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Laser Ablative Fluxless Soldering (LAFS):
60Sn-40Pb Solder Wettability Tests
on Laser Cleaned OFHC Copper Substrates

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Abstract

OFHC copper substrates, cleaned by laser ablation under argon and helium gas, were tested for solder wettability by 60Sn-40Pb using an area-of-spread method. The wettability of copper surfaces cleaned under both argon and helium gas was found to equal or exceed the wettability obtained on this surface in air using a standard RMA flux. The area of spread on copper substrates cleaned under helium was eight times larger than the area of spread of substrates cleaned under argon. The enhanced spreading observed on the substrates cleaned under helium gas was found to be due to surface roughness.

1.0 Introduction

Solder alloys are used extensively as a joining material in electronic circuits. Most of the techniques commonly employed to form joints with solder involve the use of a chemical flux. The primary function of the flux in the soldering process is to improve the wetting of joining surfaces by the molten solder alloy. Wetting of these surfaces is essential to the formation of a strong metallurgical bond. The flux accomplishes this function by breaking up surface oxides and other surface residues at the joining surfaces, allowing the active element in the solder (usually tin) to react directly with the base metal. The flux also protects both the solder and the joining surfaces from oxidation and enhances heat transfer from the heat source to the solder alloy and base metal.1)

However, fluxes by their very nature contain components such as acids and halide salts that are corrosive to metals. These chemicals remain as residues on circuit components after formation of the solder joint. If not removed, these flux residues can promote corrosion of metallized conductive paths in the circuit, eventually leading to failure due to an open conduction path. Flux residues can also decrease the resistivity of the substrate between adjacent conduction paths on a printed circuit board resulting in leakage currents. In electronic systems where high reliability is a major concern, assembled circuit boards are washed extensively to remove all traces of flux residue. The two solvents most widely used to deflux printed circuit boards are 1,1,1-trichloroethane and 1,1,2-trichloro-1,2,2-trifluoroethane.2)

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DISCLAIMER

The United States Clean Air Act, reauthorized in 1991, requires U.S. industries to eliminate all non-essential uses of these two solvents, as well as many other chlorinated hydrocarbons and chlorofluorocarbons, over the next decade. This phase-out will include the use of these solvents in cleaning applications. Electronics manufacturers must either adopt alternative cleaning solvents for use in the defluxing of electronics assemblies or utilize new soldering processes that do not require the use of a chemical flux.

Several fluxless soldering processes are currently being developed.[3] These processes utilize either reactive gases (hydrogen or organic acid vapors), plasmas (hydrogen or inert gas), or mechanical activation (i.e. ultrasonics) to either chemically or mechanically breakup metal oxide films on joining surfaces. In this paper, we present the results of initial wettability tests for a new fluxless soldering process. We have named this process laser ablative fluxless soldering (LAFS). LAFS utilizes laser ablation in a noble gas environment to remove surface oxides and other contaminants from joining surfaces. Laser ablation is used extensively in thin film processing, especially to etch organic polymers in microelectronics fabrication.[4] However, to the best of our knowledge, this technology has not been previously utilized in soldering applications.

The LAFS joining process must be performed under a noble gas environment to prevent contamination of joining surfaces by reactive gases in the ambient atmosphere. In the ablative step, a Q-switched pulsed laser beam is mechanically scanned across all joining surfaces to remove surface oxides. The very short ($\approx$ 10 nsec) pulses of laser radiation rapidly heat and vaporize very thin layers (100 to 5000 Å) of surface material. The vaporized material rapidly condenses on contact with the cooler ambient gases forming submicron particles that are easily carried away from the surface by a flowing gas stream. These particles can be totally removed from the process gas steam using a submicron total capture filter. The filter canister is the final disposal container for this waste material. However, if the ablated material contains precious metals, these metals can be easily recovered from the filter medium. The noble gas can also be recycled after purification in a titanium chip tube furnace. In the LAFS process, the noble gas environment also functions to prevent recontamination of the laser ablated surface during the period between completion of the ablation step and application of solder to the joining surfaces. Solder application and joint formation can be accomplished using many of the standard techniques normally employed in flux based solder processes.

Laser ablative fluxless soldering exhibits some very attractive process characteristics not present in other controlled atmosphere fluxless soldering techniques. No reactive chemicals are employed in the laser ablative cleaning process. Therefore, there is no possibility that the process will leave behind any type of residue on the surface that could accelerate corrosion or any other form of material degradation. The incident laser energy can be adjusted to allow selective removal of the metal oxide film without significant overetching into the metal substrate. Etching terminates at the interface between the oxide film and the substrate due to the high surface reflectivity of the metal.[5] Because etching is limited to the oxide film, the waste generation rate of the laser ablative cleaning process is extremely small. For an oxide film formed on a copper surface in air at room temperature (typically 100 Å thick), the waste generation rate for the ablation step in this fluxless soldering process will be roughly 60 mg of metal oxide per square meter of surface cleaned.

The laser ablative cleaning process can also be performed with very high spacial resolution. Complete control of beam size and position allow selective removal of surface oxides over complex surface patterns. Since the solder will not wet surfaces from which the oxide has not been removed, a simple mechanism is available for the control of solder spreading. The Q-switched laser also exhibits a very short duty cycle. As a result, the time averaged laser power absorbed by the ablated surface is small, resulting in minimal heating of joining surfaces or adjacent structures. This allows application of the process on or near thermally sensitive components. The combination of high spacial resolution and low thermal impact makes LAFS an attractive process for application on high density printed circuit boards. Because no solvents or reactive chemicals are utilized by, or as a result of this process, chemical/materials compatibility is not an issue.

A soldering process cannot form an acceptable joint between two materials if it does not induce wetting of those materials by the solder alloy. The objective of this study is to characterize the wettability of oxygen free high conductivity (OFHC) copper by 60Sn-40Pb (wt. %) solder following removal of the surface oxide by laser ablation. The results of this study will provide a quantitative assessment of the ability of the LAFS process to form solder joints using these materials.

2.0 Experimental Procedure

All substrates used as wettability test specimens in this study were 1 cm square coupons of OFHC copper 0.3 mm thick. Each substrate was oxidized by heating in air at 220° C for approximately 2 minutes until the surface exhibited a uniform brown tint. This surface tint corresponds to an oxide thickness of 200 to 400 Å.6) The oxide film thickness normally encountered on air oxidized copper solder pads in commercial electronics manufacturing is normally less than 100 Å thick.6) Consequently, the oxidized substrates used in this study represent a conservative test of the cleaning step in the laser ablative fluxless soldering process.

