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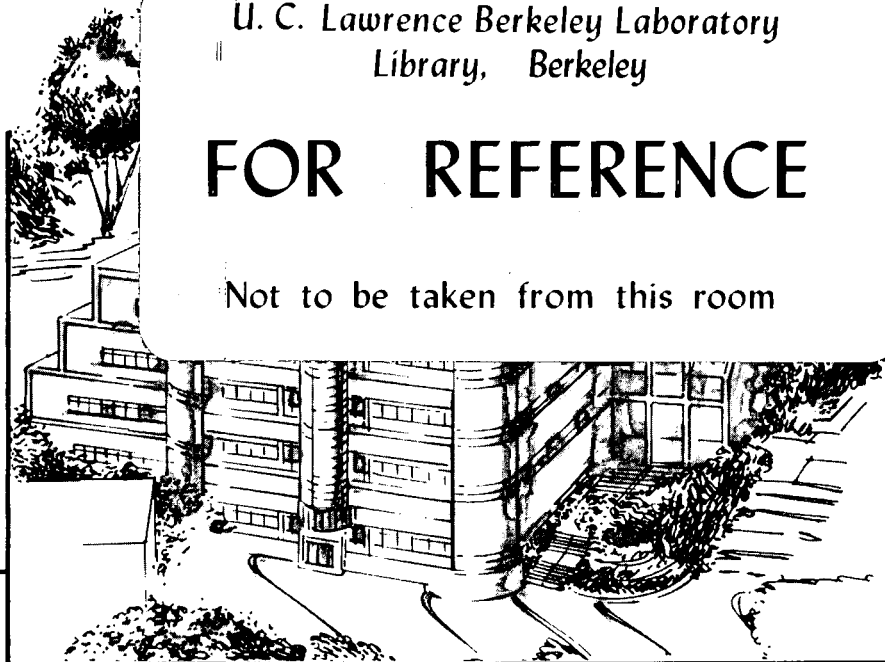## Effect of Surface Condition on the Solderability of Pre-tinned Cu Sheet

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Materials and Chemical Sciences Division

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ABSTRACT

The reliability and integrity of pre-tinned copper-clad printed circuit (PC) boards are serious concerns in the manufacture of electronic devices. The nature of wetting during soldering of Cu is discussed, and the results of some preliminary experiments on the solderability of pre-tinned Cu are described. The results suggest that pre-tinning with a Pb-rich solder, such as 95Pb-5Sn, is preferred to pre-tinning with eutectic solder, since the latter can develop exposed intermetallics during aging or baking that wet poorly. The results are interpreted by examining the growth morphology of Cu-Sn intermetallics during aging.

INTRODUCTION

A solder joint is made by bringing molten solder (usually Pb-Sn) into contact with a metal surface (usually copper or nickel) with which the solder forms a bond. The problem of forming a good bond (solderability) has both thermodynamic and kinetic features. There must be an adequate thermodynamic driving force to provide wetting at the solder-metal interface, and the kinetics of wetting must be such that the bond is achieved in the relatively short time that can be made available in a typical manufacturing process.

The thermodynamics of wetting can be understood on the basis of two equations, which also provide a convenient framework for discussing basic steps that are included in almost every soldering operation. The first is the *Young equation*[1], which is illustrated in Figure 1. When a liquid drop is placed on a solid surface that is nominally flat and rigid, it spreads over the surface until the *contact angle,* θ, between the liquid-vapor (LV) and solid-liquid (SL) interfaces along its periphery reaches the equilibrium value given by the equation

$$\cos(\theta) = (\sigma_{SV} - \sigma_{SL})/\sigma_{LV} \qquad (1)$$

where σ_{SV}, σ_{SL} and σ_{LV} are, respectively, the surface tensions of the solid-vapor, solid-liquid, and liquid-vapor interfaces. For good wetting the contact angle should be as small as possible; ideal wetting occurs when the right-hand side of equation (1) is greater than 1, in which case $\theta = 0$ (the smallest value it can have) and the liquid spreads freely over the

solid surface to form a continuous film. It follows that wetting is promoted when σ_{SV} is as large as possible while σ_{SL} and σ_{LV} are as small as possible.

The second important thermodynamic relation is the *Gibbs Relation*, which states that any spontaneous change that occurs at an interface that separates two given phases must satisfy the relation

$$\Delta\sigma \leq 0 \qquad\qquad (2)$$

that is, any spontaneous change in the interface lowers the interfacial tension. This relation suggests how one may manipulate the terms in equation (1) to promote wetting.

First, consider the choice of substrate and solder to minimize σ_{SL}. The Gibbs relation suggests that σ_{SL} can be effectively lowered by choosing a solder that has a rapid, spontaneous interfacial interaction with the metal substrate. Common solders contain Sn, which reacts spontaneously with copper or nickel at normal soldering temperatures to form intermetallic compounds. In the case of Cu, these are the ε-phase (Cu_3Sn) and the η-phase (Cu_6Sn_5), which are largely responsible for the wetting of copper by Pb-Sn solders.

