# FLUXLESS SOLDERING WITH CONTROLLED ATMOSPHERES

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# OUTLINE

- Ackowledgements and References
- Controlled Atmosphere Soldering Technology
- Vacuum Soldering
- Inert Atmosphere Soldering
- Reducing and Reactive Atmosphere Soldering
- Activated Acid Atmosphere Soldering
- Summary

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# REFERENCES

- R. J. Klein Wassink, Soldering in Electronics, Electrochemical Publications Ltd., Ayr, Scotland, Second Edition, 1989.
- C. Lea, A Scientific Guide to Surface Mount Technology, Electrochemical Publications Ltd., Ayr, Scotland, 1988.
- F. M. Hosking (Principal Investigator), Fluxless Soldering to Reduce Solvent Usage, DOE Waste Minimization Technology Development Task Plan, ADS 4095, May 90.

# *WHAT IS FLUXLESS SOLDERING*

- *Fluxless soldering is the fabrication of solder joints utilizing various soldering technologies without the application of a chemical flux.*

- *Fluxless soldering requires a clean, oxide free surface if wetting is to occur.*

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# *WHY FLUXLESS SOLDERING?*

- ***Reduce exposure to hazardous flux fumes.***
- ***Eliminate long term corrosion of soldered electronic components caused by entrapped flux residues.***
- ***Reduce the use of halogenated solvents and their waste products generated during flux residue removal.***
- ***Compliance with OSHA, EPA and Montreal Protocol regulations and agreements.***

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# WHAT ARE THE ALTERNATIVES TO FLUXLESS SOLDERING

- *Water Soluble Fluxes*
- *"No Clean" or Low Solids Fluxes*
- *New Cleaning Solvents (eg. terpene)*
- *Aqueous-based Cleaning*

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# FLUXLESS SOLDERING TECHNOLOGY HAS MANY FACETS

- Thermodynamic/Kinetic Analytical Support
- Controlled Atmosphere Soldering Technology (Vacuum, Inert/Reducing Gases, Reactive Gases, Activated Acid Vapors) <<<<<
- Thermal/Mechanical Surface Activation Soldering
- Metallization Technology
- Inhibitor and Protective Coating Technology

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# CONTROLLED ATMOSPHERE SOLDERING

- Vacuum Soldering
- Inert Atmosphere Soldering (Ar, N)
- Reducing/Forming Atmospheres (H, H/Ar, H/N)
- Reactive Atmospheres (Reducing Plasmas)
- Activated Atmospheres (Inert or Reducing Gases With Acid Vapors)

# *There are many interrelated variables that influence wettability during controlled atmosphere soldering*

- *Base Metal (Cu, Ni, Kovar, FeNi)*
- *Solder Alloy (melt temperature, wetting, strength)*
- *Precleaning (mechanical or chemical)*
- *Base Metallization (Au, Cu, Ni)*
- *Atmosphere Purity (low $O_2$/$H_2O$)*
- *Atmosphere Flow Rate*
- *Atmosphere Mixture*
- *Thermal Profile*

oxide free surface to start with

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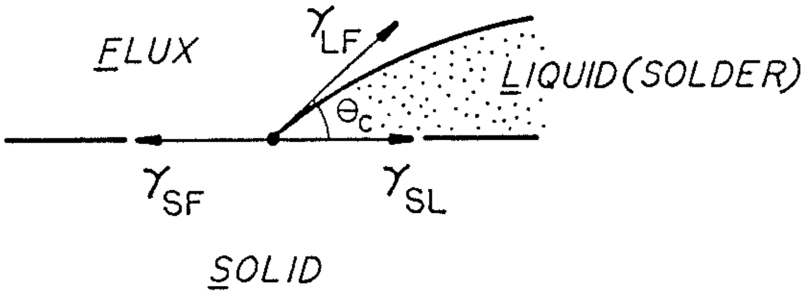
# Solder Wettability Depends on the Liquid Solder Reacting and Spreading Over an Oxide Free Surface

## Young's Equation (Equilibrium)



$$\boxed{\gamma_{SF} - \gamma_{SL} = \gamma_{LF}\cos\theta_c}$$

## Wetting Improves as "ø" Decreases

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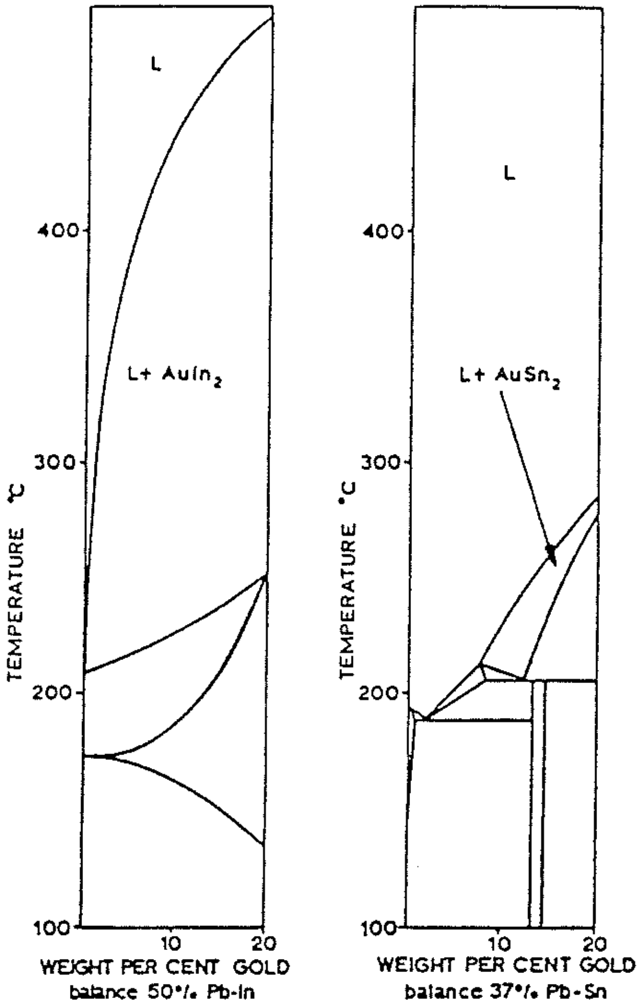
# Comparison of Au Solubility with 50In-50Pb and 63Sn-37Pb (Pseudobinary Equilibrium Diagrams*)



* F. G. Yost, Gold Bulletin, <u>10</u> (#4), October 1977.