The laser ablative cleaning of copper substates and subsequent wettability tests were performed in a stainless steel chamber under an atmosphere of noble gas. A schematic diagram of the chamber is shown in Figure 1. The copper substrates were placed in the chamber a hot plate. The chamber was closed and evacuated to 0.1 torr pressure to remove the ambient air. The chamber was then backfilled with noble gas to an absolute pressure of 625 torr. This evacuation/back fill cycle was repeated two more times to ensure that all of the oxygen and nitrogen gas in the chamber had been removed. The noble gases used in this study were either 99.999% pure helium or 99.999% pure argon. Nitrogen gas cannot be used in the laser ablative cleaning step due to the very high gas temperatures (3000 to 10,000 K) generated by the laser ablation process in the near surface region above the substrate. These temperatures are high enough to dissociate diatomic nitrogen resulting in rapid nitridation of the substrate surface.

Laser ablative cleaning of copper substrates was accomplished by scanning a pulsed laser beam across the surface of the substrate. The coupon was maintained at a temperature of 220° C during the cleaning process. Any circulation of the noble gas in the chamber was due entirely to convection. The laser used for ablative cleaning was a Q-switched Nd:YAG laser with an output wavelength of 1.064 μm, a pulse length of 10 nsec, and a pulse repetition frequency of 10 Hz. The irradiance profile of the laser beam was gaussian in shape with a diameter ($1/e^2$ points) of 5.9 mm. The pulse energy of the laser was 850 mJ. The laser beam was scanned across the substrate surface at a linear rate of 5 mm/sec with a 5 mm separation between adjacent scan tracks. The beam was directed onto the copper substrate through a UV grade quartz window located in the top of the chamber. The beam was incident on the substrate surface at an angle of 2° with respect to surface normal to prevent optical feedback into the laser cavity. No laser beam focusing element was employed.

The wettability of the laser cleaned substrate surfaces was measured using an area-of-spread (sessile drop) method.7) This wettability test measures the contact angle of the solder on the substrate at equilibrium. A decrease in contact angle corresponds to an increase in surface wettability. In the sessile drop test, a solder drop of known volume is deposited on a substrate surface at a temperature which is greater than the melting temperature of the solder. The molten solder is allowed set on the surface of the substrate until the apparent spreading of the solder drop on the surface is complete (2 minutes). The solder and the substrate are then cooled to room temperature. The contact angle of the solder with respect to the substrate is determined from the area of spread of the solder on the substrate assuming that the solder forms a perfect spherical cap on the substrate surface. The contact angle θ is given by the equation:

$$\text{Tan}\ \theta = \frac{2\ b\ (j - k)}{b^2 - (j - k)^2}$$

where b is the radius of the base of the spherical cap, j and k are coefficients given by the following formulas:

$$j = \left\{ \left[\left(\frac{3\ V}{\pi} \right)^2 + b^6 \right]^{1/2} + \frac{3\ V}{\pi} \right\}^{1/3}$$

$$k = \left\{ \left[\left(\frac{3\ V}{\pi} \right)^2 + b^6 \right]^{1/2} - \frac{3\ V}{\pi} \right\}^{1/3}$$

and V is the initial volume of the solder drop.

All wettability tests were conducted at a substrate temperature of 220° C. Solder was placed in contact with the laser cleaned substrate surface within one minute after completion of the laser ablative cleaning step. The solder was deposited on the substrate surface in the form of a small ball using a pair of needle nose tweezers mounted on the end of a wobble stick. The tweezers were loaded with sufficient compressive force to hold a solid ball but would release the ball once the solder became molten. The tips of the tweezers were oxidized to prevent the adhesion of molten solder. Each solder ball contained 9 mg of solder composed of 60 wt.% Sn and 40 wt.% Pb. The solder contained no chemical flux. The density of the solder at this composition was 8.5 g/cm^3. The solder was allowed to equilibrate on the substrate surface at 220° C for two minutes and then rapidly cooled to room temperature. The area of spread of the solder drop was measured at room temperature by planimetry from magnified optical photographs of the copper substrates.

Selected wettability test specimens were cross-sectioned to reveal the microstructure of the solder/copper interface. This microstructure was examined using a combination of optical metallography, scanning electron microscopy, electron microprobe, and electron backscatter imaging techniques. The metallography samples were etched with an ASTM standard E407 #26 ferric chloride etch. The elemental composition of the interface was examined with a JEOL JXA-8600 electron microprobe x-ray analyzer operated at an acceleration potential of 25 kV and a beam current of 31 nA. The x-ray spacial resolution of these quantitative measurements is approximately 1 μm. Calibration of x-ray line positions and intensities was accomplished using pure metal standards or binary compounds for all elements reported. A $\Phi(\rho,Z)$ algorithm was used to convert the raw count data into weight percentages.8)

3.0 Results

3.1 Wettability Tests

Four oxidized copper substrates were cleaned by laser ablation under a helium inert gas environment and six substrates were cleaned under an argon environment. Copper surfaces cleaned under helium gas exhibited a matted surface finish with a burnt orange color. Surfaces cleaned under argon gas exhibited the normal metallic copper color.

The results of surface wettability tests on the laser cleaned copper substrates for 60Sn-40Pb solder are summarized in Table 1. Substrates cleaned under the two different gases showed a remarkable difference in surface wettability. The solder droplet obtained on substrate #8, which was cleaned under argon gas, is shown in Figure 2. The solder on this substrate formed a near spherical cap with an approximately round base. This result was typical of all solder droplets formed on copper substrates cleaned under argon gas. The solder contact angles calculated from the area of spread of the solder on these substrates ranged from 12° to 22°. As a baseline for comparative purposes, the contact angle measured for 60Sn-40Pb solder on OFHC copper in air using Alpha 611™ flux (Alpha Metals Inc.) was 23°.9) This flux is a rosin based, mildly activated (RMA) flux widely used in electronics manufacture.

The solder droplet obtained on substrate #9 is shown in Figure 3. This substrate was cleaned by laser ablation under helium gas. On this substrate, the 9 mg solder ball has spread out to cover almost the entire surface of the copper coupon. Similar results were obtained for the other three copper substrates cleaned under helium gas. The area of spread of the solder on these surfaces was typically 7 to 12 times larger than the area of spread observed on surfaces cleaned under argon gas. This indicates that the contact angle of 60Sn-40Pb solder on surfaces cleaned under helium is much smaller than the contact angle on surfaces cleaned under argon. The actual values calculated in Table 1 for the contact angle of 60Sn-40Pb solder on the substrates cleaned under helium gas are all less than 1°. However, these values are not expected to be very accurate because the geometric form of the solder droplet on the substrate surface does not approximate a spherical cap, and because the topography of the surfaces cleaned under helium are highly convoluted (see below). Because of the extremely large area of spread of the solder on copper substrates cleaned under helium gas, the solder layer on these surfaces is expected to be extremely thin. Assuming the solder coverage across the surface is uniform, the solder thickness on the four substrates cleaned under helium gas should fall between 12 and 16 μm based on the areas of spread for these substrates listed in Table 1.

