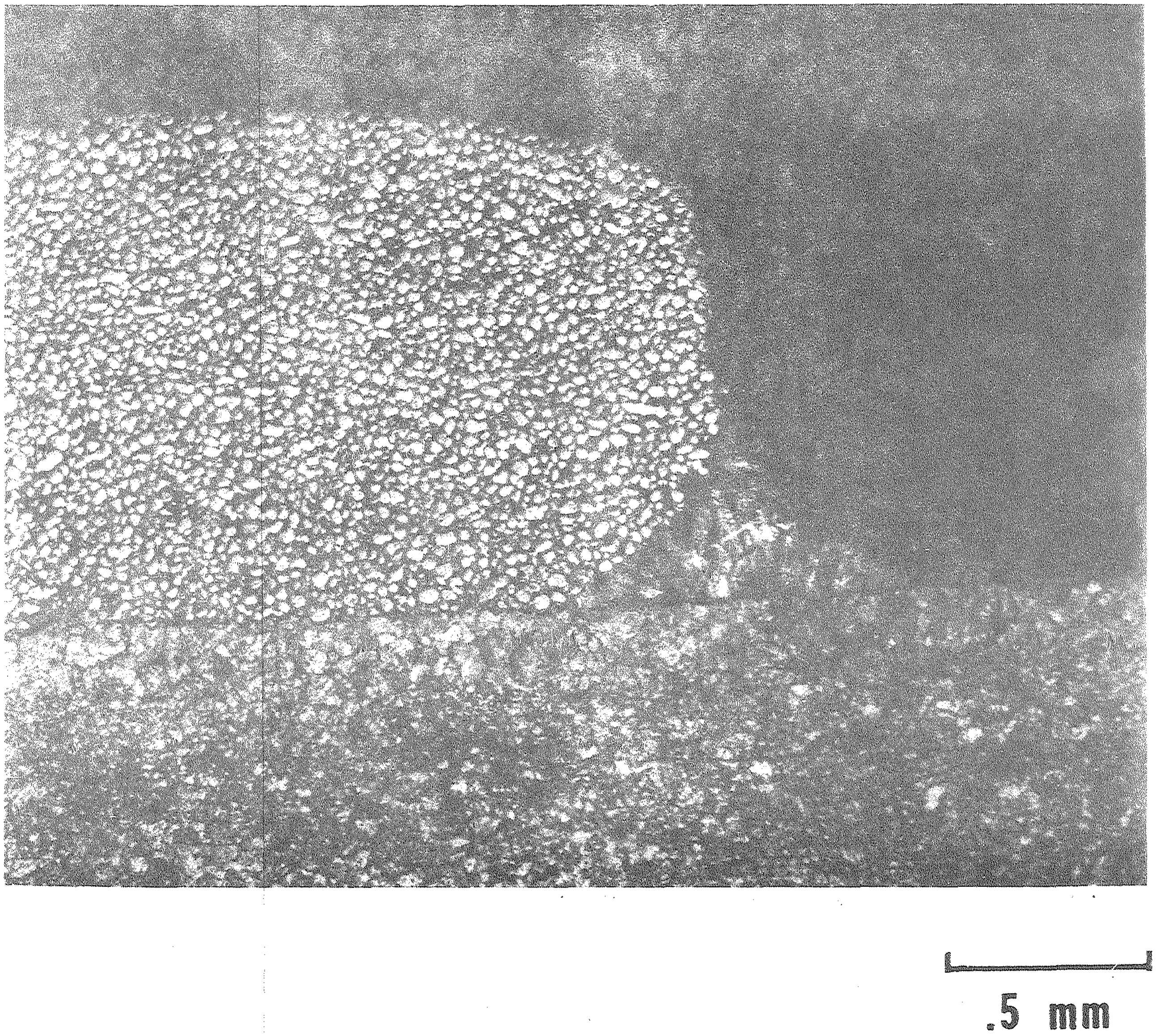

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Fig. 14. Micrograph of a cross-section of the liquidus on copper solidus, 780°C. The eutectic liquid is at the base and side of the drop.

solidus primary phase and a fine two-phase eutectic structure. On heating through 780°C, the eutectic structure melted, forming a drop of 53 wt% eutectic liquid and 47 wt% copper solidus assuming equilibrium conditions. Most of the liquid flowed out to the drop edge. The primary phase and a small amount of liquid remained at the drop center. On continued heating, the edge of the drop was essentially the case of eutectic liquid on either pure copper or copper solidus. Since the eutectic composition was unsaturated with respect to copper at 900°C, the substrates at the drop edge were preferentially dissolved.