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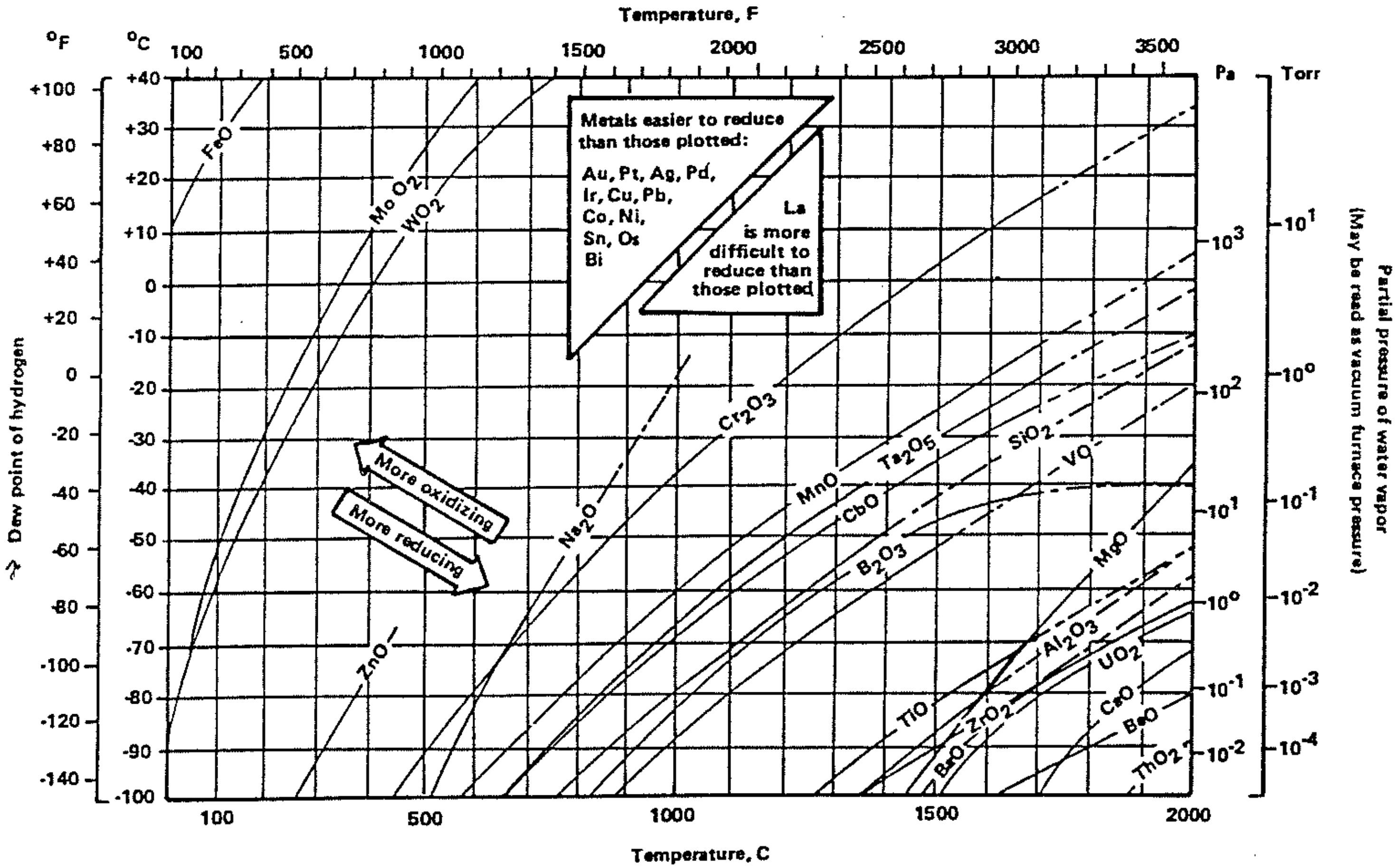
# VACUUM SOLDERING TECHNOLOGY

## Vacuum Soldering Characteristics

- *Base metal and solder alloy oxidation are minimal in a vacuum as a consequence of low oxygen.*
- *Oxides cannot be reduced in a vacuum at normal soldering temperatures. Vacuum soldering requires pretinned (hot dipped or plated) or nonoxidized surfaces (eg. Au).*
- *Vacuum levels must be controlled to prevent vaporization of solder alloy constituents.*
- *Heating and cooling rates are difficult to control in vacuum and require special processing.*

← must start
with an
oxide free
surface

# Metal-Metal Oxide Equilibria in Hydrogen and Vacuum



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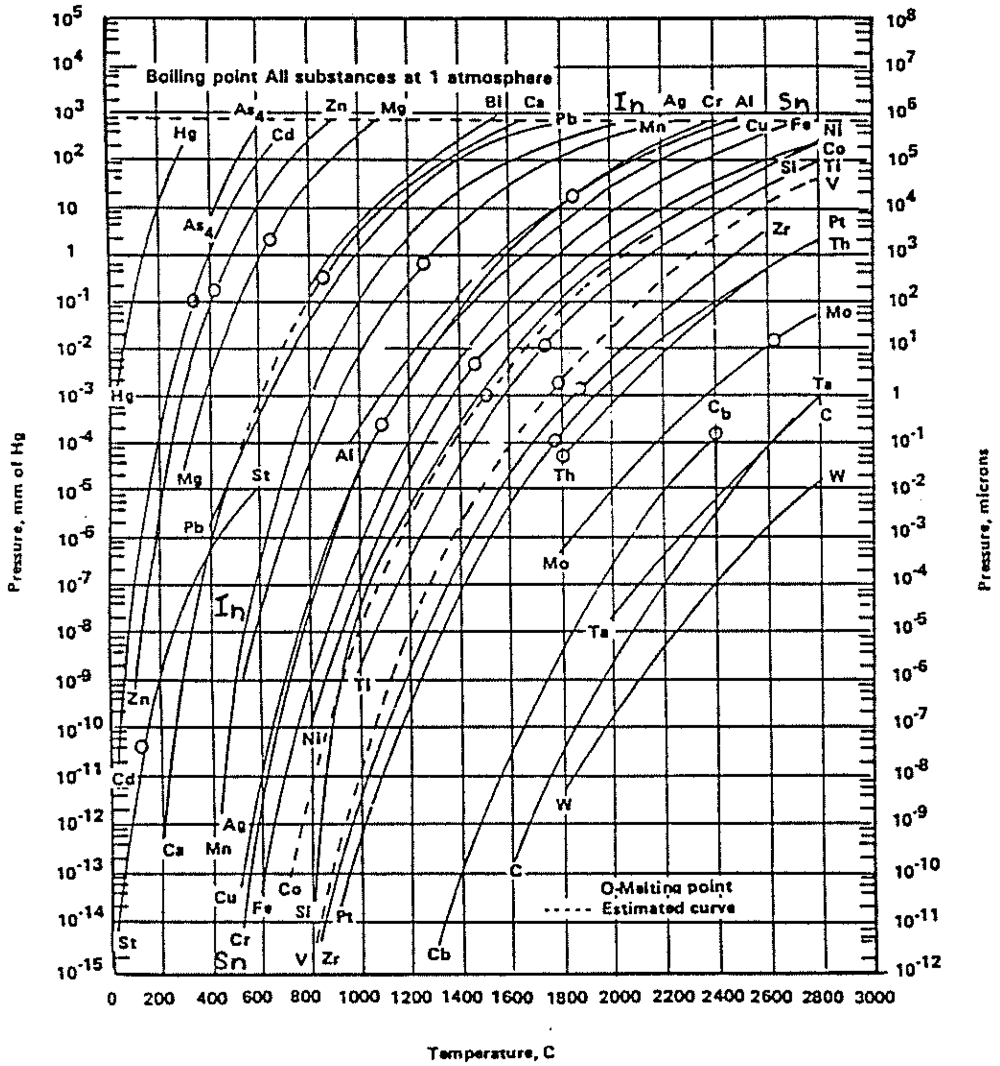
~~Added~~ need to work with Au.