3.2 Test Specimen Cross Section for a Copper Substrate Cleaned Under Argon Gas

Figure 4 shows a scanning electron microscope (SEM) image of the interfacial region between the solder and the copper substrate on sample #2 at low magnification. This substrate was cleaned by laser ablation under argon gas. The dark region in the lower portion of the SEM image is the copper substrate. The lighter region in the upper portion of the image is the solder. The interfacial boundary on this sample is very flat. No large gaps, voids, or cracks were observed between the solder and the substrate at any position along the interface.

An optical micrograph of the interfacial region on sample #2 is shown in Figure 5. The light region in the lower portion of the micrograph is the copper substrate. The dark region in the upper portion of the micrograph is the solder. A thin intermetallic layer is clearly visible between the substrate and the solder. The presence of this intermetallic layer indicates that a reaction has occurred between the copper substrate and one or more elements in the solder as the solder spread across the substrate. The intermetallic layer is composed of finger-like projections whose growth appears to originate at the copper boundary and extend into the solder. These finger-like projections exist in a range of sizes up to 5 μm in length and 2 μm in width. The intermetallic phase covers the entire boundary of the copper substrate.

Figure 6 shows an electron microprobe quantitative line scan for copper, tin and lead across the interfacial region on sample #2. The scan starts in the copper substrate and proceeds into the solder along a direction perpendicular to the copper/solder interface. The intermetallic zone begins at a position of 5 μm along the scan line and extends to 8.5 μm for a total width of 3.5 μm. The weight concentrations of copper and tin observed in this intermetallic region correspond to atomic concentrations of 52 at.% Sn and 43 at.% Cu. Examination of the equilibrium phase diagram indicates that a process temperature of 220° C, ε-Cu_3Sn and η-Cu_6Sn_5 phases would be expected to form at the copper-solder interface.10) The equilibrium Cu-Pb diagram shows that these two metals are virtually insoluble at this temperature. The ratio of atomic concentrations of copper to tin observed in the intermetallic zone on sample #2 is a very close match to Cu_6Sn_5. This intermetallic layer appears to contain approximately 3 at.% Pb as an impurity. Similar qualitative results were obtained at other positions along the interfacial region of the sample. At positions beyond the intermetallic zone along the scan line, the solder consists of lead rich granular phases suspended in a solid matrix rich in tin. This granular structure, which can be seen in Figure 4, is typical of bulk 60Sn-40Pb solder.[11)]

3.3 Test Specimen Cross Section for a Copper Substrate Cleaned Under Helium Gas

An SEM image of the interface region between the solder and the copper substrate on sample #13 is shown in Figure 7. This sample was cleaned by laser ablation under helium gas. The dark region in the upper portion of the SEM image is the epoxy mounting medium in which the sample is mounted. The lighter region in the lower portion of the image is the copper substrate. The solder is present as the bright layer directly above the copper. The boundary in this sample between the copper substrate and the solder is highly convoluted when compared to the boundary observed in Figure 4 for the copper substrate cleaned under argon gas. The maximum depth of the convolutions in this image is 50 μm. The solder is spread very thinly over the surface of this substrate as predicted from the area of spread value listed in Table 1. At all positions examined along the substrate surface, there is just sufficient solder present to fill the depth of the convolutions. Examination of regions of the substrate surface on sample #13 that are not covered by solder show the same degree of convolution. This indicates that the convolutions were caused by the laser ablative cleaning process and not by reaction of the copper substrate with the elemental components of the solder. The transformation of the substrate surface to a highly convoluted state during laser ablative cleaning under helium gas dramatically increases the exposed surface area of the copper substrate. Based on the magnitude of the convolutions present in Figure 7, the surface area of sample #13 is estimated to be greater than the surface area of sample #2 by a factor of 10.

An electron backscatter image of the solder layer on sample #13 is shown in Figure 8 at higher magnification. The dark region at the bottom of the image is the copper substrate. The dark region at the top of the image is the epoxy mounting medium. The lighter regions in the center of the image represent the high atomic weight phases in the solder containing tin and lead. Three different phases can be observed in the solder layer on this sample. The three phases are indicated by the letters A, B, and C in the figure. The results of electron microprobe analysis of the three phases at the indicated positions are given in Table 2. Phase A, which lies predominantly in the layer closest to the copper substrate, corresponds very closely to the stoichiometry for Cu_3Sn. Phase B is similar in stoichiometry to Cu_6Sn_5. This phase is confined predominantly to a thin layer, less than 1 μm thick, in the interfacial region between phases A and C. Phase C contains the bulk of the lead originally present in the solder but is severely depleted in tin. The composition of this phase is 19 at. % Sn, 73 at. % Pb, and 5 at. % Cu. The normal composition of 60Sn-40Pb is 72 at. % Sn and 28 at. % Pb.

<u>4.0 Discussion and Conclusions</u>

The data listed in Table 1 indicate that the wettability by 60Sn-40Pb solder of OFHC copper surfaces cleaned under argon or helium gas by laser ablation equals or exceeds the wettability obtained on this substrate using a common RMA flux in air. Wettability tests are a strong indicator of whether or not a soldering process is capable of forming a functional solder joint with a given solder alloy-base metal system. However, the microstructure of the interface between the solder alloy and the base metal also has a strong influence on the strength of the solder joint.

For copper substrates cleaned under argon gas, a cross section of the solder-copper interface reveals the presence of a Cu_6Sn_5 intermetallic layer between the copper and the solder which is nominally 2 μm thick. No voids between the copper and the solder are observed. The presence the Cu_6Sn_5 intermetallic layer at the interface indicates that reactive mixing has occurred between copper from the substrate and tin from the solder. The formation of this intermetallic layer is thought to be an important step necessary for the wetting of copper substrates by tin based solders.11) The microstructure of the bulk solder adjacent to this interface exhibits the granular structure typical of bulk 60Sn-40Pb solder. Solder joints with this microstructure generally have good bond strength.

On copper substrates cleaned under helium gas, the solder spread out into an excessively thin layer on the surface. The topography of the initial laser cleaned surface on these substrates was found to be highly convoluted. This convoluted surface topography forms a densely packed interconnecting network of grooves on the surface of the substrate. Each groove contains just enough solder to fill its depth. Very little solder is observed on top of the hills between the grooves. The confinement of the solder to the grooves on the surface of these substrates indicates that capillary forces played a dominant role in the solder spreading on these surfaces.12) The enhanced spreading of solder observed on the copper substrates cleaned under helium gas is due primarily to this capillary effect. The copper substrates cleaned under argon gas show a much smoother surface topography. Consequently, the geometric effect of capillary forces on these surfaces is greatly reduced and less solder spreading is observed.