With the pure copper substrates the liquid retained at the drop center dissolved both the primary phase and the substrate to reach saturation. Since the chemical potential of copper in the substrate was higher than that of copper in the primary phase, the solution of the substrate was preferential. For the solidus substrates, the copper chemical potential was the same for both substrate and primary phase, and since the primary phase had a much greater surface area exposed to the liquid, little of the substrate at the drop center was dissolved. Thus, more solution occurred at the drop center in the case of liquidus on pure copper than in the case of liquidus on solidus.

X-ray line scans of the pure copper substrates revealed that silver had diffused both at the drop center and at the drop edge. Diffusion was expected since the substrates were unsaturated with silver. No diffusion occurred in the case with the solidus substrates.

The surfaces of both substrates showed the liquid at the drop edge spreading along grain boundaries (Fig. 15). Again, the liquid did not spread evenly across the grains, and the appearance of the edge of

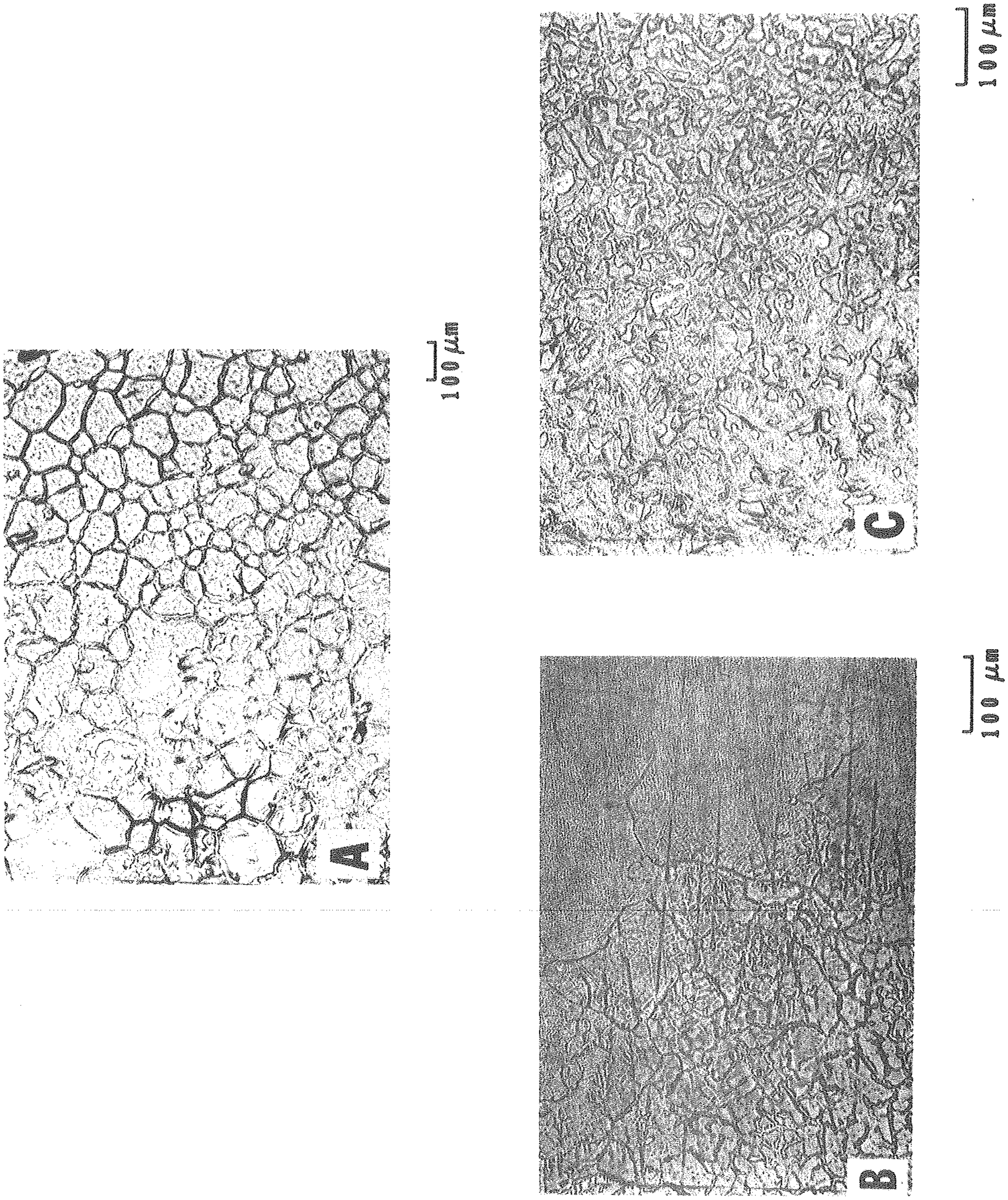

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Fig. 15. Micrographs of the substrate surfaces at the edge of spreading. Spreading was from left to right.
(A) Liquidus on copper solidus, 900°C.
(B) Liquidus on pure copper, 900°C, right at the edge of spreading.
(C) Liquidus on pure copper, 900°C, closer to the drop center.

spreading on the substrates was similar to that occurring with the eutectic liquid (Fig. 12).