# Relationship Between Temperature and Vapor Pressure



## Note

- In and Sn curves lie to the right of the Pb curve (lower vapor pressures)
- Bi, Zn, and Cd curves lie to the left of the Pb curve (higher vapor pressures).

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# *Base Metal-Solder Alloy Reaction During Soldering Is Very Sensitive to Time and Temperature*

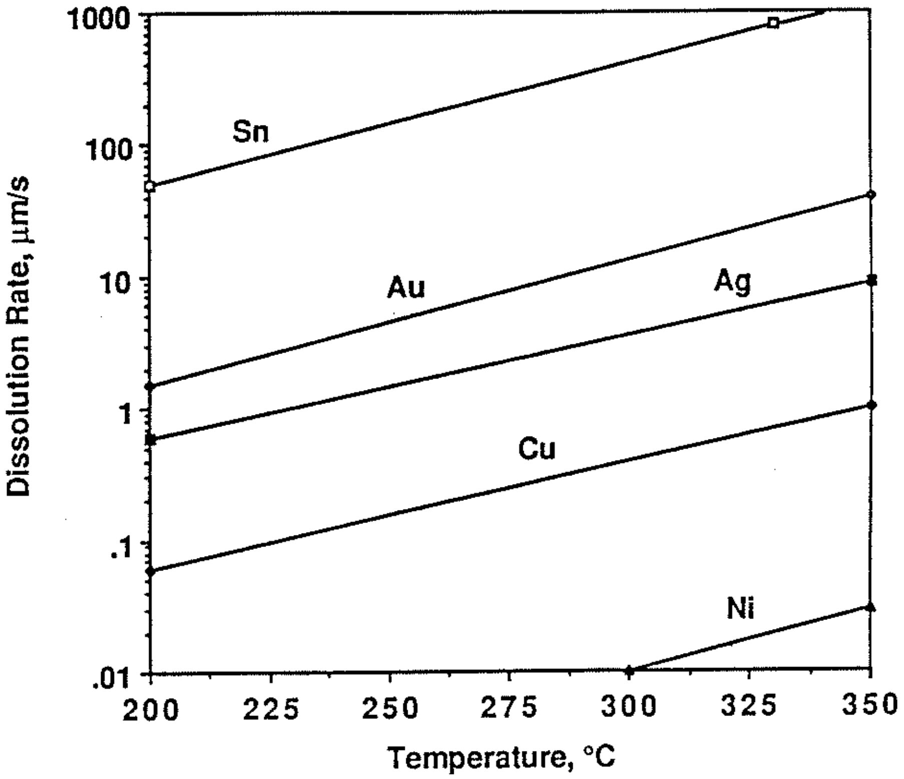
$$dD/dt = A\exp(-Q/kT)$$

*(Dissolution Rate)*

| *Elemental Reaction* | *Typical IMC* |
|---|---|
| *Au-Sn* | $AuSn_4$ |
| *Au-In* | $AuIn_2$ |
| *Cu-Sn* | $Cu_6Sn_5$, $Cu_3Sn$ |

## *EXAMPLE*

Dissolution Rate of Metals by Liquid 60Sn40Pb



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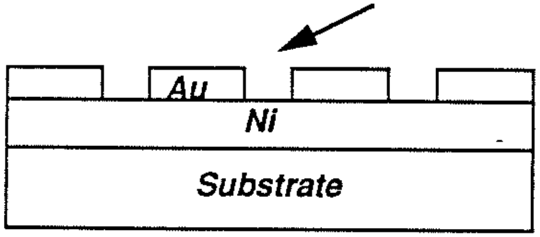
# Oxide Free Surfaces Are Necessary If Vacuum Soldering Is to Succeed



*Oxidation and Corrosion Transport Through Thin, Porous Au Surface*

- *Au metallizations can provide an oxide free, solderable (fluxless) surface.*
- *Control of the Au thickness is critical; too thick and Au intermetallics will embrittle the joint; too thin and porous Au will allow oxidation of the underlying metal.*
- *Recommended Au thickness is 50-75 $\mu$in. (1.3-1.9 $\mu$m).*
- *Fraction of Au in a 63Sn-37Pb solder joint should not exceed 3 wt. %.*

↑ embrittlement

# VACUUM SOLDERING EXAMPLE

Application: Attach ferrite discs to Cu support rings

Base Materials:
- OFHC Cu
- Sputtered Ti/Mo/Cu ferrite with an overplate of 100 µin. Ni and 20 µin. Au

Solder Alloy (wt.%): 63Sn-37Pb

Flux: None

Soldering Temperature: 250°C (≤ 1 min.)