The tin in the solder on copper substrates cleaned under helium gas has reacted extensively with the copper base metal. The solder volume confined to the grooves on the surface of these substrates is severely depleted in tin. Cu_3Sn is the predominant intermetallic phase formed at the copper-solder interface. In solder joints formed with flux in air, Cu_6Sn_5 is the predominant intermetallic phase observed at the interface between copper and 60Sn-40Pb solder.1) Cu_6Sn_5 was the only intermetallic phase observed on copper substrates cleaned under argon gas. The predominance of the Cu_3Sn phase as opposed to the Cu_6Sn_5 phase on copper substrates cleaned under helium gas suggests that the extent of reaction between tin and copper on this substrate was enhanced by the high surface area of base metal exposed to the solder, but limited by the availability of tin. The formation of thick Cu_3Sn intermetallic layers and tin depleted lead rich layers at copper-solder interfaces has previously been associated with solder joint embrittlement.1) However, the microstructure of the interface between the solder alloy and the base-metal on the copper substrates cleaned under helium gas in this study is an artifact of the limited amount of solder present at this interface. A greater solder volume at the interface would be expected to result in less tin depletion in the solder and predominantly Cu_6Sn_5 formation at the interface. This would result in a more favorable interface microstructure for solder joint formation.

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Table 1

Summary of contact angle measurements for OFHC copper substrates cleaned by laser ablation under argon or helium gas.

Sample ID	Inert Gas	Area-of-Spread (cm^2)	Contact Angle
#7	He	0.69	0.75°
#9	He	0.74	0.68°
#13	He	0.85	0.55°
#21	He	0.87	0.53°
#1	Ar	0.085	17°
#2	Ar	0.078	19°
#3	Ar	0.106	12°
#4	Ar	0.072	22°
#8	Ar	0.104	13°
#16	Ar	0.092	15°

Table 2

Summary of quantitative electron microprobe analysis of the three phases observed in Figure 8 at the copper-solder interface of a copper substrate cleaned under helium gas.

Phase	Elemental Composition (at. %)		
	Cu	Sn	Pb
A	73.8	25.0	0.1
B	47.4	48.4	2.5
C	4.8	19.0	72.9

Figure Captions

Figure #1	Schematic diagram of chamber configuration used for 60Sn-40Pb solder wettability tests on OFHC copper substrates cleaned by laser ablation under argon and helium gas.
Figure #2	Nine milligram 60Sn-40Pb solder droplet on OFHC copper substrate cleaned by laser ablation under argon gas. The graduations on the lower edge of the figure are spaced at 0.5 mm intervals.
Figure #3	Nine milligram 60Sn-40Pb solder droplet on OFHC copper substrate cleaned by laser ablation under helium gas. The graduations on the lower edge of the figure are spaced at 1.0 mm intervals.
Figure #4	Scanning electron microscope image of the copper-solder interface on a copper substrate cleaned by laser ablation under argon gas. The dark region in the lower portion of the image is the copper substrate. The lighter region in the upper portion of the image is the solder.
Figure #5	Optical micrograph of the copper-solder interface for a copper substrate cleaned by laser ablation under argon gas. The surface of this sample received a standard ferric chloride etch. The light region in the lower portion of the micrograph is the copper substrate. The dark region in the upper portion of the micrograph is the solder.
Figure #6	Electron microprobe quantitative line scan for Cu (solid line), Sn (short dashed line), and Pb (long dashed line) across the intermetallic zone of a copper-solder interface formed on a copper substrate cleaned by laser ablation under argon gas. The scan starts in the copper substrate and proceeds into the solder along a vector perpendicular to the copper-solder interface.
Figure #7	Scanning electron microscope image of the copper-solder interface on a copper substrate cleaned by laser ablation under helium gas. The dark region in the upper portion of the image is the epoxy mounting medium. The lighter region in the lower portion of the image is the copper substrate. The solder is present as the bright layer directly above the copper.
Figure #8	Electron backscatter image of the copper-solder interface on a copper substrate cleaned by laser ablation under helium gas. The dark region at the bottom of the image is the copper substrate. The dark region at the top of the image is the epoxy mounting medium. The lighter regions at the center of the image represent the high atomic weight phases in the solder containing tina and lead: A) Cu_3Sn phase, B) Cu_6Sn_5 phase, C) Pb rich phase.

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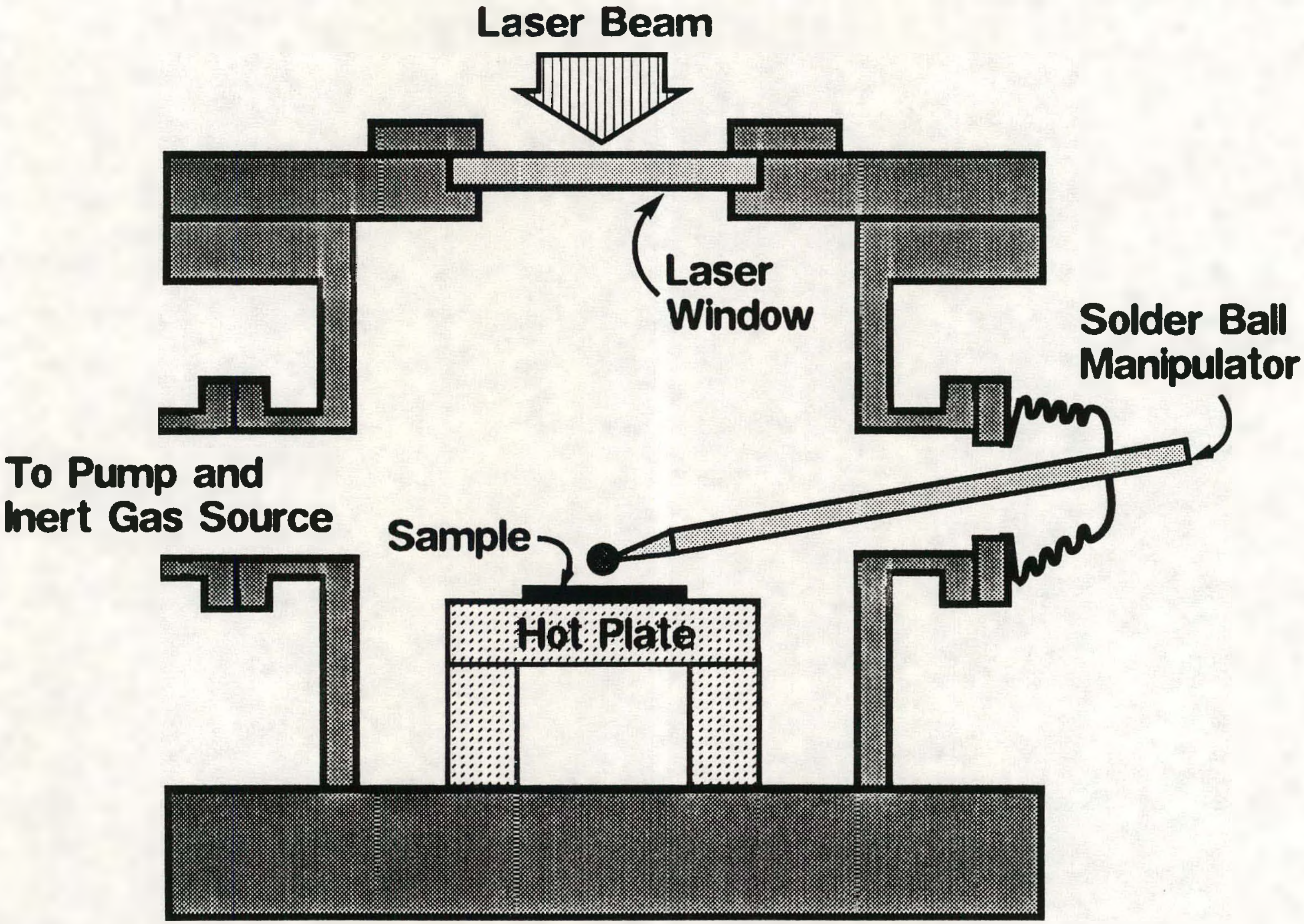

