



# **2007 IBSS Meeting Chicago, Illinois Nov 12-14, 2007**

## **Comparison of Metal-Ceramic Brazing Methods**

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**Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.**





# Outline

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**Purpose**

**Background information**

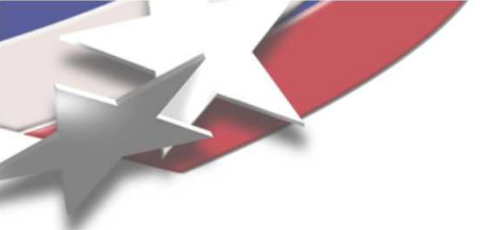
**Examples of ceramic-metal brazes**

**Methods that require surface modification.**

- Mo-Mn metallization
- Thin-film metallization

**Methods requiring no surface modification.**

- Active brazing
- Direct brazing



# Purpose

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**Presentation motivation is twofold:**

- **Document the of methods currently used to braze metals to non-metals, particularly oxide ceramics, and show some positive and negative attributes of each method.**
- **Additionally, a goal is to compile the results from many years of brazing to create document that could be used by future designers, showing what tensile strengths can be reasonably expected using these methods and braze filler metal combinations.**



# **Metal-Ceramic Brazing: Background**

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**Brazing is a method of joining materials.**

- 1) Takes place  $\geq 450^{\circ}\text{C}$**
- 2) Parent substrate materials are not melted**
- 3) Braze filler metal is drawn into or held within the braze joint by capillary attraction**

**Standard brazing practices do not work on non-metallic (oxide, carbide, nitride) surfaces, failing to meet the 3<sup>rd</sup> requirement shown above.**

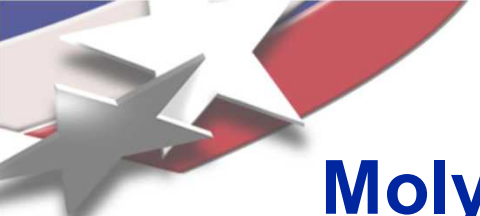
**Brazing to a nonmetallic surface requires 1) surface modification\* or 2) the use of non-standard braze filler metals.**

**\*direct brazing methods are an exception**

# Some Examples of Metal-Ceramic Brazes

- High-voltage insulators/devices
- Vacuum breaks
- Electronic packages and connectors
- Structural brazing





# **Molybdenum-Manganese / Nickel Plate**

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## **Procedure:**

**A coating of molybdenum (or sometimes tungsten) and manganese particles mixed with silicates and glass additives and volatile carriers is applied to the ceramic surface to be brazed.**

**The coating is fired in a wet hydrogen environment at 1450-1600°C leaving a “glassy” metallic coating 300-500 micro-inches thick.**

**The coating is subsequently plated with 0.001-0.003 inch layer or nickel.**

**The nickel plating is sinter-fired at 850-950°C in a hydrogen atmosphere leaving a finished metallic surface that can be readily brazed using standard braze filler metals.**

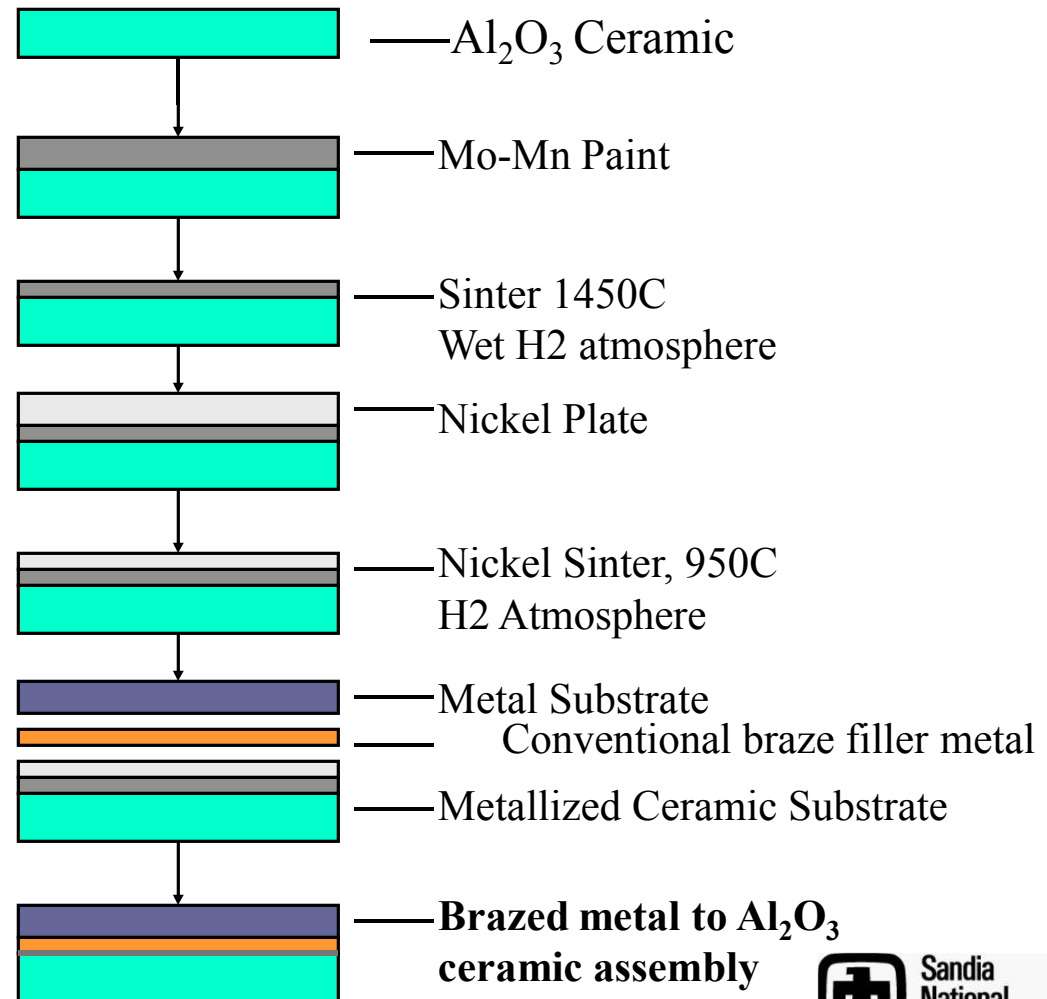
# Molybdenum-Manganese / Nickel Plate

## Advantages

- Mature technology
- Proven history
- Easily brazed using standard filler metals
- Commercial Suppliers Available