Vacuum Level: $5 \times 10^{-5}$ torr

Cooling Method: Furnace cool or argon quench

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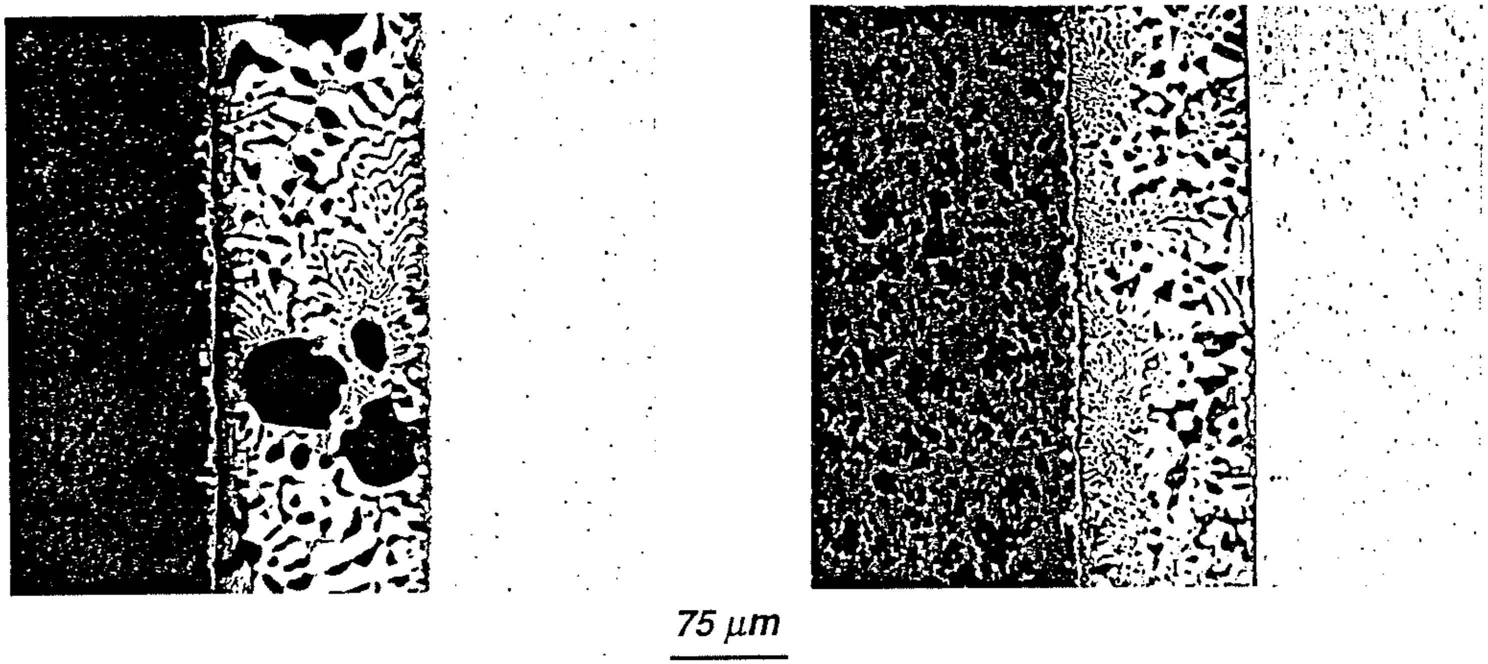
# Quality of Vacuum Soldered Ferrite-SnPb-Cu Joints Is Dependent on the Furnace Cooling Rate



Furnace Cool
(Slow)

Argon Quench
(Fast)

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# Vacuum Soldering
# Reqires Special Conditions For Success

- *Metallized Base Surface (eg. Au)*
- *"Clean" Solder Alloy*
- *"Clean" Vacuum*
- *Minimum Exposure to the Molten Solder*
- *Controlled Cooling of the Joint (Once Solid)*

# *Infrared Vacuum Heating Significantly Improves the Thermal Response During Soldering*

- *Conventional resistive vacuum heating is relatively slow and results in excessive reaction between the molten solder and base surface. Voids, dewetting, and low joint strength can result.*

- *Infrared vacuum soldering depends on quickly radiating heat to the work area and reduces the time that the solder is molten. More parts can also be processed per unit of time.*

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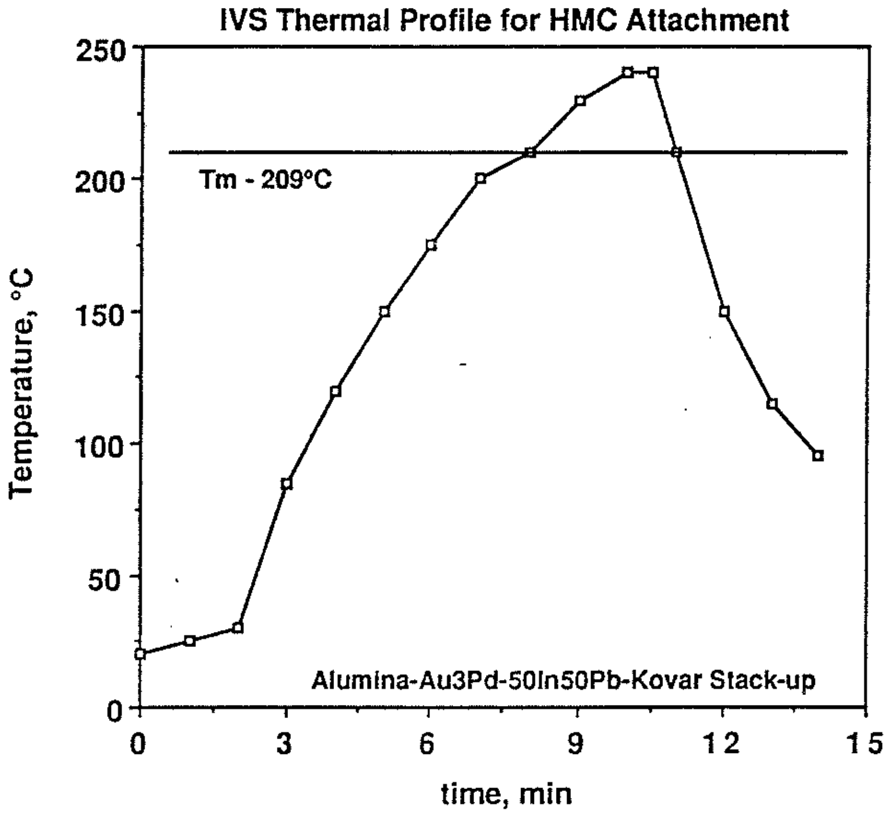
# Typical Thermal Profile During Infrared Vacuum Soldering



*IVS Temperature History for HMC Attachment*

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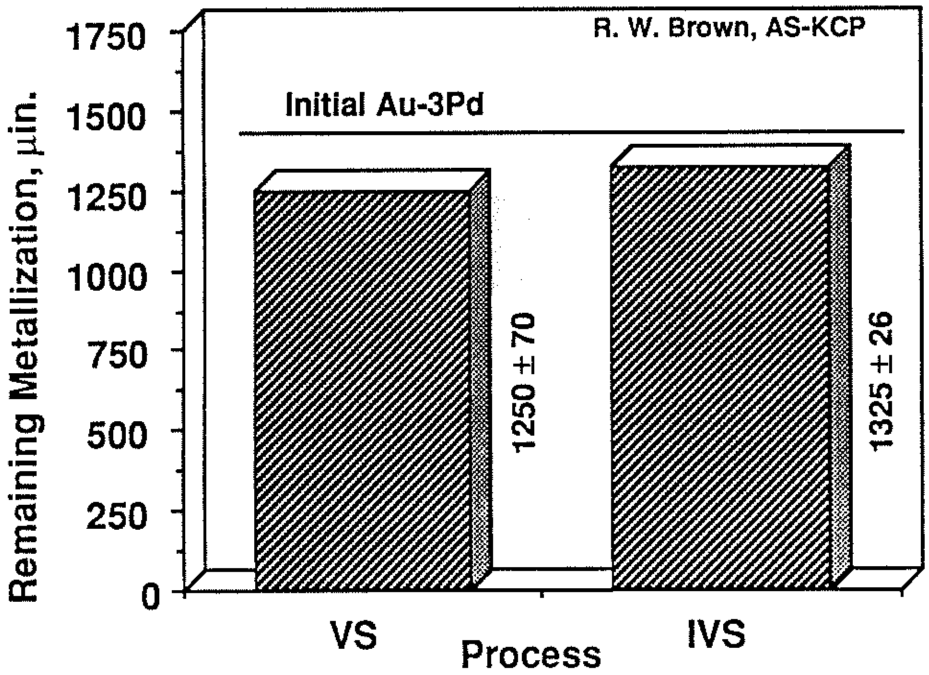
# *Remaining Au-3Pd Metallization After Soldering**