Second, consider the preparation of the metal surface to maximize σ_{SV}. When a metal surface is exposed to air it adsorbs surfactants, oxidizes, and attracts dirt. Equation (2) shows that all of these spontaneous processes lower σ_{SV}, and, hence, inhibit wetting. Cleaning the surface, for example, with a reactive flux, raises σ_{SV} and promotes wetting. However, strongly reactive fluxes introduce chemical agents that are often undesirable contaminants. It is, hence, common in the manufacture of electrical components to "pre-tin" metal surfaces that are to be soldered by coating them with a thin, protective layer of tin or Pb-Sn solder (gold plating is also used). The pre-tinned layer protects the metal substrate from oxidation and contamination, and is, at least in theory, easily dissolved or wet by molten solder. The wetting process is usually assisted by a mild flux that helps clean the surface of the pre-tin layer and adsorbs at the LV interface, lowering σ_{LV}.

The kinetics of wetting during soldering are largely determined by the kinetics of the reactions that occur on the interface. In the case of Pb-Sn solder contact with clean, bare copper, the pertinent reaction is the formation of the appropriate Cu-Sn intermetallic at the interface. At normal soldering temperatures the preferred intermetallic is the η-phase (Cu_6Sn_5). This is the Sn-rich intermetallic in the Cu-Sn system[2] (Figure 2). It is preferred since Sn diffuses rapidly through the liquid solder, so the copper supply at the growing intermetallic interface is the rate-limiting consideration. However, η-phase formation is limited to temperatures below about 400°C in the Cu-Sn binary; the ε-phase (Cu_3Sn) forms when soldering is done at higher temperatures.

In the case of solder contact with a pre-tin layer, the kinetics of wetting are determined by the rate of reaction between the solder and the pre-tin layer. Ordinarily, the pre-tin layer presents a solder surface to the wetting solder, and the kinetics of wetting are limited by the rate of melting or dissolution of the pre-tin coating. The rate of wetting is increased by a fine grain size in the coating, which permits liquid solder penetration along

grain boundaries, but is decreased by oxidation of the pre-tin surface, and is particularly slowed if the pre-tin layer with exposed intermetallics is to react at the wetted interface.

One of the troublesome problems that is commonly encountered in soldering pre-tinned components is the loss of solderability during storage or baking prior to soldering[3,4,5]. Pre-tinned components are often stored for some period of time before assembly, and are often baked by exposure to a relatively high temperature before soldering to remove moisture that slow soldering kinetics. It is then sometimes found that the components wet poorly, requiring the rejection or costly re-work of soldered parts. We have recently been engaged in a study of that problem. The following experiments suggest some of its sources, and possible remedies.

EXPERIMENTAL

The experiments studied the wetting of copper by eutectic Pb-Sn solder (63Sn-37Pb, by weight), using several different surface preparations of the copper to simulate situations that might be encountered during manufacturing. The prepared surfaces included (1) clean, bare Cu, (2) Cu pre-tinned with a thin layer of eutectic solder, (3) Cu pre-tinned with a thin layer of 95Pb-5Sn solder, and (4,5) Cu pre-tinned with eutectic or 95Pb-5Sn solder, then aged at 170°C for 6 days to simulate an aged and baked condition.

All the specimens were made of OFHC Cu sheet cut to 25.4 mm x 25.4 mm x 0.84 mm coupons. Although the actual pre-tinning temperatures varied with the solder composition, the general procedure was the same. The Cu specimens were mechanically polished using a 600 grit silicon carbide paper and chemically microetched with a 50% diluted nitric acid until uniform bubbles evolved from the surface. The specimens were rinsed in water and in ethyl alcohol, and were kept in mildly activated rosin type (RMA) flux until pre-tinning for approximately 10-20 minutes. The solder bath temperature for 63Sn-37Pb solder was 245°C and for 5Sn-95Pb solder was 360°C. The specimens were immersed in the molten solder bath for 5 seconds and then air-cooled, resulting in an average solder thickness of about 10 μm. For aging, the 63Sn-37Pb and 5Sn-95Pb pre-tinned specimens were individually encapsulated in argon-filled quartz tubes and held at 170°C for 6 days.

The kinetics of wetting were studied in a wetting balance in which Cu samples with prepared surfaces are partially immersed in a molten bath of eutectic solder. The force on the specimen is measured as a function of time after immersion. As the interfacial reactions that accomplish wetting proceed, the solder meniscus climbs on the partially immersed copper surface, and the downward force on the specimen increases. The testing device used was a Multicore Universal Solderability Tester (MUST), which is a commercially available unit. The test machine was interfaced with a computer for data acquisition and control, using software developed here. The test parameters are listed in Table 1. Prior to the test, the specimens were dipped in RMA flux. Three specimens were tested for each condition.

The surface characterization was performed using a scanning electron microscope (SEM). For the cross-sectional optical microscopy, the samples were cut from the tested

specimens and mounted in epoxy. A conventional polishing technique was used. The intermetallics were identified by using an X-ray diffractometer.

RESULTS AND DISCUSSION

The wetting curves corresponding to the different surface conditions are shown in Figures 3 and 4 and are displayed as a function of the wetting force with time. The time to immersion depth was the same for all specimens, and the buoyancy force is subtracted, so the force plotted is the true wetting force due to the solder meniscus developed at the interface.

Cleaned Cu

The cleaned copper surface is rapidly wet by the eutectic solder, as shown in Figures 3 and 4. Wetting is completed within 2 sec. of immersion, and the wetting force stabilizes at about -0.4 N/m. The irregularities in the wetting curve are primarily due to the action of the flux, which flows into the solder bath from the upper part of the specimen.