## Disadvantages

- Time consuming
- Multiple-step process
- Requires specialized equipment
- Nickel plating depletion
- Expensive



# Molybdenum-Manganese / Nickel Plate

## ASTM-F19 Tensile Button Test Results

| Filler Metal            | Non-metal Substrate | Metal Substrate | Brazing Temperature | Furnace Atmosphere | Tensile Strength     |
|-------------------------|---------------------|-----------------|---------------------|--------------------|----------------------|
| 50Au/50Cu               | 94% Alumina         | Fe-29Ni-17Co    | 1000°C-3 min        | Dry Hydrogen       | 17.1 ksi<br>±1.8 ksi |
| 65Cu/35 Au              | 94% Alumina         | Fe-29Ni-17Co    | 1040°C/3 minutes    | Dry Hydrogen       | 14.5 ksi             |
| 72Ag-28Cu               | 94% Alumina         | Fe-29Ni-17Co    | 810°C/3 minutes     | Dry Hydrogen       | 14.3 ksi             |
| 77Au-13Ag-10Ge          | 94% Alumina         | Fe-29Ni-17Co    | 495°C/3 minutes     | Dry Hydrogen       | 15.6 ksi<br>±0.2 ksi |
| 77Au-13Ag-10Ge (2x thk) | 94% Alumina         | Fe-29Ni-17Co    | 455°C/5 minutes     | Dry Hydrogen       | 16.1 ksi<br>±1.0 ksi |

### Test Samples:

### ASTM-F19 Tensile Buttons

(94% alumina with Fe-29Ni-17Co interlayers)

- Tensile strength (crosshead speed = 8.38E-03 mm/sec)
- Hermeticity Data (helium leak rates <2E-09 atm-cc/sec)



# Molybdenum-Manganese / Nickel Plate

**Alumina**

72Ag-28Cu, 810C - 3 min, dry H<sub>2</sub>  
Al-500 with Mo/Mn Metallization  
and Ni Plate, 500X

**Mo-Mn Reaction Layer**

**Ni Plating**

**Filler Metal**

**Fe-29Ni-17Co**

50  $\mu\text{m}$



# Thin-Film Metallization

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## Procedure:

**A combination of materials, usually 2 or 3, are deposited onto the nonmetallic surface using a physical vapor deposition (PVD) method such as evaporation or sputtering.**

**The first layer deposited, usually titanium, is typically 0.05-0.25 $\mu\text{m}$  thick.**

**The top layer is a noble metal such as gold, platinum or palladium that is 0.25-1.0 $\mu\text{m}$  thick.**

**Occasionally an additional layer is used as a diffusion barrier layer. When used it is applied prior to the noble metal layer.**

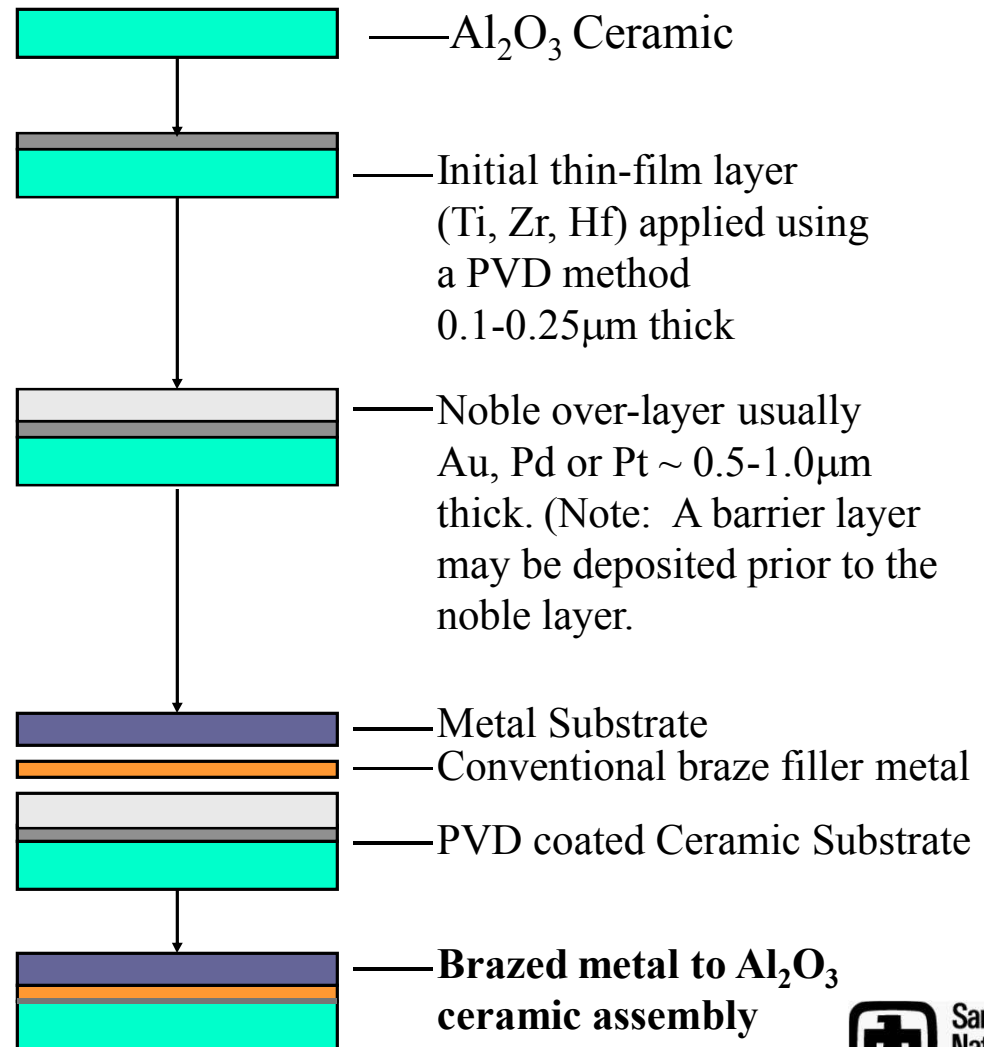
# Thin-Film Metallization

## Advantages

- **Materials Variety**
- **Proven history**
- **Easily brazed using standard filler metals**