*Average Au-3Pd consumed by Vacuum Soldering (VS) is 33 to 123 μin.*

** Alumina-Au3Pd-50In50Pb-Kovar HMC Attachment*

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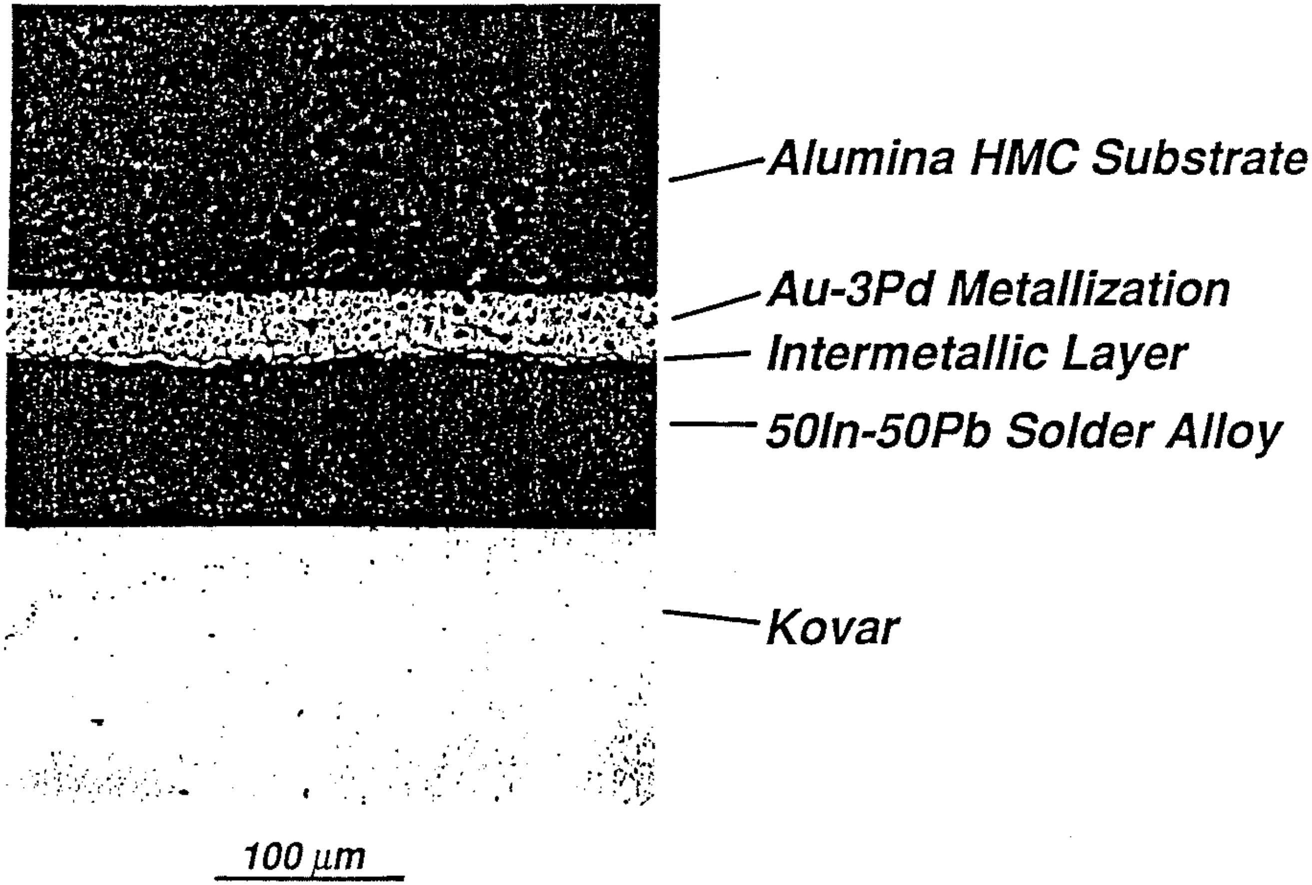
# Infrared Vacuum Soldering of a Thick Film Network to a Kovar Mounting Plate with 50In-50Pb

R. W. Brown, AS-KCP



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# *Conditions Necessary for Successfully Soldering in an Inert Atmosphere*

- ***Pretinned Surface (Hot Dipped or Plated)***
- ***Cleaned and Protected Surface***
- ***Nonoxidizing, Metallized Surface (eg. Au)***

***Inert Atmospheres Only Serve as a Protective Gas Cover During Soldering and Do Not Reduce Existing Surface Oxides!***

# INERT ATMOSPHERE SOLDER PROCESSING

- Direct flushing of the parts and work area with argon or nitrogen inert gas prior to soldering is adequate.

clean area
backfill with
dry inert atm.

- The cleanest inert atmosphere is obtained by first evacuating the soldering chamber and then backfilling with the inert gas.

- A dynamic gas flow is preferred over a static gas cover.

- Inert atmospheres can be applied to batch and continuous soldering processes.

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# REDUCING OR FORMING ATMOSPHERE SOLDERING

- *Reducing atmosphere soldering technology utilizes molecular $H_2$, $H_2$-Ar, and $H_2$-$N_2$ cover gases.*
- *The kinetics for oxide reduction with reducing-forming atmospheres are very poor at soldering temperatures below 300°C.*
- *Auxiliary heat sources (eg. hot stage, infrared, or laser) can facilitate the process.*

Ar | N equal

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# Reduction of Metal Oxides by Hydrogen is Thermodynamically Feasible

$MO + H_2 \dashrightarrow M + H_2O$ (where M = metal )

This reaction requires a dry hydrogen atmosphere, otherwise the released water will react with and reoxidize the metal:

$$M + H_2O \dashrightarrow MO + H_2$$

<u>However</u>, the kinetics for hydrogen reduction of metal oxides at typical soldering temperatures (≤ 300°C) are not favorable. Reducing gases should be considered only when soldering with high temperature (> 300°C) solder alloys.