The structure of the intermetallic formed at the interface during the wetting of bare Cu by eutectic solder is well known from previous studies. The surface and cross-sectional views of the wetted interface are shown in Figure 5. The primary intermetallic is the Cu_6Sn_5, η-phase. At the wetting temperature, 245°C, the equilibrium Cu_6Sn_5 intermetallic has the ordered, η structure, which mutates to the long period superlattice η' structure at 186°C[6]. The structure is basically hexagonal, and is reflected in the morphology of the growing intermetallic grains, which tend to form elongated spikes or whiskers perpendicular to the interface[6]. Eventually, a thin layer of ϵ-phase (Cu_3Sn) forms at the intermetallic-Cu interface, creating a composite layer of two intermetallic structures.

Cu Pre-Tinned with 95Pb-5Sn

The surface state of the pre-tinned Cu surface is shown in Figure 6a. The 95Pb-5Sn pre-tinning layer forms a thin, rough film of η-phase intermetallic on the copper surface. The intermetallic depletes Sn from the pre-tin coating, which raises its melting point. However, the pre-tinned layer melts on contact with the 245°C solder bath. The interfacial intermetallic then partially dissolves to re-establish the wetted interface.

The wetting curve for Cu pre-tinned with 95Pb-5Sn is shown in Figure 4a. The wetting force increases rapidly to asymptote at a value of $\approx$ -0.36 N/m. The incubation time for the initiation of wetting is slightly longer than that for pure copper, largely due to the need to dissolve the pre-tinned layer. While the measured asymptotic value of the wetting force is slightly less than that on pure copper, this value is subject to experimental error (due, for example, to the alignment of the specimen in the bath) and is somewhat imprecise. A direct measurement of the height of the meniscus on specimens observed after wetting yields a meniscus height about 3% greater than that on pure copper, which suggests that the pre-tinned layer promotes wetting. The surface state after wetting is shown in Figure 6b. The intermetallic layer appears finer-grained than that originally

present in the pre-tinned layer, which suggests that the original intermetallic is removed and reconstituted during wetting, either by dissolution or thermal spall from the interface.

The pre-tinned layer was aged at 170°C for 6 days to simulate shelf aging and baking prior to soldering. The state of the aged surface is shown in Figure 7a. During aging spikes or whiskers of the η-phase grow through the pre-tinned layer and expose their tips at the free surface. The cross-section of the layer in Figure 7c reveals a thin intermetallic coating from which the η-phase spikes protrude. The Cu-Sn phase diagram (Figure 2) suggests that the η-phase will eventually convert into the Cu-rich ε-phase. This has not happened after 6 days aging, possibly for kinetic reasons associated with the morphology of the layer (there may be a thin ε-phase layer at the Cu interface that is undetected in this work).

The wetting curve for the aged 95Pb-5Sn sample is shown in Figure 4b. The wetting kinetics are very nearly the same as for the unaged specimen. The only apparent change is in the meniscus height measured after wetting, which is « 6% below that on the unaged specimen, suggesting a slightly negative contribution to wetting. The relatively small effect of the exposed intermetallic is consistent with its low areal fraction in the surface of the pre-tinned layer.

Cu Pre-Tinned with 37Pb-63Sn

The wetting curve of an unaged sample pre-tinned with 37Pb-63Sn is shown in Figure 4c. Good wetting is obtained, and the kinetics of wetting resemble those of 95Pb-5Sn specimen. The interfaces of both the pre-tinned layer and the wetted sample are coated with a thin, rough layer of primarily η-phase.

The microstructure of the eutectic pre-tinned layer changes significantly during aging for 6 days at 170°C. As shown in Figure 8, the η-phase converts into the Cu-rich ε-phase. The residual Pb dewets from the intermetallic, and withdraws into discrete, irregular islands on the interface, so that the residual surface contains a significant fraction of ε-phase. The kinetics of wetting are dramatically slowed (Figure 4d). The wetted surface has a final cross-section like that shown in Figure 8d. The ε-phase is coated with an irregular layer of the Sn-rich η-phase. The poor quality of bonding at the interface is apparent from the figure.

There are two reasons for poor wetting at the aged interface. First, the ε-phase intermetallic oxidizes on exposure to air[7,8] and is poorly wet by solder. Wetting requires the breakdown of the oxide coating through the action of the molten solder and flux, and is hence retarded. Second, the Cu-Sn phase diagram shows that the equilibrium phase in contact with a Sn-rich medium is the Sn-rich η-phase rather than the Cu-rich ε-phase. As suggested by the cross-section in Figure 8d, the wetting reaction involves the conversion of ε-phase to η-phase at the wetted interface, which may be a kinetically slow process since it requires the dissolution of ε-phase. The cross-section suggests that good bonding is only attained over those portions of the interface where η-phase has formed. Since the reaction is incomplete, only partial bonding is obtained.

CONCLUSION

The results of the preliminary experiments reported here illustrate the effectiveness of pre-tinning in maintaining the solderability of Cu surfaces. Pre-tinning with Pb-rich solder (95Pb-5Sn) is particularly effective since solderability is preserved even after a relatively long aging treatment. On the other hand, pre-tinning with eutectic solder risks the loss of solderability during aging or baking due to surface exposure of an ε-phase intermetallic with poor wetting properties.

ACKNOWLEDGEMENT

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Table 1: Wettability Test Parameters

IMMERSION TIME:	10 s
IMMERSION DEPTH:	4 mm
IMMERSION SPEED:	15 mm/s
SPECIMEN WIDTH:	25.4 mm
SPECIMEN THICKNESS:	0.84 mm
BUOYANCY FORCE:	6.934E-03 N/m

Figure Captions

Figure 1.　Schematic illustration of typical contact angle: (a) $\theta > 90°$, no wetting or de-wetting; $\theta < 90° > 0°$, adequate wetting; $\theta = 0°$, complete wetting.