## Disadvantages

- **Requires specialized equipment**
- **Masking required**
- **Size constraints**



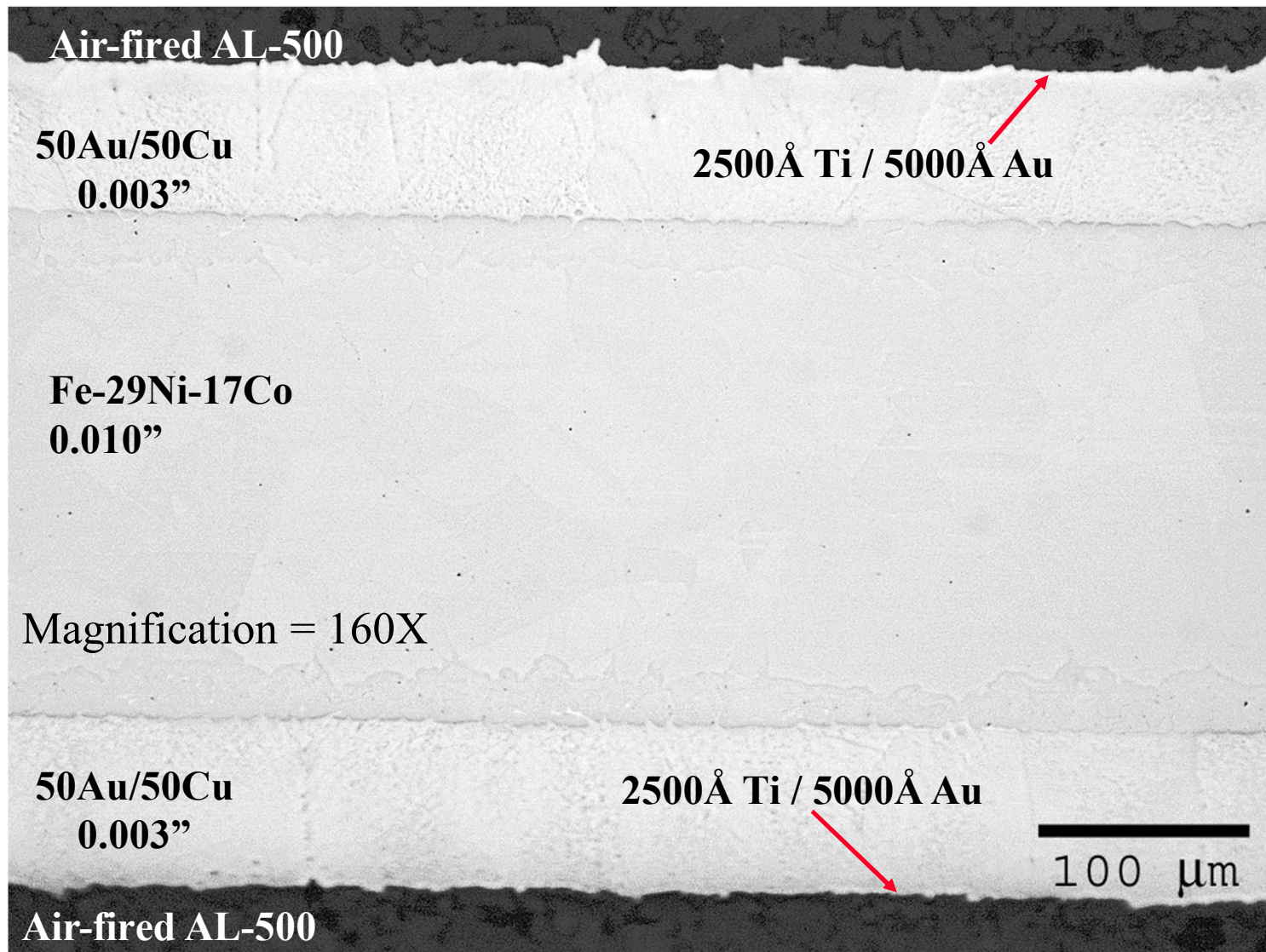


# Thin-Film Metallization

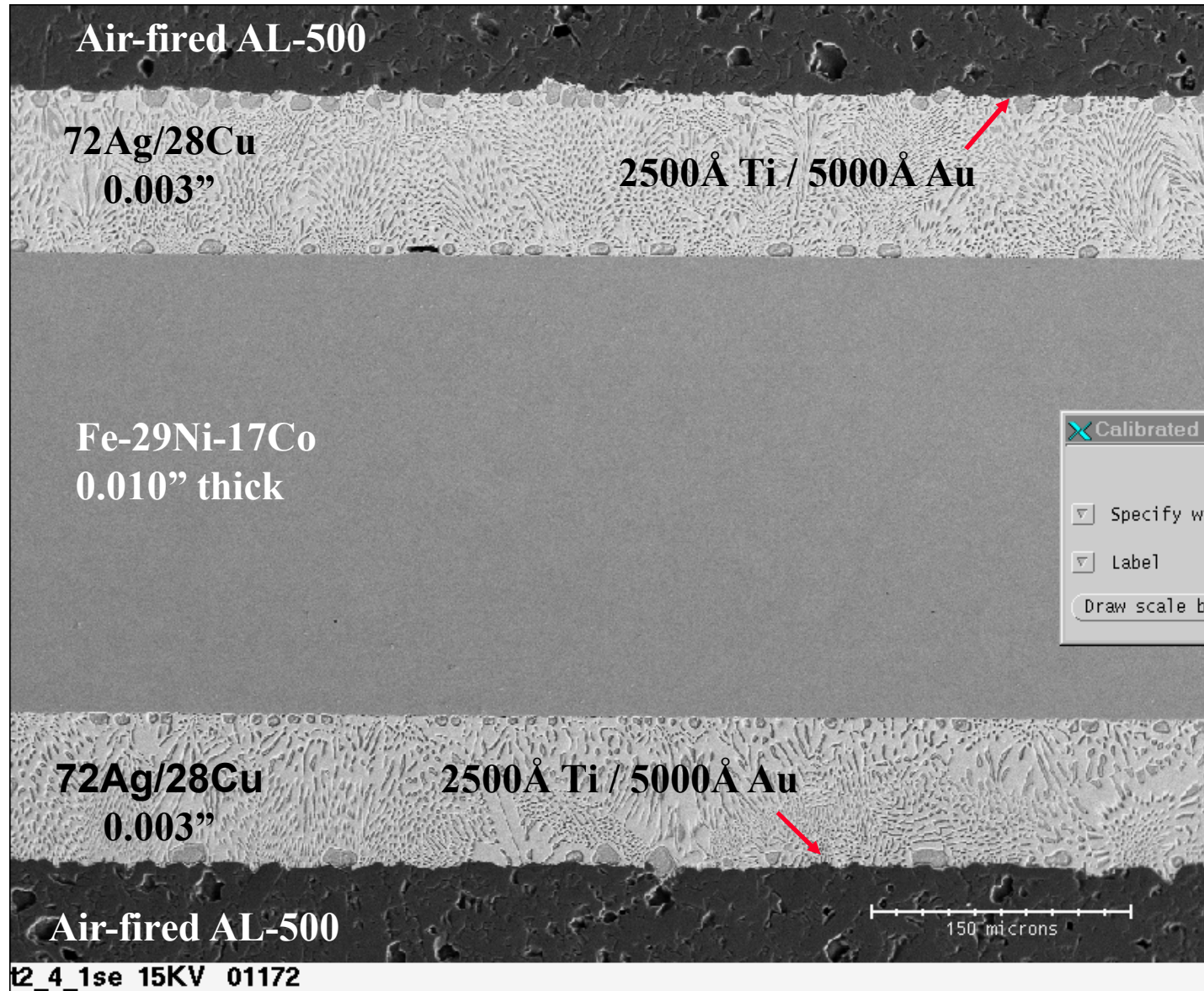
## ASTM-F19 Tensile Button Test Results

| Filler Metal   | Substrates                  | Thin-Films                        | Brazing Temperature/Time | Furnace Atmosphere | Tensile Strength |
|----------------|-----------------------------|-----------------------------------|--------------------------|--------------------|------------------|
| 50Au/50Cu      | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.5mmAu              | 1000°C/3 minutes         | Dry Hydrogen       | 14.8 ksi         |
| 50Au/50Cu      | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.5mmAu              | 1020°C/10 minutes        | Dry Hydrogen       | 12.9 ksi         |
| 72Ag-28Cu      | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.5mmAu              | 810°C/3 minutes          | Dry Hydrogen       | 13.0 ksi         |
| 50Au/50Cu      | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.02mmPd/<br>0.5mmAu | 1000°C/3 minutes         | Dry Hydrogen       | 16.1 ksi         |
| 50Au/50Cu      | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.02mmPd/<br>0.5mmAu | 1020°C/10 minutes        | Dry Hydrogen       | 11.8 ksi         |
| 63Ag-27Cu-10In | 94% Alumina<br>Fe-29Ni-17Co | 0.25mmTi/<br>0.5mmPt              | 755°C/2 minutes          | UHP Argon          | 13.2 ksi         |
| 63Ag-27Cu-10In | 951 LTCC<br>Fe-29Ni-17Co    | 0.25mmTi/<br>0.5mmPt              | 755°C/2 minutes          | UHP Argon          | 8.2 ksi          |
| 63Ag-27Cu-10In | 951 LTCC<br>Fe-29Ni17Co     | 0.5mmTi/<br>0.5mmAu               | 755°C/5 minutes          | UHP Argon          | 6.5 ksi          |
| 63Ag-27Cu-10In | 951 LTCC<br>Fe-29Ni-17Co    | 0.5mmTi/<br>0.5mmPd               | 755°C/5 minutes          | UHP Argon          | 3.8 ksi          |