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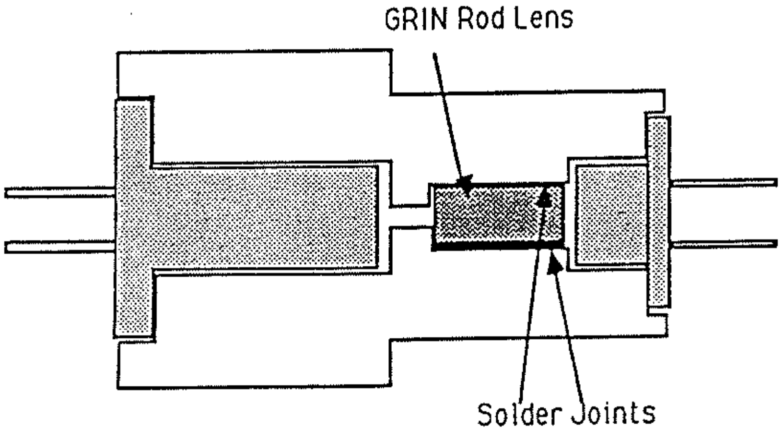
# EXAMPLE OF REDUCING ATMOSPHERE SOLDERING

## *Fluxless Soldering of an Optoelectronic Package*



*Graded Index Rod Lens*

- *Base Materials- Ni plated Kovar housing and metallized (Cr-Pt-Au) borosilicate glass lens*
- *Solder Alloy - 60Sn-40Pb*

### *Processing Steps*

*a) fire Ni plated Kovar housing in hydrogen at 900°C*
*b) immediately assemble lens-housing with solder preform and transfer into vacuum retort*
*c) solder in hydrogen at 240°C*

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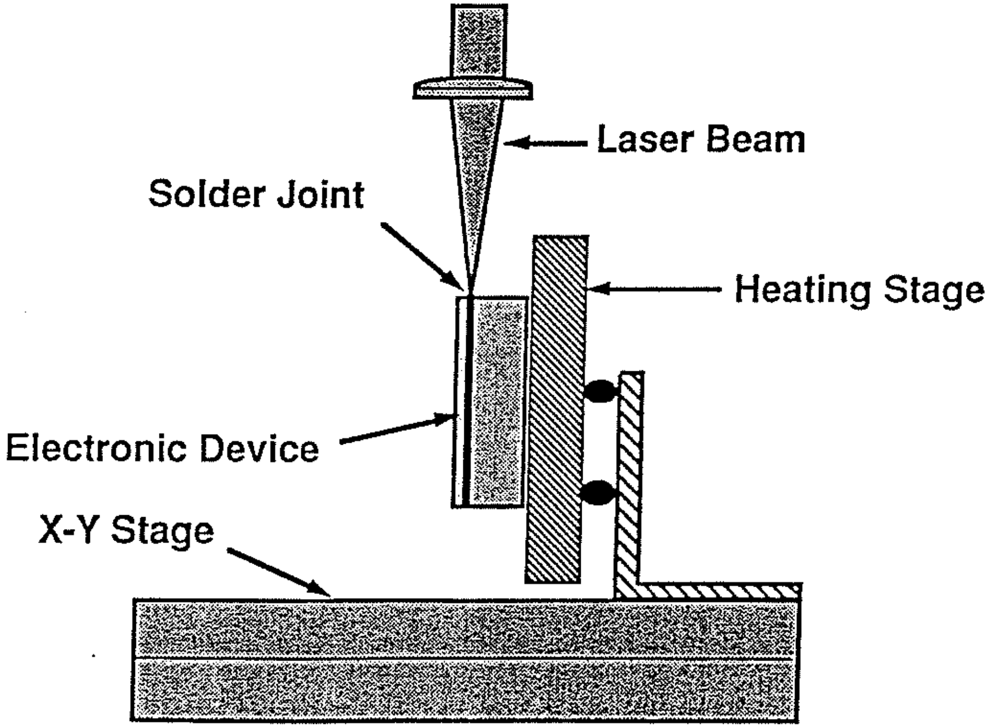
# *Laser Inert/Forming Atmosphere Soldering of Discrete Electronic Devices*

## *100W CW Nd:YAG Laser*



***Objective*: Attach discrete electronic components in a protective inert or forming cover gas with laser heating and no fluxing.**

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# Laser Atmosphere Soldering Example

Base Metal: Ni (175 μin.) and Au (50 μin.) electroplated Kovar (Fe-29Ni-17Co)

Solder Alloy: 63Sn-37Pb (183°C)

Flux: None

Soldering Atmosphere: Forming Gas (5% $H_2$-Ar)

Heat Source: 100W CW Nd:YAG Laser

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# Optical Micrographs of SnPb Laser Solder Joints

## Ni-Au Plated Kovar Base Plates
## (30W, 0.015", 5 ipm test parameter)

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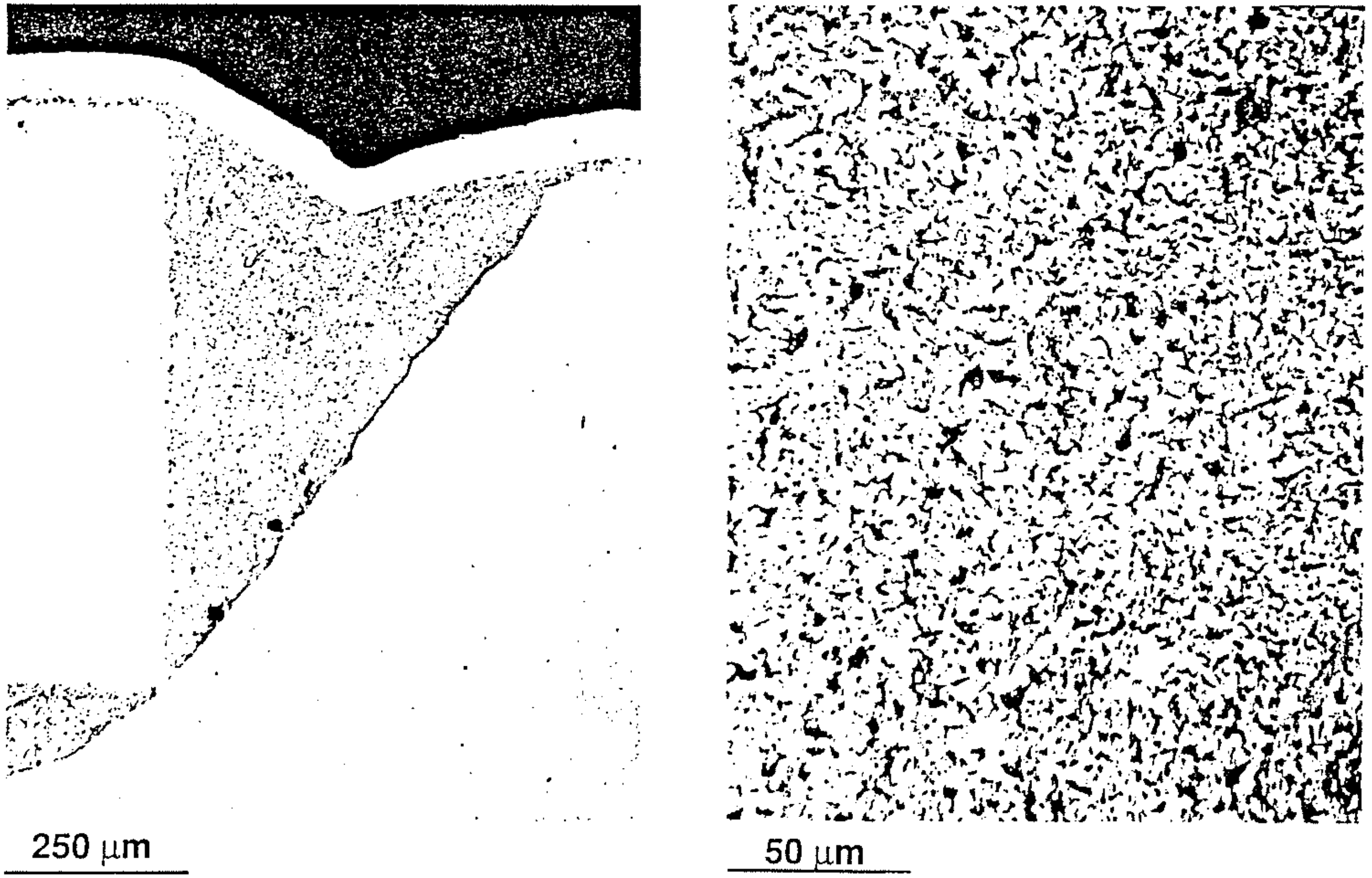
# Optical Micrographs of SnPb Laser Solder Joints