Capillary forces between the liquid and the primary phase at the drop center kept all the liquid from spreading, and the balance between these forces and the spreading forces resulted in the bell-shaped drops. Again, no conclusions can be made concerning the theoretical model due to the shape of the drops and the effect of grain boundaries.

C. EUTECTIC LIQUID ON PURE COPPER AND ON COPPER SOLIDUS AT 780°C

The experiments at 780°C were designed to avoid the difficulties associated with the disproportionation of the two-phase liquidus drop on melting. Table I shows that the same types of nonequilibrium conditions were set up as in the cases with the liquidus drops in the 900°C experiments. The temperature at which the eutectic drop melted was the same temperature as the experiment, so care was taken not to overshoot the melting point. On both types of substrates the liquid spread as soon as melting occurred.

For eutectic liquid on the solidus substrate, the system was in chemical equilibrium, and an equilibrium contact angle had been expected. No interfacial reaction was observed, but the edge of the spreading revealed the liquid being pulled along grain boundaries (Fig. 16B). X-ray line scans indicated that the solidus substrates were homogeneous with no preferential concentration of either silver or copper at grain boundaries, indicating that reactions were not occurring at grain boundaries. Although the system was in chemical equilibrium, spreading occurred due to capillary forces at grain boundary grooves. The lesser amount of spreading in comparing Fig. 16B with Figs. 12 and 15 can be