Figure 2.　A binary Cu-Sn phase diagram.

Figure 3.　Wetting profile of clean, bare Cu substrate.

Figure 4.　Wetting profiles: (a) Cu pre-tinned with 95Pb-5Sn; (b) Cu pre-tinned with 95Pb-5Sn aged at 170°C for 6 days; (c) Cu pre-tinned with 37Pb-63 Sn; (d) Cu pre-tinned with 37Pb-63 Sn aged at 170 °C for 6 days.

Figure 5.　SEM micrographs of the wetted interface of Cu specimen: (a) surface; (b) cross-section. XBB 912-1138

Figure 6.　SEM micrographs of Cu pre-tinned with 95Pb-5Sn: (a) surface before wetting; (b) surface after wetting. XBB 912-1139

Figure 7.　Cu pre-tinned with 95Pb-5Sn aged at 170°C for 6 days: (a) and (b) SEM micrographs of the surface before and after the wetting; (c) and (d) optical micrographs of the cross-section before and after the wetting. XBB 912-1140

Figure 8.　Cu pre-tinned with 37Pb-63 Sn aged at 170°C for 6 days:(a) and (b) SEM micrographs of the surface before and after the wetting; (c) and (d) optical micrographs of the cross-section before and after the wetting. XBB 912-1137

(a)

(b)

liquid metal

θ

θ

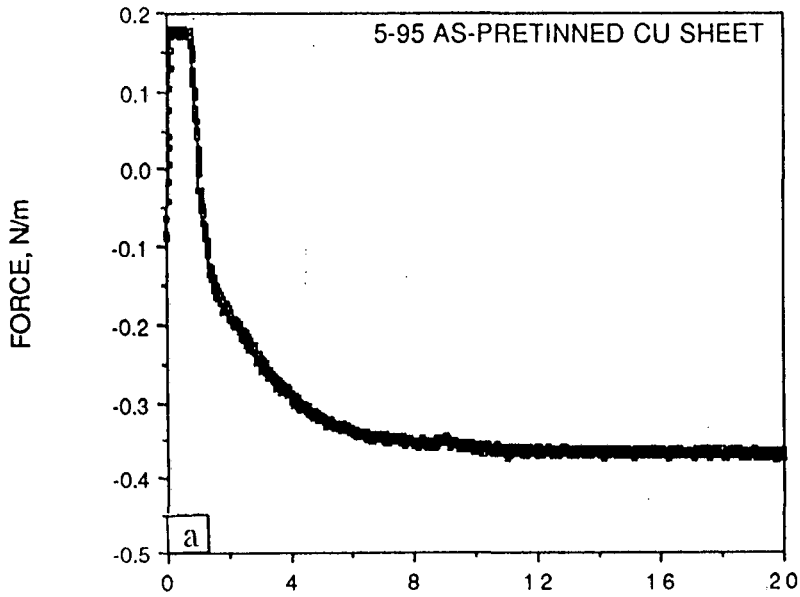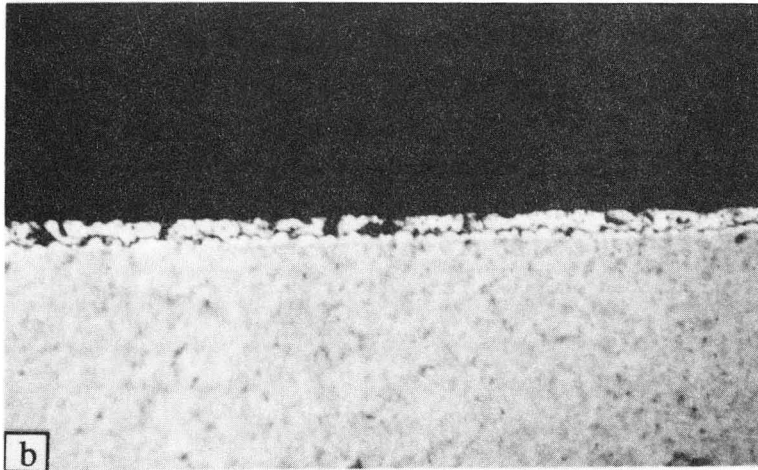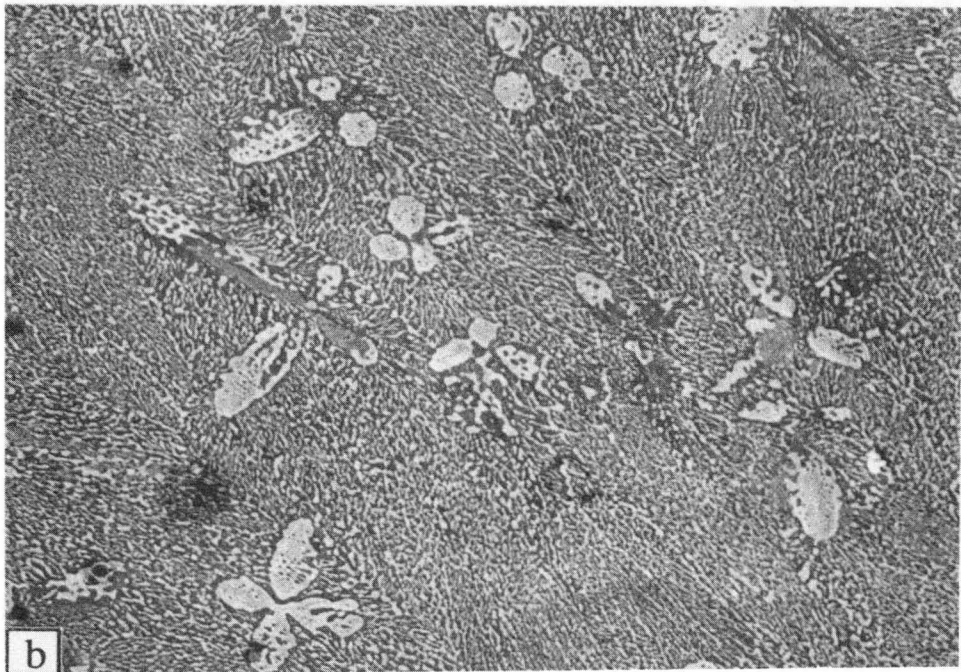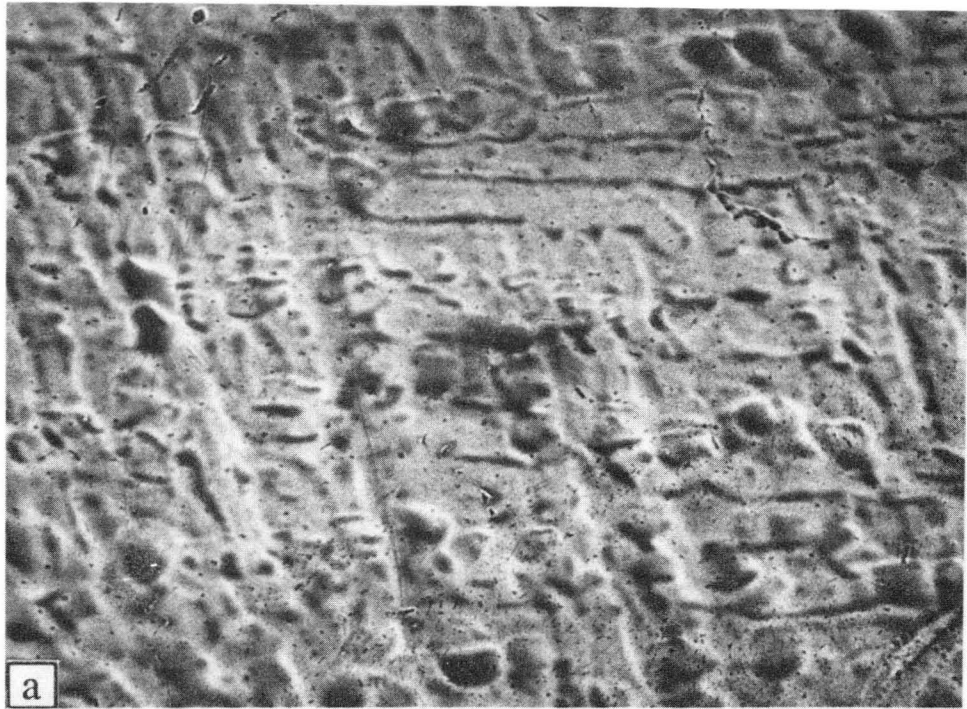liquid metal