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Figure #1

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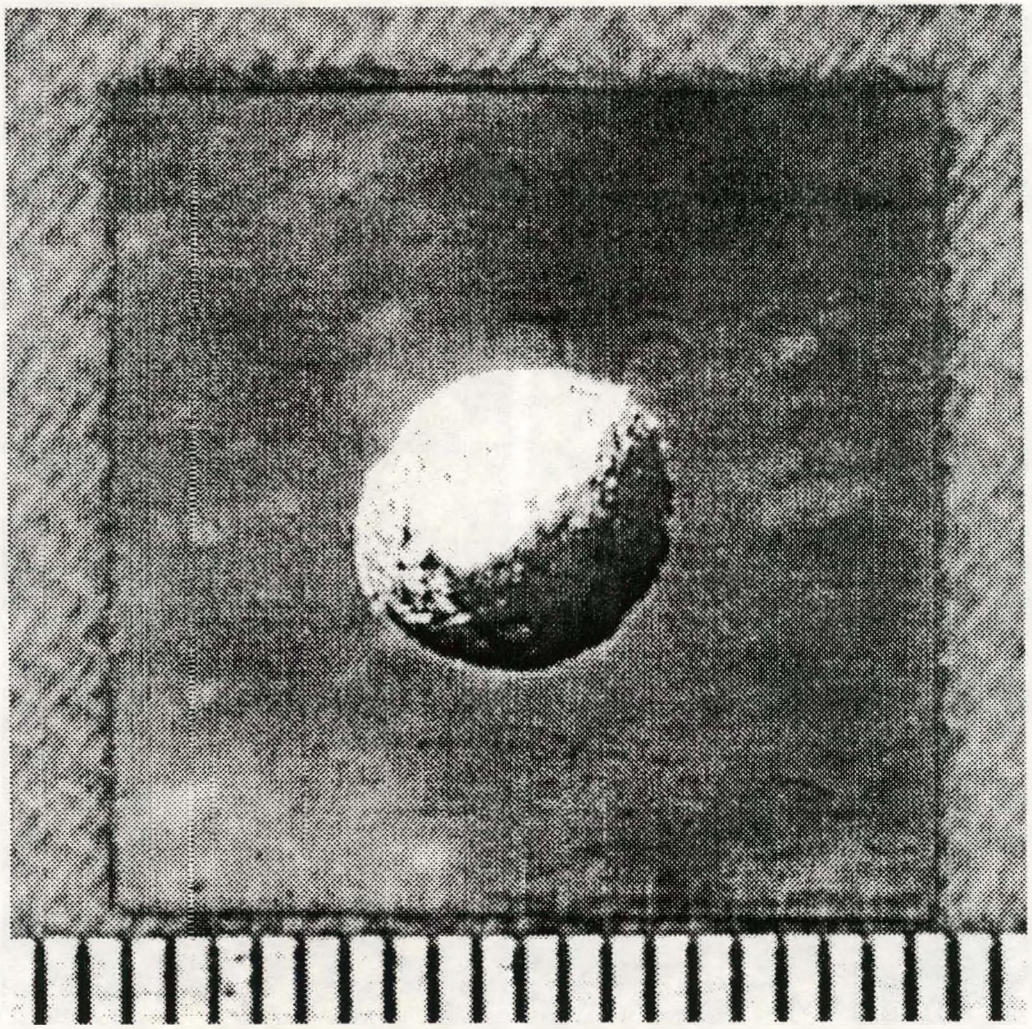

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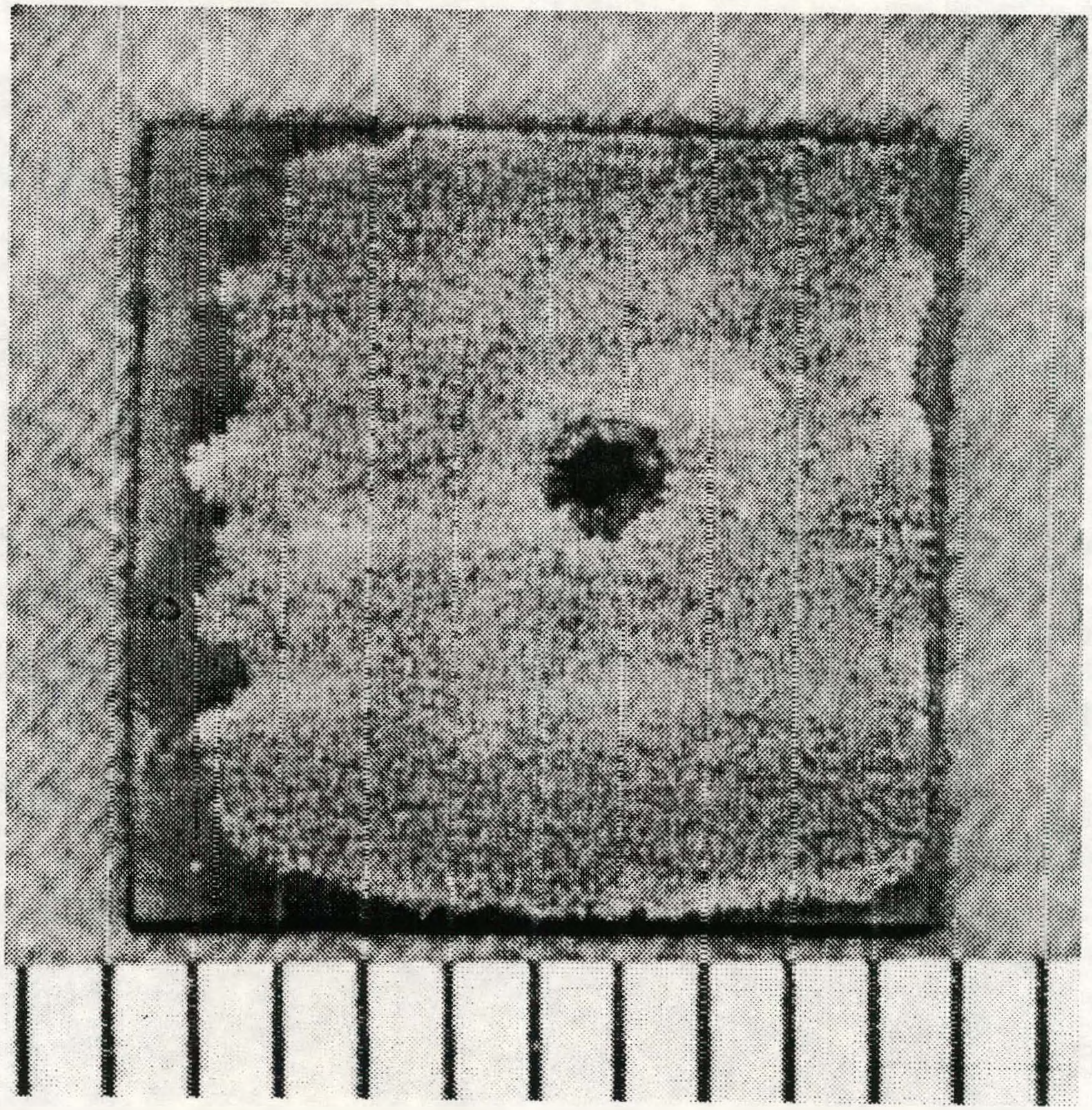