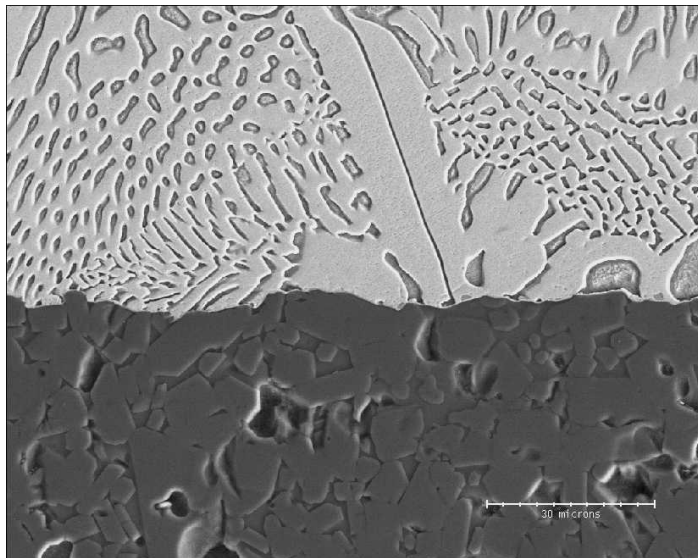
# Thin-Film Metallization



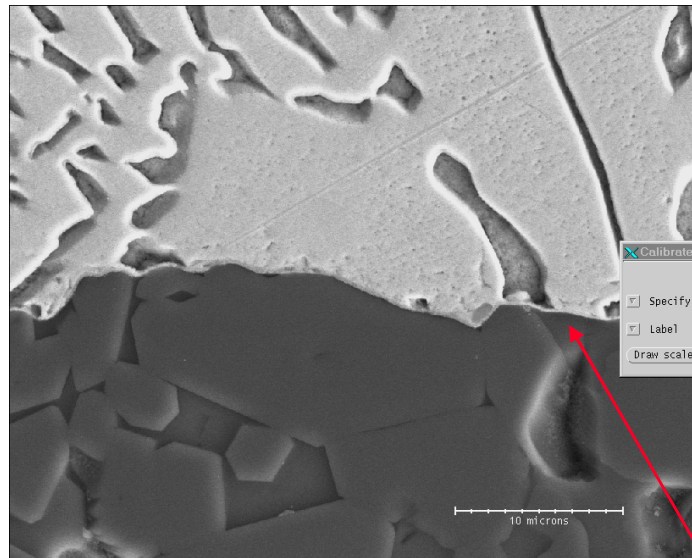
# Thin-Film Metallization



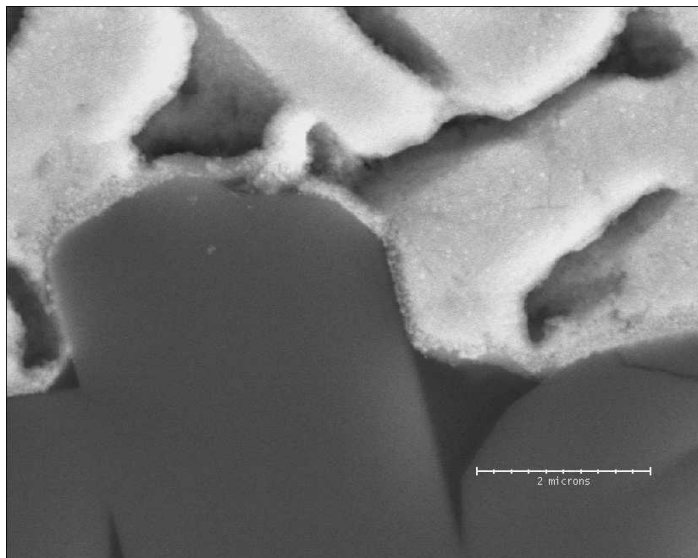
# Thin-Film Metallization



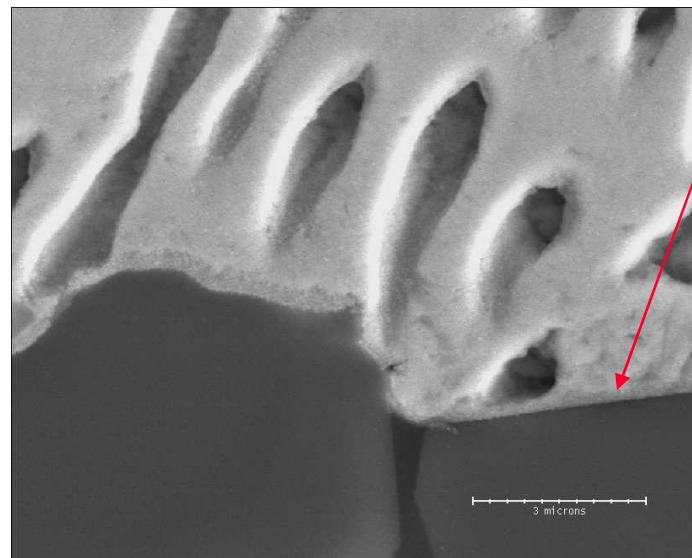
t2\_4\_2se 15KV 01172



t2\_4\_3se 15KV 01172



t2\_4\_5se 15KV 01172



t2\_4\_6se 15KV 01172

Sample T-2-4:  
810°C-3 min,  
Dry H<sub>2</sub>  
2500Å  
Ti/5000Å Au  
on Air Fired  
Al-500

Ti/Au Thin-  
Film Layer

# Active Filler Metal Brazing

## Procedure

- Active filler metal brazing lets one use standard brazing techniques when making metal to ceramic brazements.
- The metal and nonmetal substrates are cleaned, the active filler metal preform or paste is applied within the braze joint area.
- The braze is performed, usually in an inert or ultra-high vacuum environment.



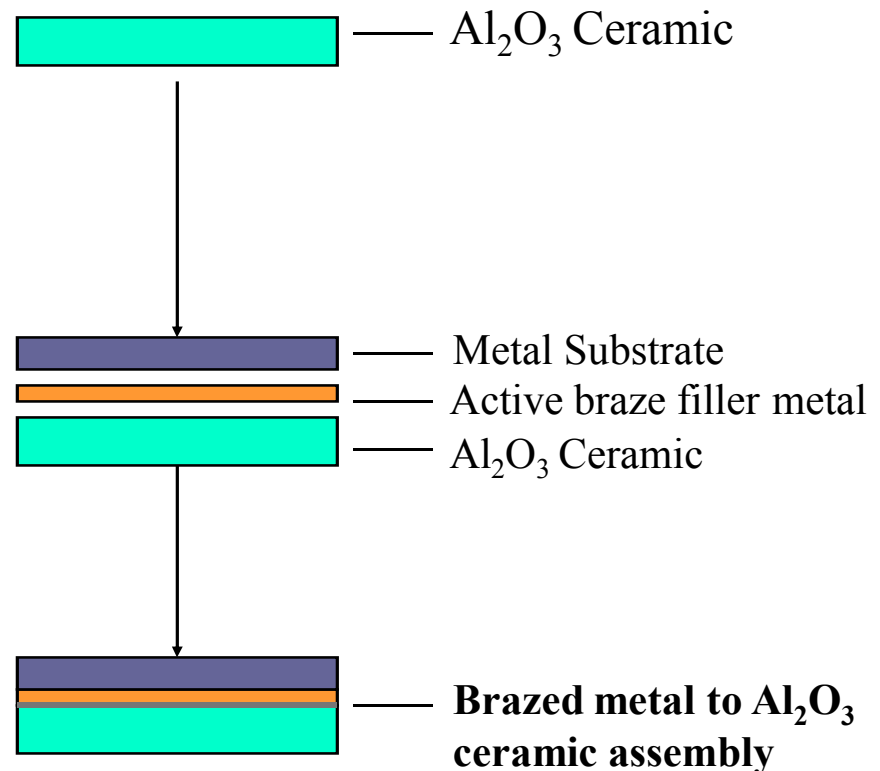
# Active Filler Metal Brazing

## Advantages

- Ease of use
- Variety of filler metal schemes & temperature ranges
- No specialized metallization equipment or processes required
- Easily brazed using standard filler metals