solid metal

(c)

liquid metal

solid metal
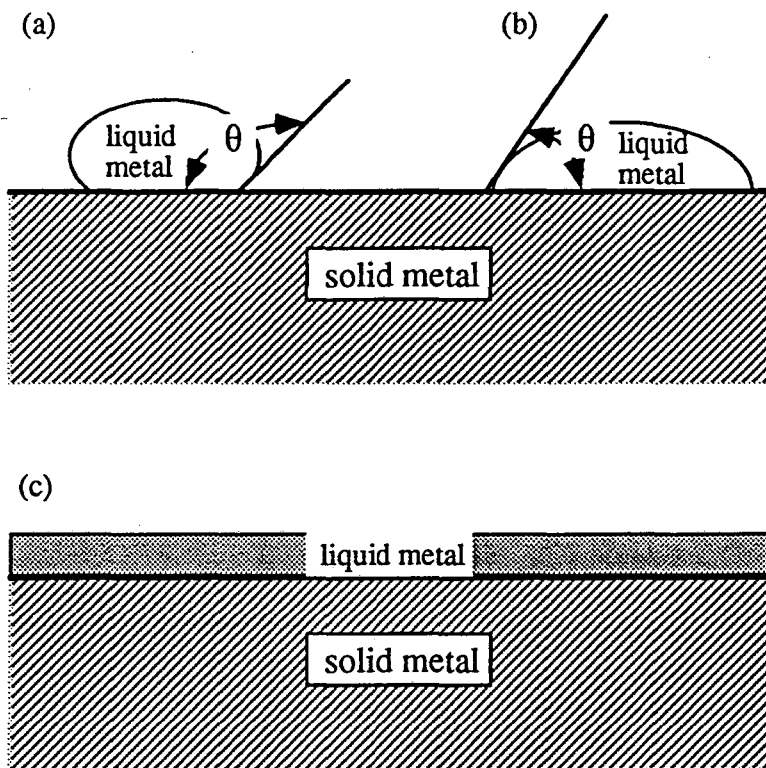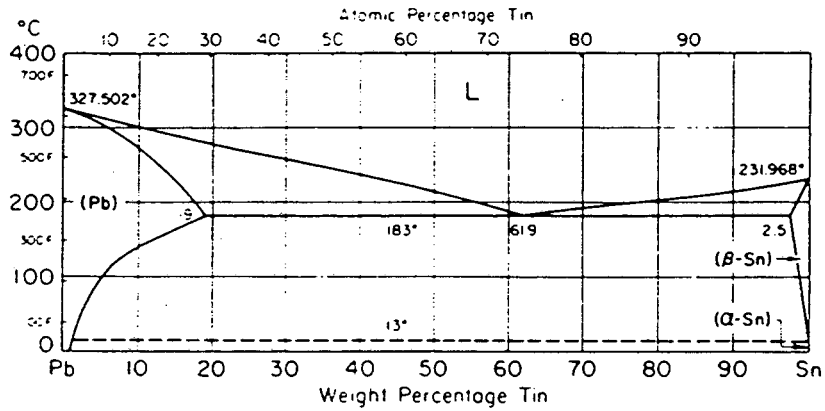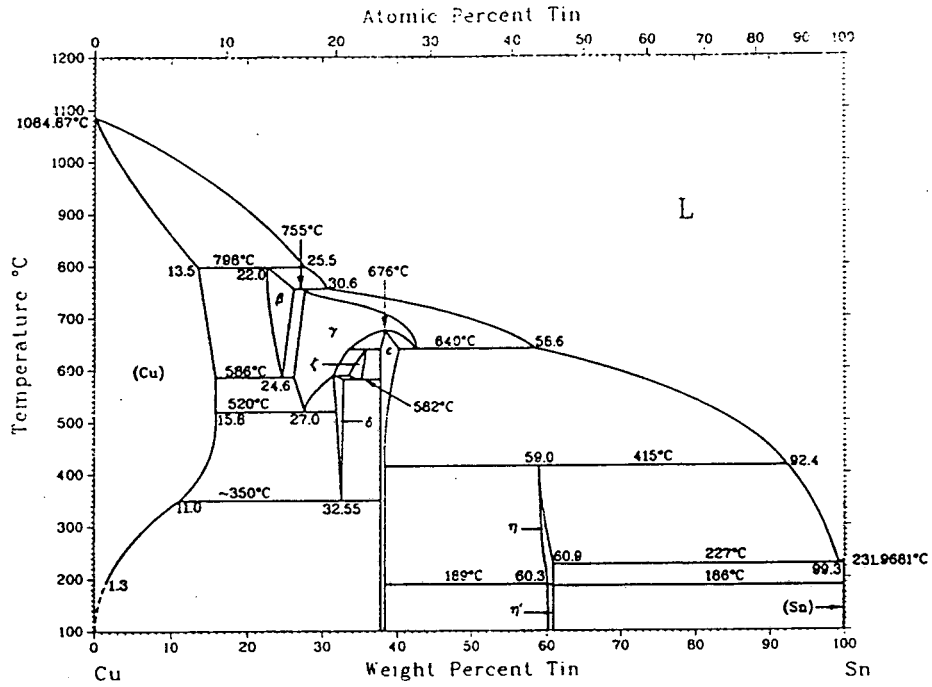