## Ni-Au Plated Kovar Base Plates
## (100W, 0.035", 30 ipm test parameter)



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# REACTIVE ATMOSPHERE SOLDERING

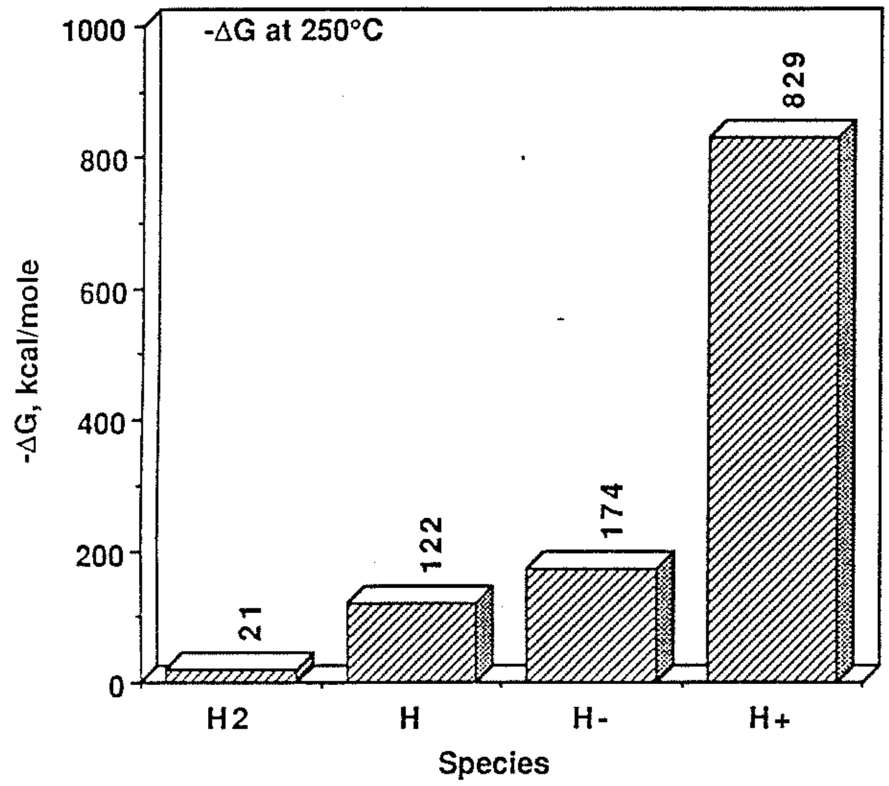
- *Atmospheres based on ionic or atomic hydrogen, hydrogen-nitrogen, or hydrogen-argon atmospheres.*

- *The reaction rates are significantly faster for oxide reduction with reactive gases.*

- *In-situ plasma cleaning and auxiliary laser or infrared heating have the greatest potential for reactive gas soldering.*

- *The effect of reactive gases on the packaging materials near the solder joint is of primary importance and the limiting factor of the process.*

# Thermodynamics of the Reduction of $Cu_2O$ at 250°C Suggests That Ionic Hydrogen Has the Best Potential



| Gas Species | Reduction Factor |
|---|---|
| $H_2$ | 1 |
| H | 6 |
| H- | 8 |
| H+ | 39 |

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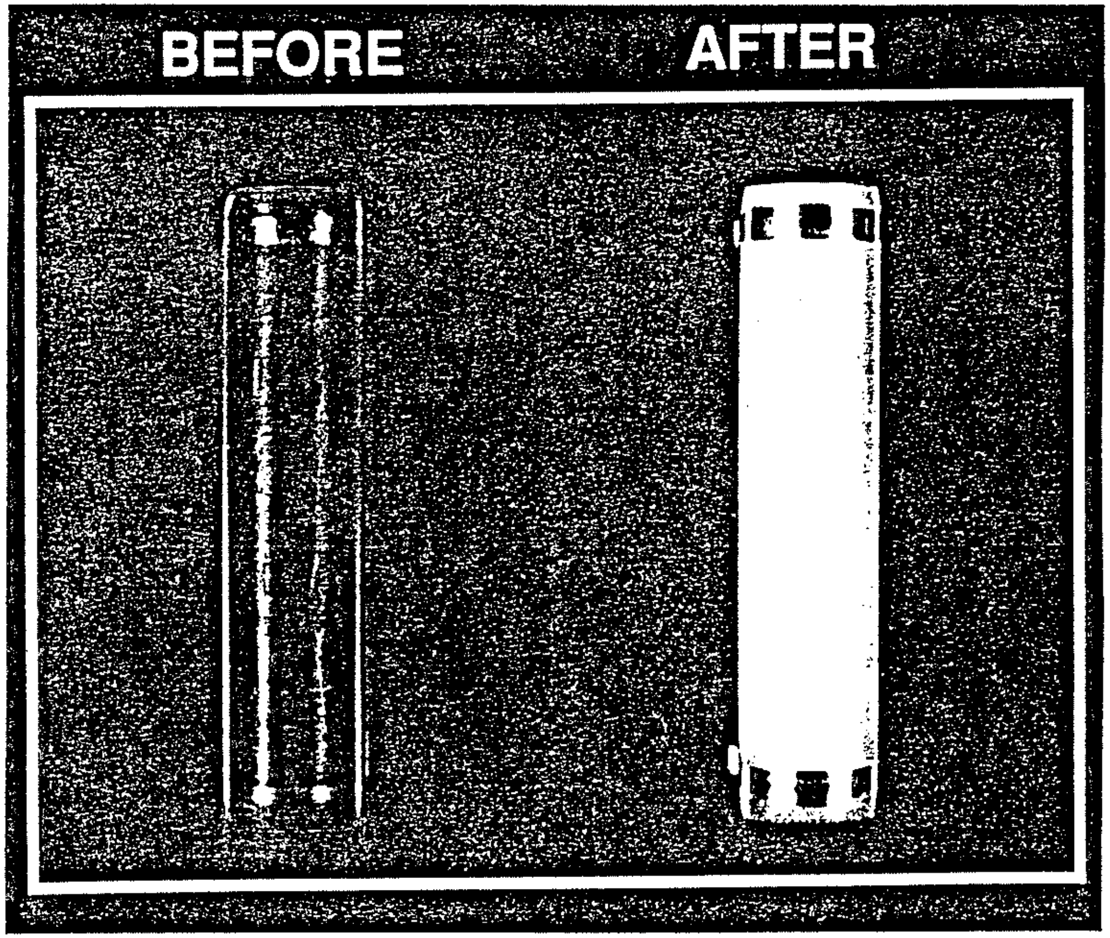
# Plasma/Cathodic Cleaning Is Very Effective in Reducing Heavily Oxidized Copper