## Disadvantages

- Requires specialized equipment/atmosphere control
- Not usable with all joint designs
- Size constraints





# Active Filler Metal Brazing

## ASTM-F19 Tensile Button Test Results

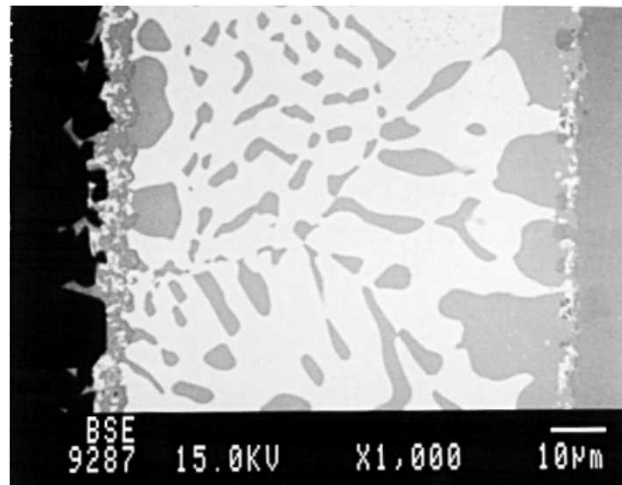
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| Filler Metal                  | Non-metal Substrate | Metal Substrate | Brazing Temperature                    | Furnace Atmosphere             | Tensile Strength   |
|-------------------------------|---------------------|-----------------|----------------------------------------|--------------------------------|--------------------|
| 59.00Ag-27.25Cu-12.5In-1.25Ti | 94% Alumina         | Fe-29Ni-17Co    | 998-1028°C/2-3 min<br>1000°C suggested | Vacuum                         | 14.5ksi<br>±1.8ksi |
| 59.00Ag-27.25Cu-12.5In-1.25Ti | DuPont 951 LTCC     | Fe-29Ni-17Co    | 755°C/5 min                            | Vacuum                         | 8 ksi ±1.8ksi      |
| 63.00Ag-35.25Cu-1.75Ti        | 94% Alumina         | Fe-29Ni-17Co    | 825-1040°C/2-10 minutes                | Vacuum                         | 11-16 ksi          |
| 63.00Ag-35.25Cu-1.75Ti        | 94% Alumina         | Fe-29Ni-17Co    | 1040°C/2 minutes                       | Dry Hydrogen                   | 14.5ksi            |
| 63.00Ag-35.25Cu-1.75Ti        | 94% Alumina         | Fe-29Ni-17Co    | 825-1040°C/2-10 minutes                | Partial pressure argon         | 11-14 ksi          |
| 62Cu-35Au-2Ti-1Ni             | 94% Alumina         | Fe-29Ni-17Co    | 1006-1026°C<br>6-8 minutes             | Vacuum                         | 11-14 ksi          |
| 97Ag-1Cu-2Zr                  | 94% Alumina         | Fe-29Ni-17Co    | 963°C, 3 minutes<br>above liquidus     | Partial pressure argon, 2 torr | 21.3ksi<br>±0.2ksi |
| 97Ag-1Cu-2Zr                  | 94% Alumina         | Fe-29Ni-17Co    | 990°C/5 minutes                        | Dry Hydrogen                   | 15.4ksi<br>±3.2ksi |
| 62Cu-35Au-2Ti-1Ni             | 94% Alumina         | Fe-29Ni-17Co    | 810°C/3 minutes                        | Vacuum                         | 14.3ksi            |

# Active Filler Metal Brazing

## 97Ag-1Cu-2Zr

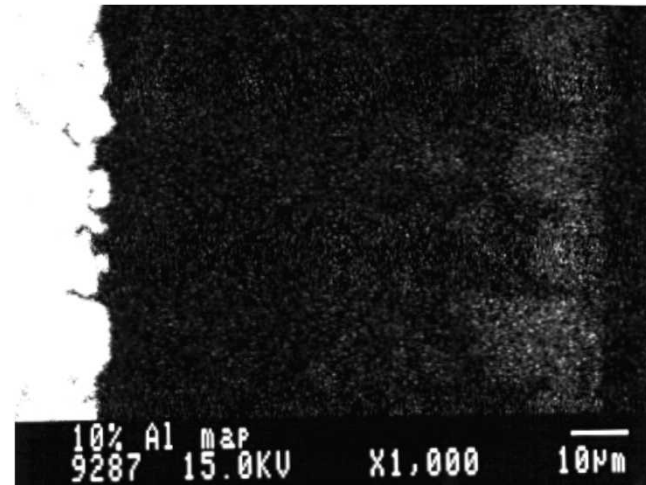
**BSE and Probe Maps for a sample brazed with 97Ag-1Cu-2Zr at 950°C, 5 min in a 12 torr argon partial pressure atmosphere**