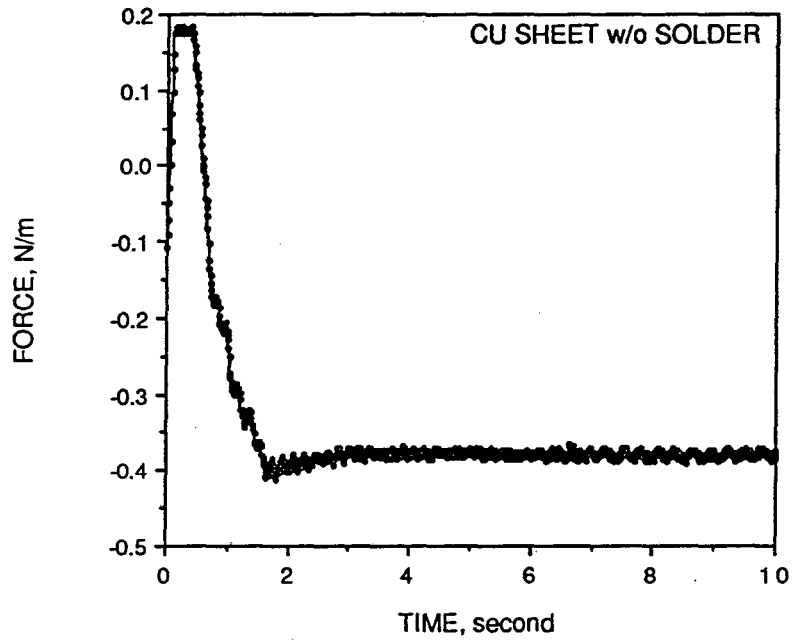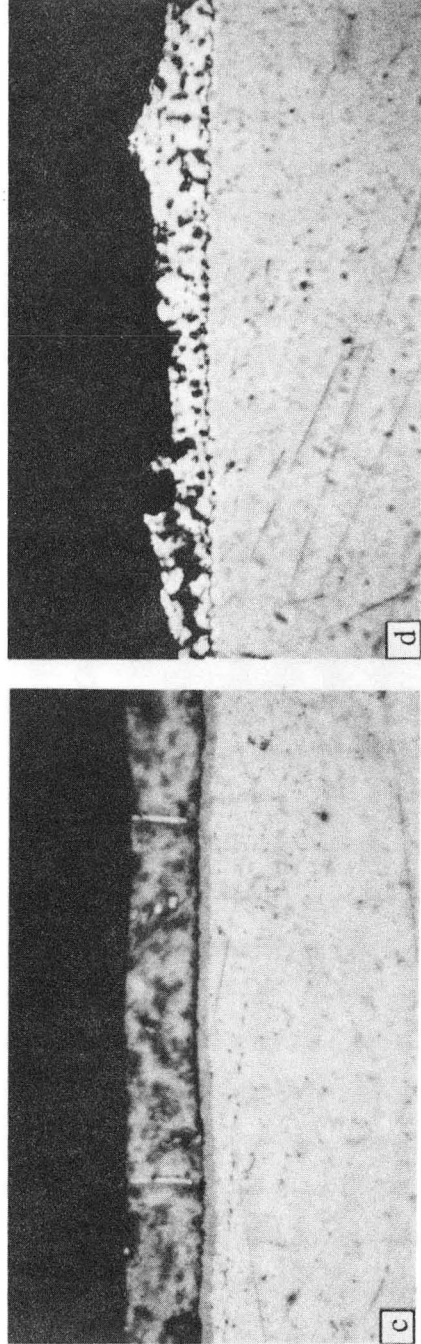
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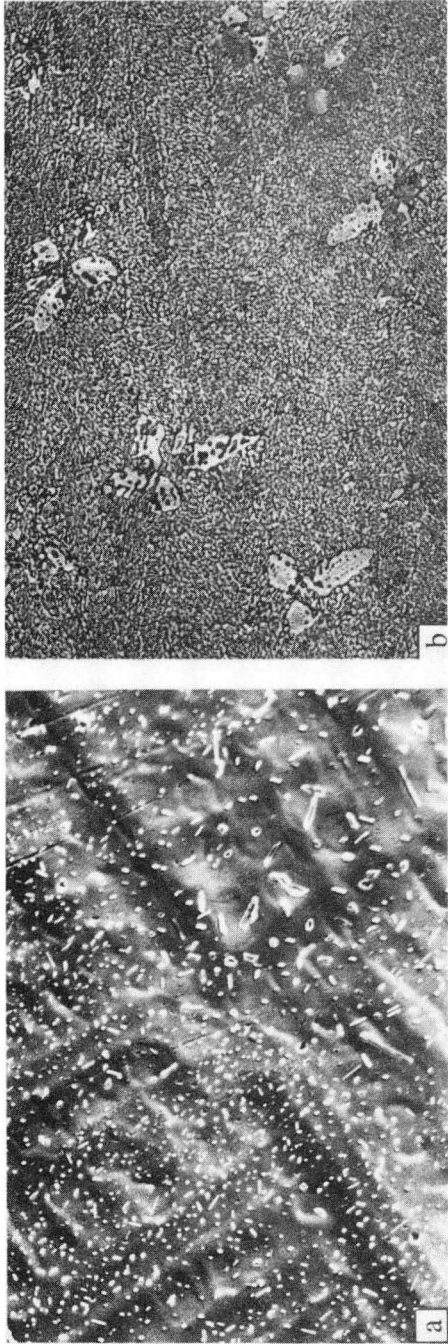
Figure 2