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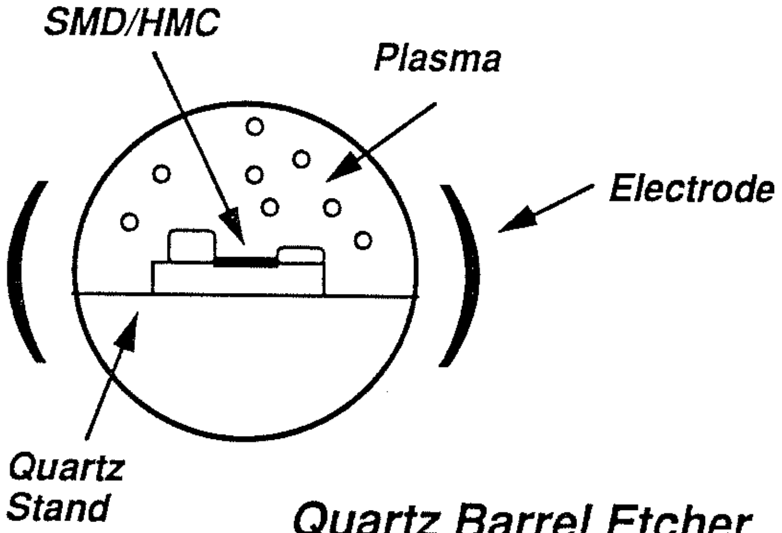
# Two Step Plasma Cleaning and Soldering Is Best Suited for Batch Processing

## EXAMPLE



Quartz Barrel Etcher

- Cleaning Variables -
  - a) power
  - b) chamber pressure
  - c) time
- Soldering (fluxless) assisted with auxiliary heating (hot stage, laser, infrared)

- Reducing plasma produced by an RF electric field.

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# ACTIVATED ACID ATMOSPHERE SOLDERING

- *These atmospheres are based on inert or forming gas covers with dilute additions of acetic or formic acid. The acid vapors are purported to accelerate oxide reduction below 300°C*
- *The technology is adaptable to batch or continuous solder processing and can be applied to primary or reflow attachment.*
- *Heating is performed with resistive or infrared elements.*

# Metal Oxide Reduction by Formic Acid Occurs at Temperatures Below 300°C

(1) $MO + 2HCOOH \text{ ---> } M(COOH)_2 + H_2O$

where, $M = \text{metal}$

(2) $M(COOH)_2$ is unstable and decomposes into

$$M(COOH)_2 \text{ ---> } M + 2CO_2 + H_2$$

(at $T > 200°C$)

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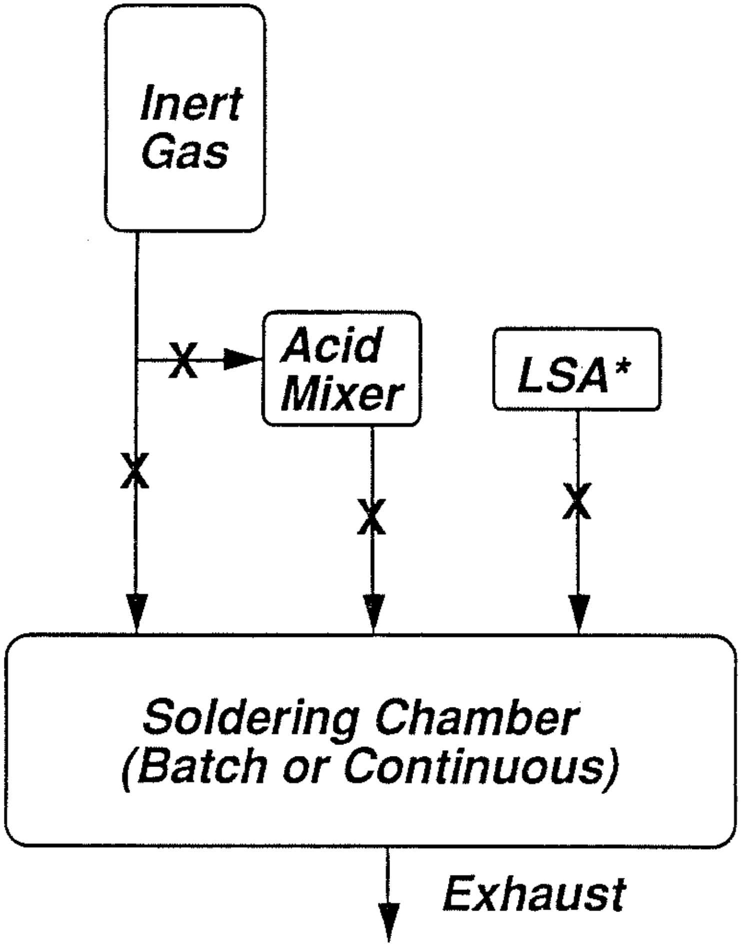
# Typical Process Variables of Activated Acid Atmosphere Soldering



<u>Example</u>

- Gas Flow Rate (10-20 cu. m/hr)
- Gas-Activator Mixture (100 g/hr of formic acid)
- Low Solids Additive (1 l/hr)
- Preheat and Soldering Temperatures
- Board Throughput

* Difficult to wet surfaces may require a dicarboxylic acid additive (eg. adipic acid). This "no clean", low solids addition can be varied from 0.5 to 1.5 % and applied with an ultrasonic atomizer in an alcohol carrier.

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# SUMMARY

- Controlled Atmosphere Soldering Technology can be applied to fluxlessly attaching SMDs and HMCs.
- Controlled Atmosphere Soldering offers a wide range of processing and heating choices.
- Controlled Atmosphere Soldering can satisfy batch and continuous solder processing.
- Controlled Atmosphere Soldering cannot satisfy every electronic packaging application. Materials compatibility with the process parameters and atmosphere must be considered.
- Soldering technologies can be combined to produce satisfactory solder joints. Controlled atmospheres and "no clean" fluxing are excellent examples.

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