Alumina

Braze

Fe-29Ni-17Co

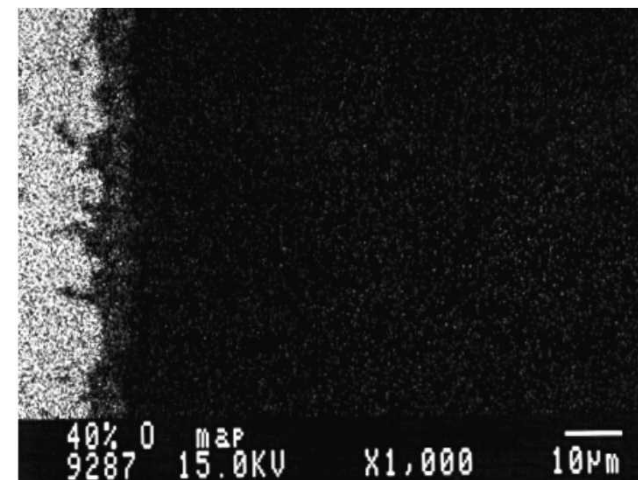
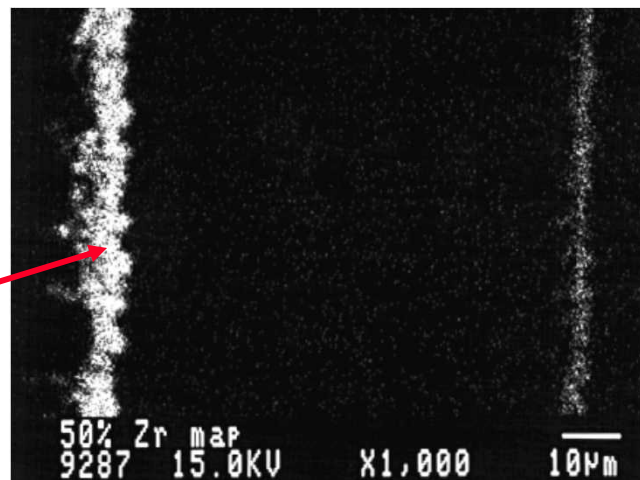


Alumina

Braze

Fe-29Ni-17Co

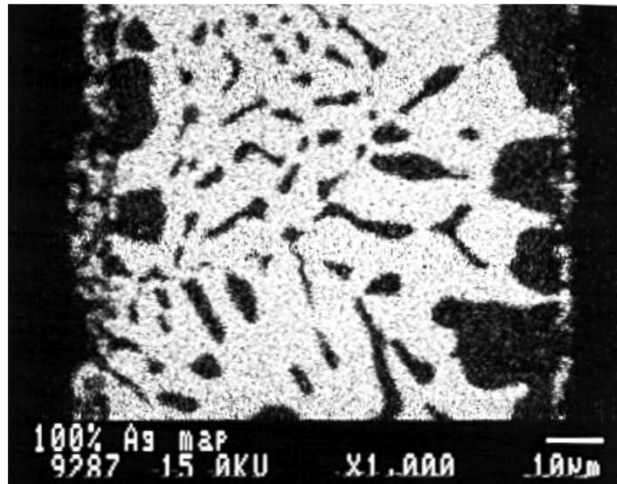
**Note that the Zr has successfully migrated to the oxide ceramic surface to allow the filler metal to “wet” properly.**



# Active Filler Metal Brazing

## 97Ag-1Cu-2Zr

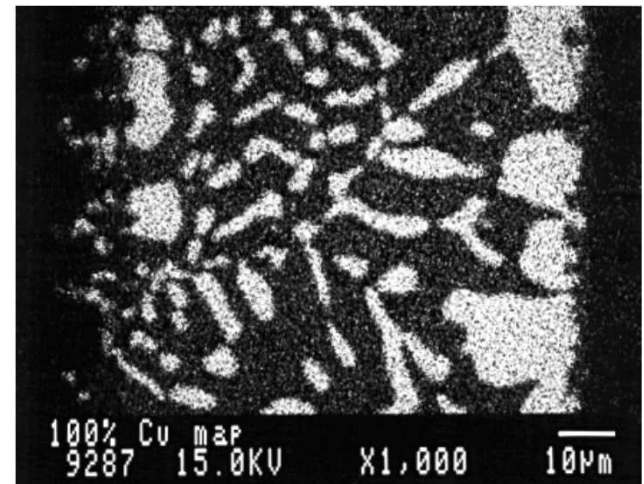
BSE and Probe Maps for a sample brazed with 97Ag-1Cu-2Zr at 950°C-5 minutes in a partial pressure atmosphere of 12 torr argon



Alumina

Braze

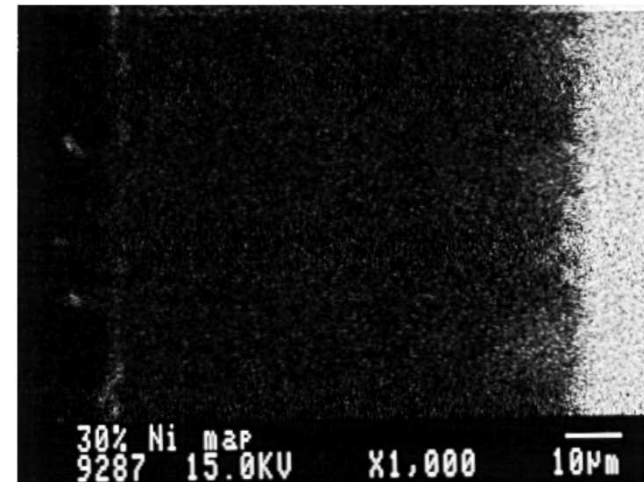
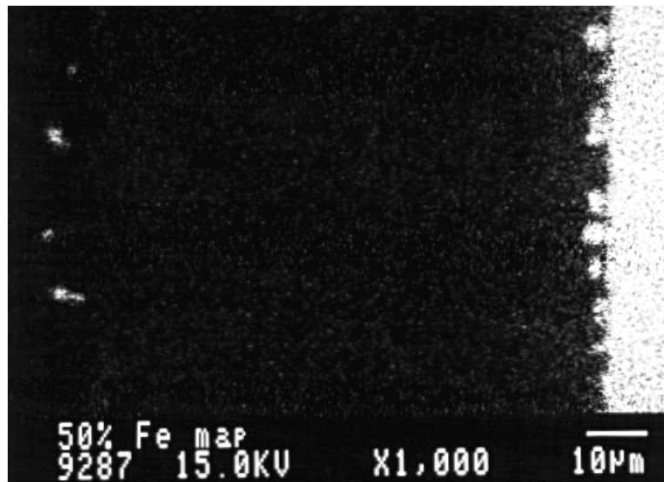
Fe-29Ni-17Co