Figure 3
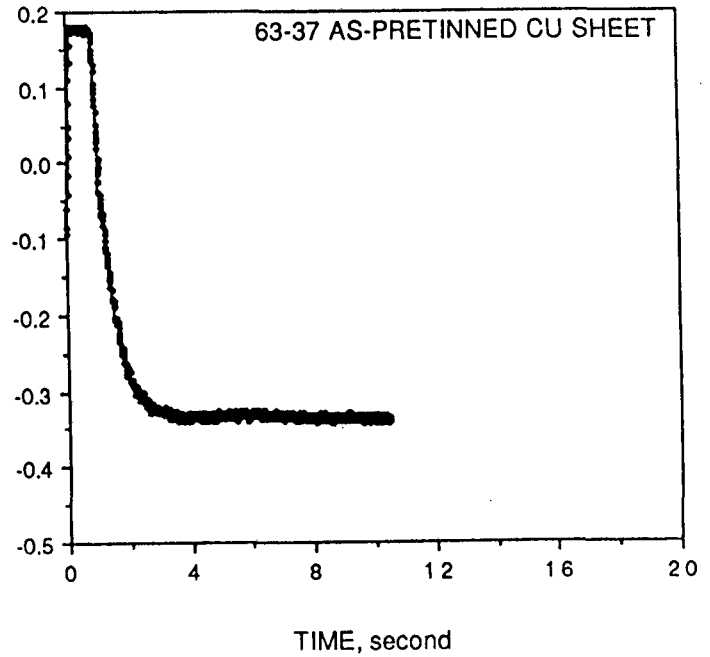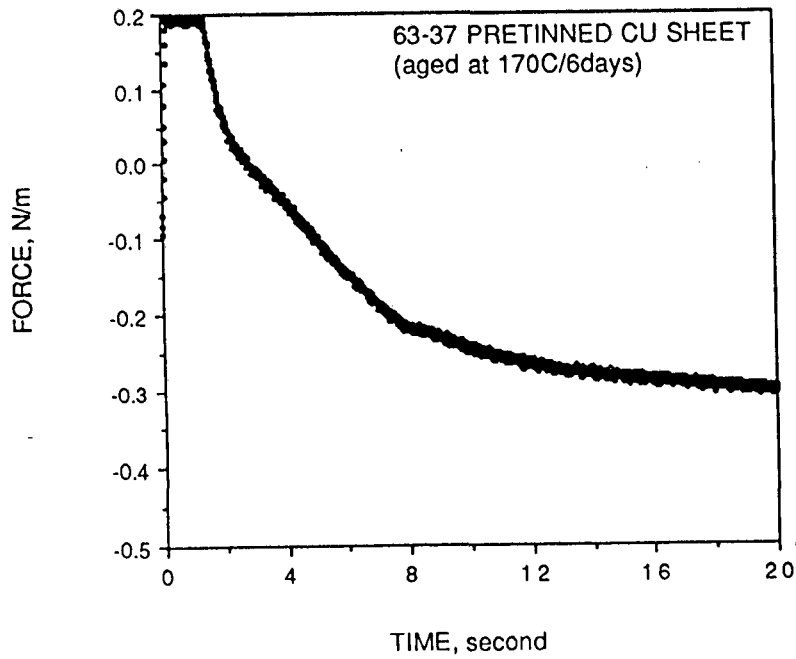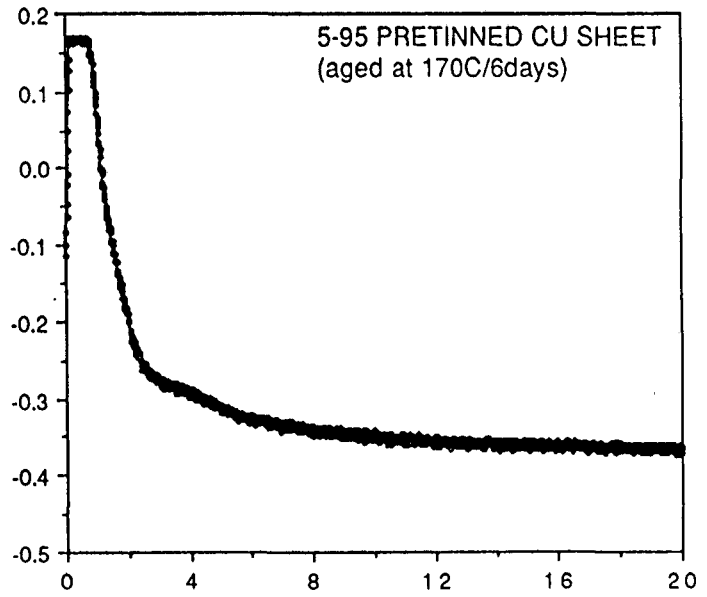
Figure 4