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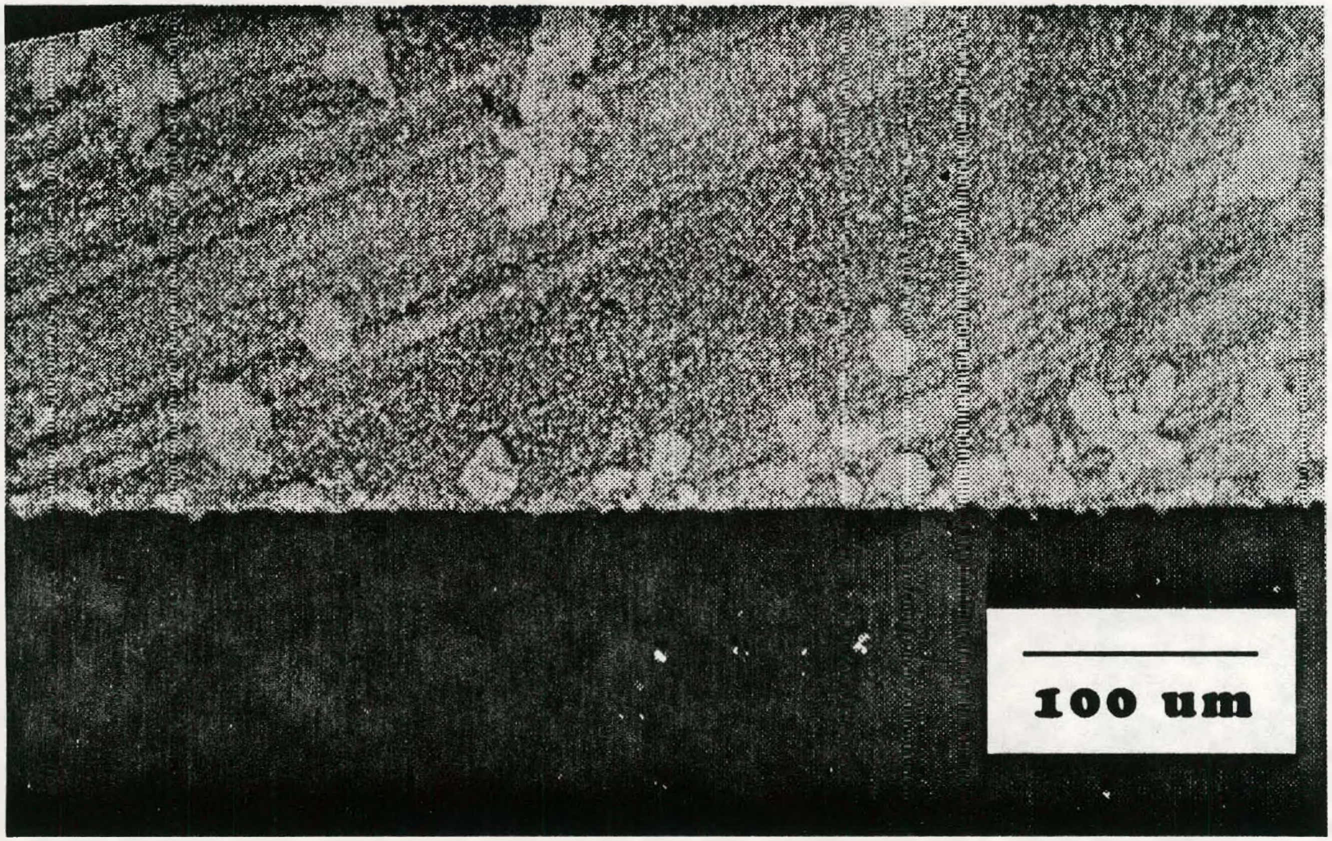