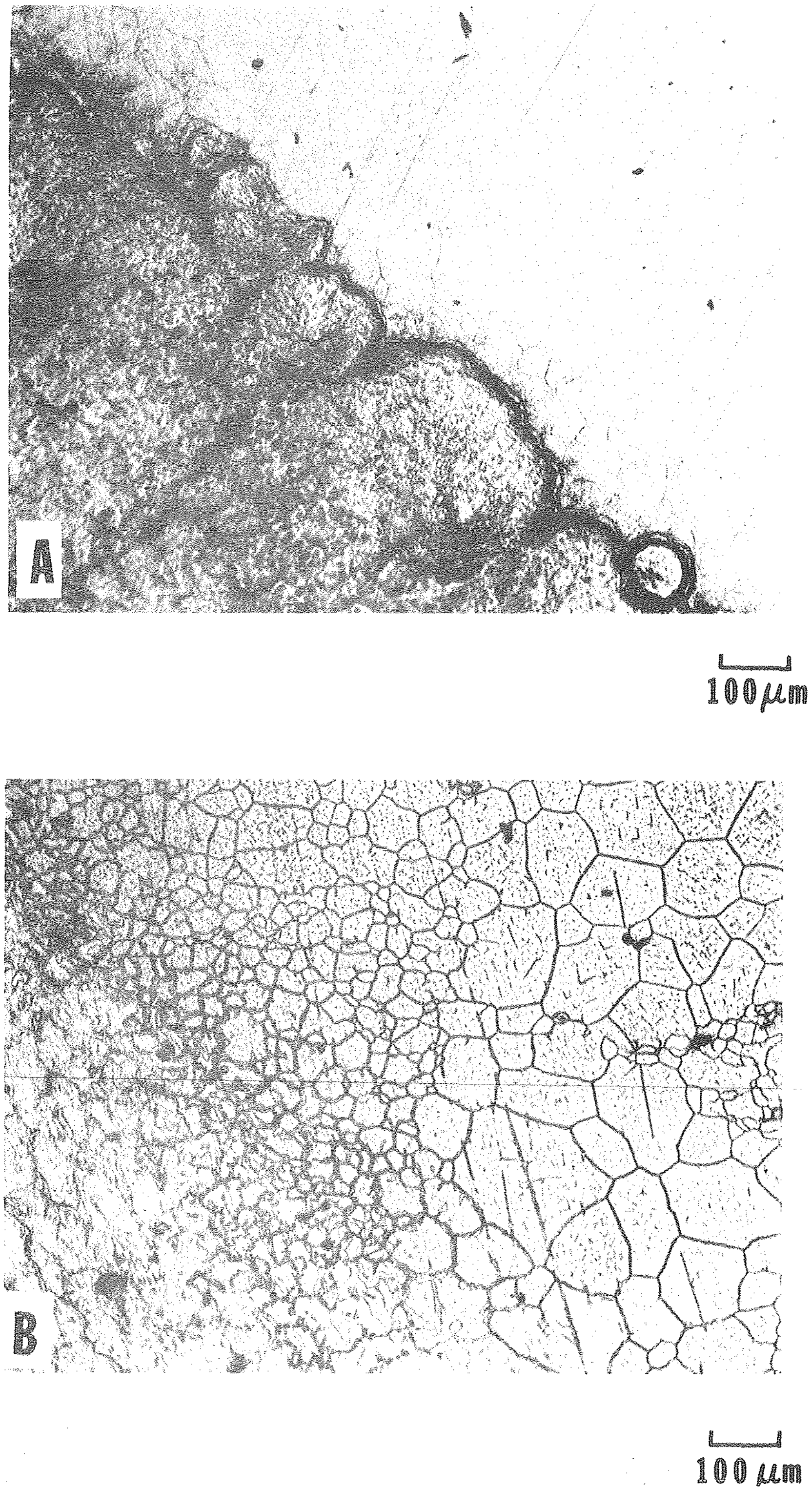

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Fig. 16. Micrographs of the substrate surfaces at the edge of spreading.
(A) Eutectic liquid on pure copper, 780°C.
(B) Eutectic liquid on copper solidus, 780°C.

attributed to less thermal grooving because of lower temperatures in the former case.

For eutectic liquid on pure copper, silver diffused into the substrate. Spreading occurred evenly across the grains (Fig. 16A), indicating that the reaction caused the spreading. This was the only case in which grain boundaries played no role. The liquid spread faster due to the reaction than due to the capillary flow along grain boundaries; thus, no grain boundary effect was seen. In terms of the theoretical model the spreading was due to the reaction of the silver diffusing into the substrate. The viscosity of the liquid was low enough and the diffusion of silver into copper was slow enough so that the flowing liquid was always in contact with unreacted solid. The free energy contribution of the diffusion reaction was great enough to cause spreading.

D. SPREADING DUE TO GRAIN BOUNDARIES

The liquid spread along the grain boundaries due to capillary forces. As the substrates were heated to experimental temperature, thermal etching of the surface grain boundaries created capillary grooves. The amount of grooving was greater at 900°C than at 700°C. When the drop melted, the liquid moved along the grooves similar to the way a liquid which wets a solid will rise in a capillary tube made of the solid. The smaller the diameter of the tube, the higher the liquid rises. The principal difference is that the weight of the liquid does not impede the flow along grain boundary grooves. The driving force is greatest at the base of the groove, where the width is the smallest. A small amount of liquid will flow along the base, making it easier for ensuing liquid to flow.

Parker and Smoluchowski[17] observed capillary flow of liquid silver on finely ground or on polished and etched iron (6 wt% Mo) surfaces. Spreading was attributed to the grooves. The same phenomena is occurring in the present study except that the capillary flow is due to thermal grooving of grain boundaries.

The necessary conditions for capillary flow are that the liquid wet the solid and that the liquid have a low enough viscosity for easy flow along the grooves. Nonwetting liquids would not be expected to spread along grooves, assuming that the system is in chemical equilibrium.

Grain boundaries have also been observed to have important effects in glass-metal and in glass-ceramic systems.[18,19] Unfortunately, grain boundaries have usually been neglected in interfacial studies. Future work is thus needed to further quantify their effect in wetting and spreading.

SUMMARY AND CONCLUSIONS

Spreading occurred due both to chemical reaction and to capillary flow along grain boundaries. When the eutectic liquid was on pure copper at 780°C, silver from the liquid diffused into the copper, and the reaction was intense enough to cause spreading without extended movement along grain boundaries. When the eutectic liquid was on the solidus at 780°C, the system was in thermodynamic equilibrium, but spreading still occurred due to capillary forces pulling the liquid along grain boundary grooves.

The eutectic liquid on pure copper at 900°C spread. Cross-sections revealed intense solution of the substrate, and the surface of the substrate at the edge of the spreading revealed the liquid spreading along grain boundaries. Spreading can be attributed both to the reactions of silver diffusing into the substrate and the liquid dissolving some of the substrate and to the grain boundaries. The eutectic liquid also spread on copper solidus at 900°C. Spreading was due to the reaction, which in this case involved the solution of the substrate by the liquid, and to the grain boundaries.

For copper liquidus on pure copper at 900°C, the disproportionation of the drop into two phases resulted in its being bell-shaped. Greater solution occurred at the drop edge because of a greater amount of eutectic liquid being there. Silver also diffused into the substrate. With copper liquidus on copper solidus at 900°C the results were similar, except that no silver diffused into the substrate. The liquid at the drop edge spread over both composition substrates due both to the reactions at the drop edge and to the grain boundaries.

The grain boundary effect was essentially the effect of capillary forces pulling the liquid along the grooved surface grain boundaries.

Penetration of grain boundaries due to reactions did not occur, although the grain boundaries were preferentially attacked when the liquid dissolved the substrates.

Similar experiments should be done with single crystal substrates to eliminate any spreading due to grain boundaries. The full consequences of interfacial reactions and spreading can then be studied. Since practical systems, however, involve solids with grain boundaries, the present theory should be expanded to include their effects.

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