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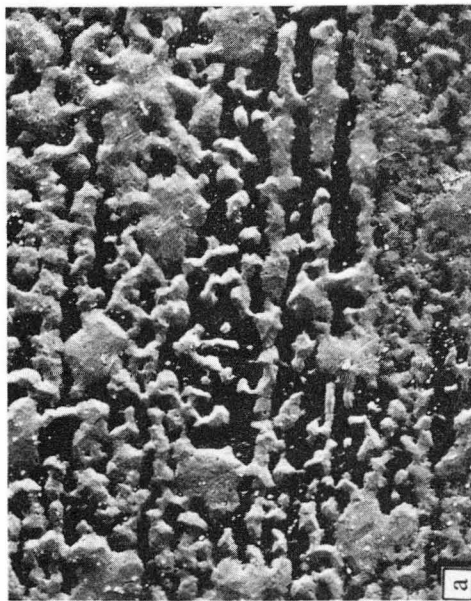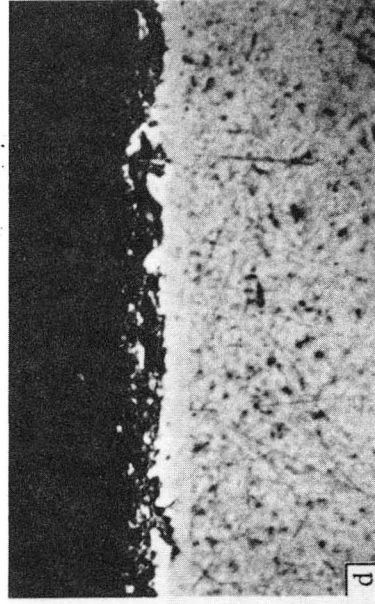

10 μm

Figure 5

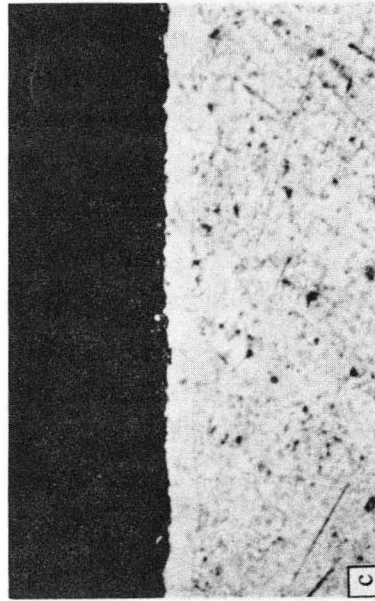20 μm

Figure 6

Figure 7

20 μm

10 μm

Figure 8

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