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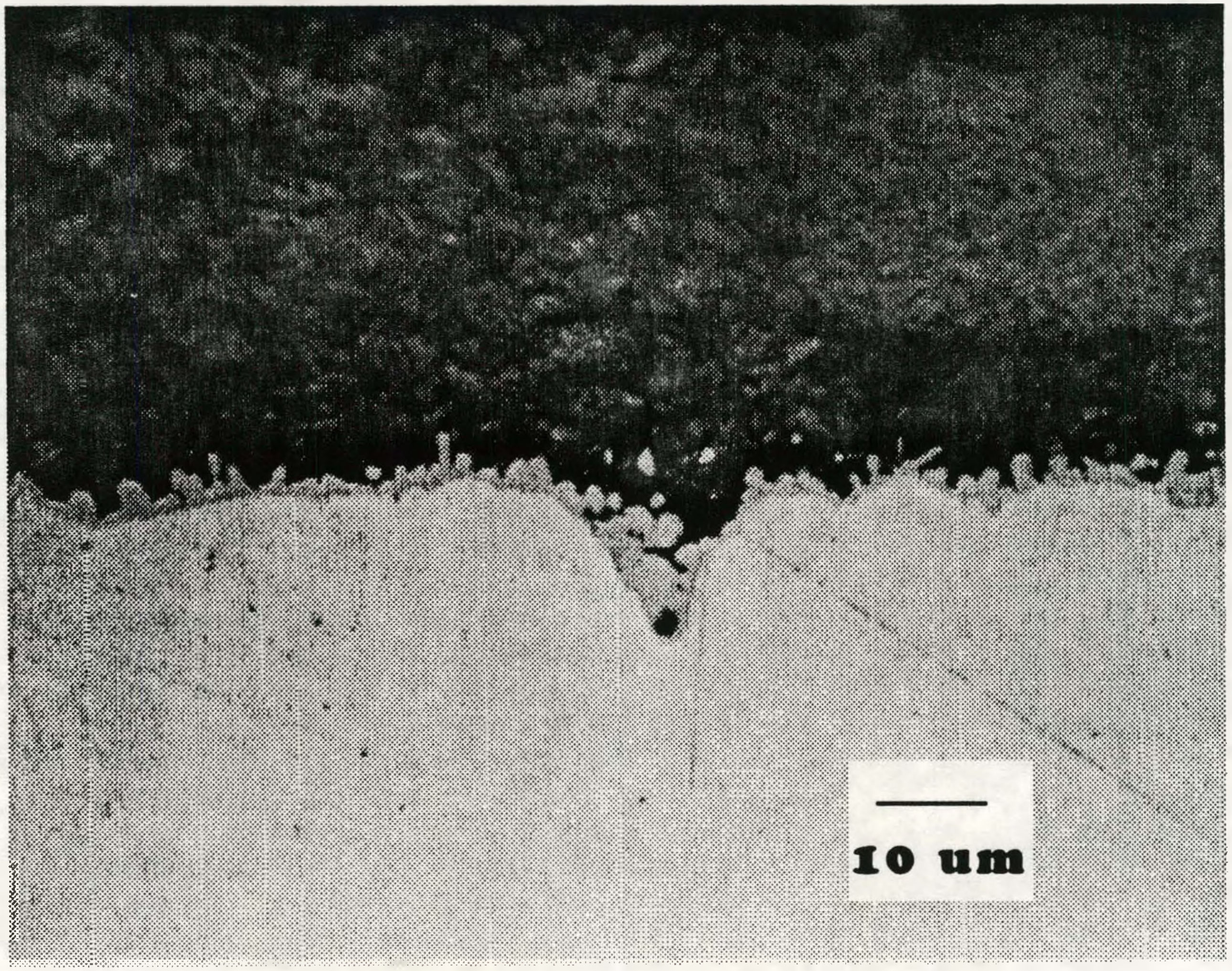

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Figure #5

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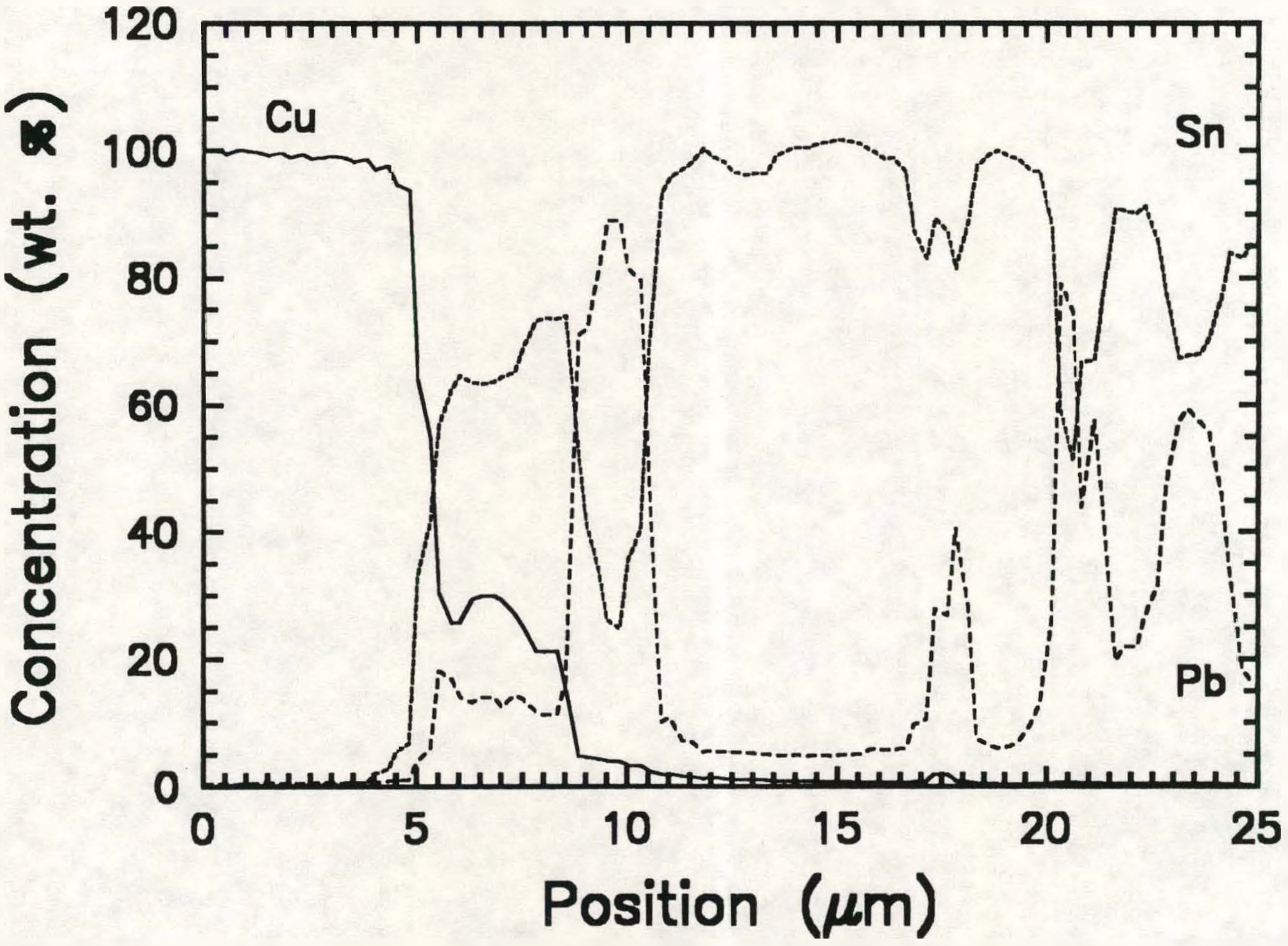

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Figure #6

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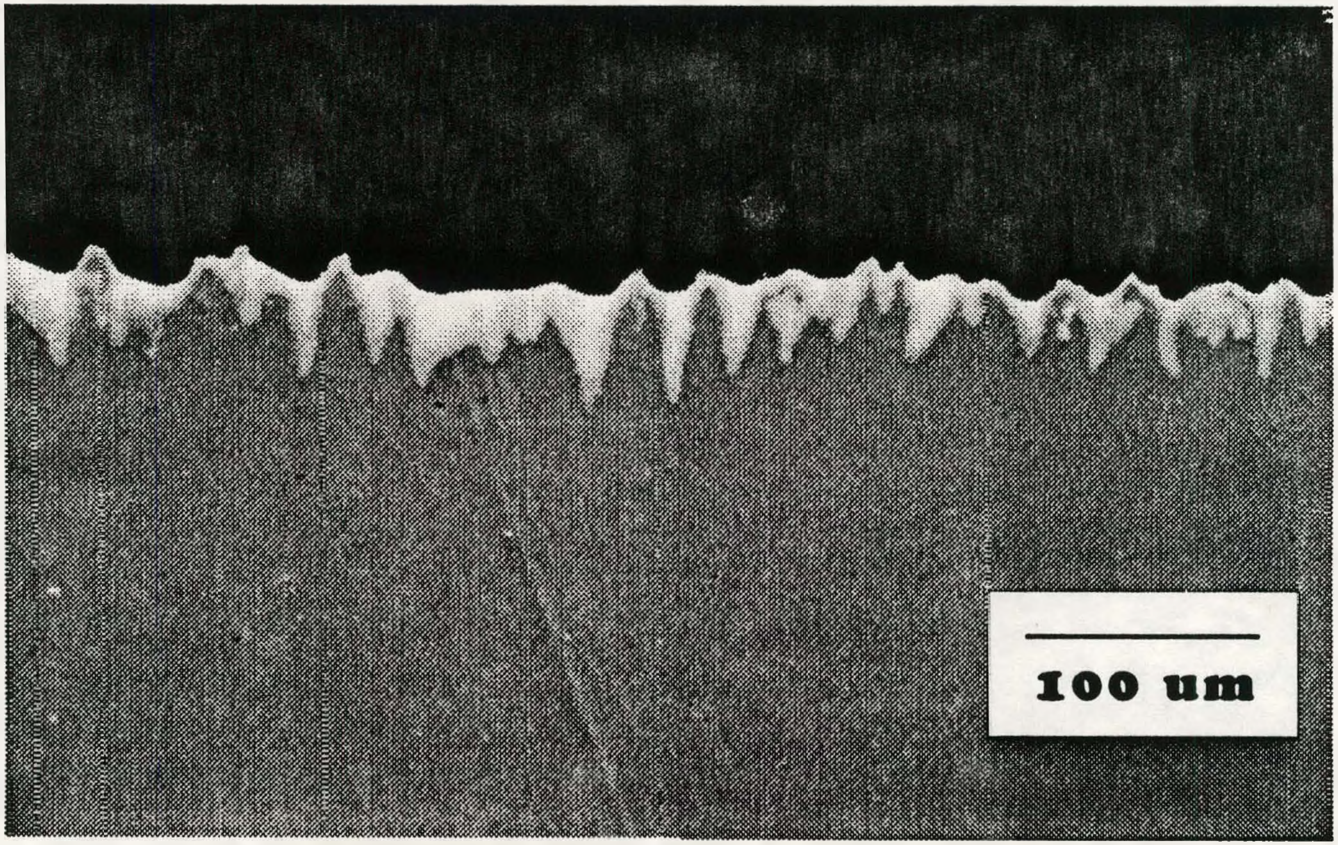

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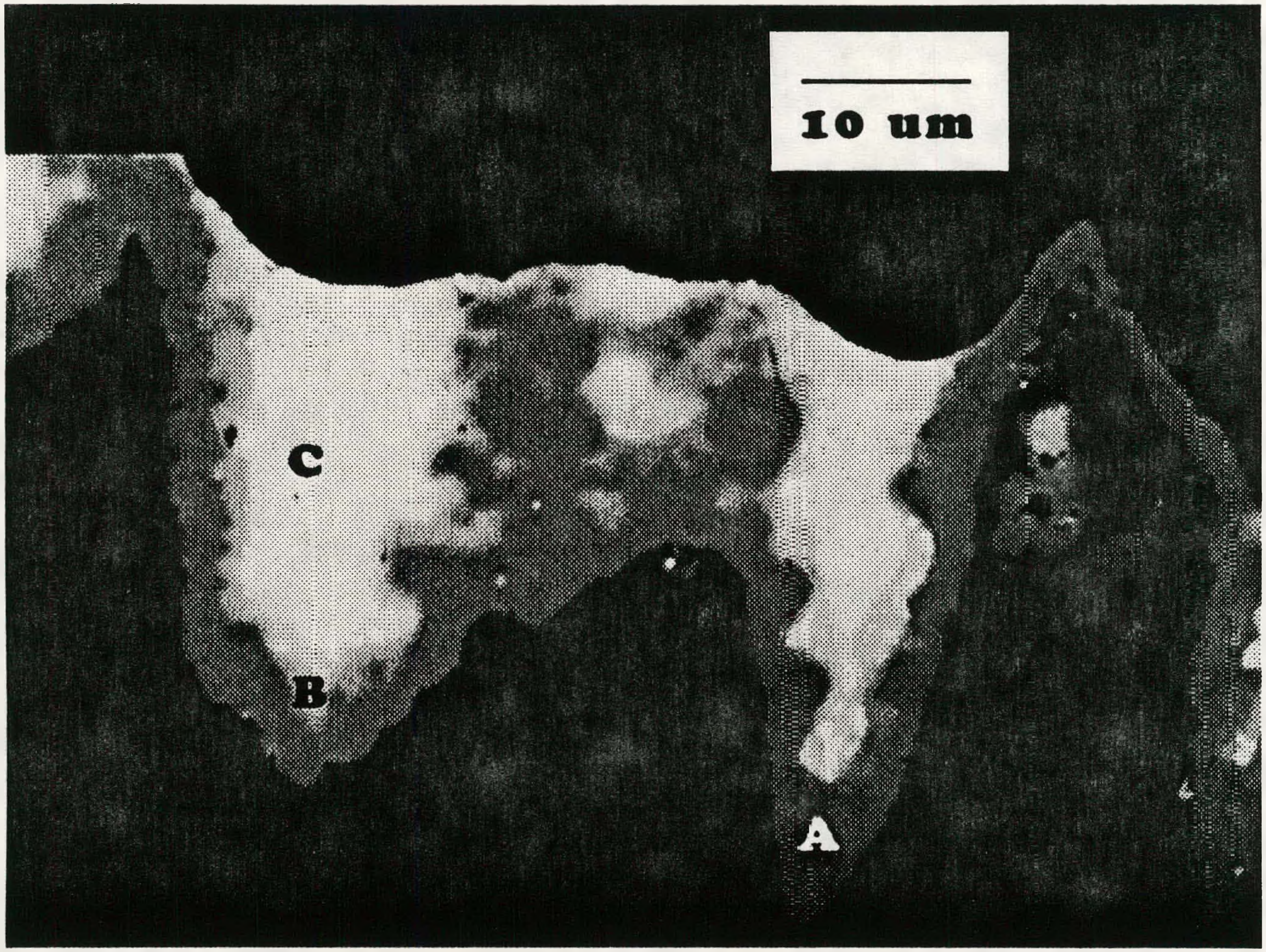

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Figure #8