Alumina

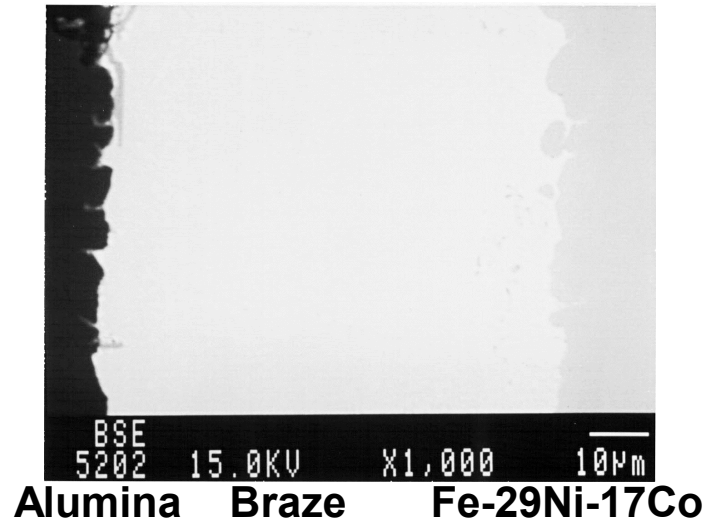
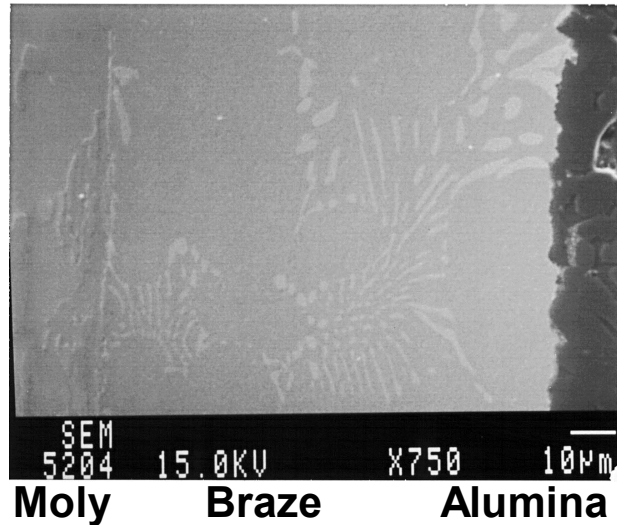
Braze

Fe-29Ni-17Co

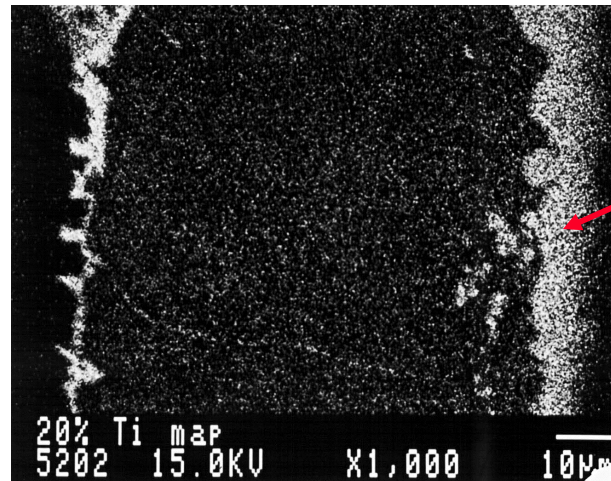
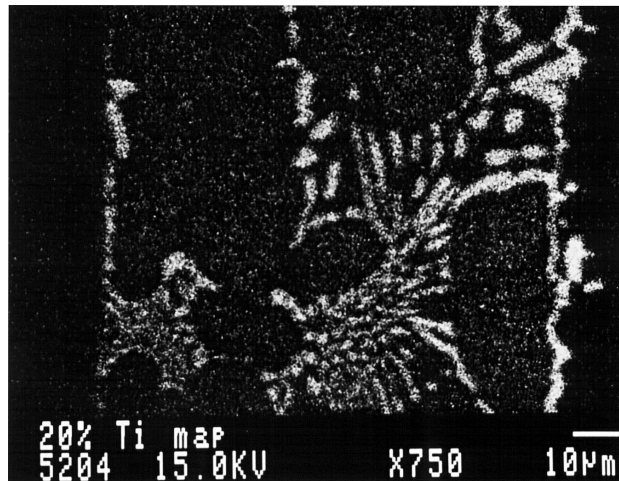


# Active Filler Metal Brazing

## 62Cu-35Ag-2Ti-1Ni

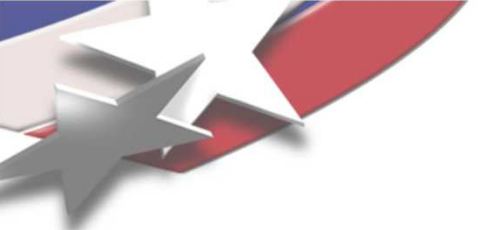


Comparison of  
molybdenum vs.  
Fe-29Ni-17Co  
metal members.



Note titanium  
penetration into  
Fe-29Ni-17Co

Reference: J. J Stephens et al - *Elevated Temperature Mechanical Properties of the 62Cu-35Au-2Ti-1Ni Braze Alloy*, 2004 AWS



# Direct Brazing

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## Procedure

- **Direct brazing lets one use conventional braze filler metals and standard brazing techniques when making metal to ceramic brazements.**
- **Specific metal substrate and braze filler metals interact to form an adherent metallic oxide layer on an oxide ceramic material.**
- **The metal and nonmetal substrates are cleaned, the braze filler metal is applied within the braze joint area.**
- **The braze is performed, usually in an inert or ultra-high vacuum environment.**

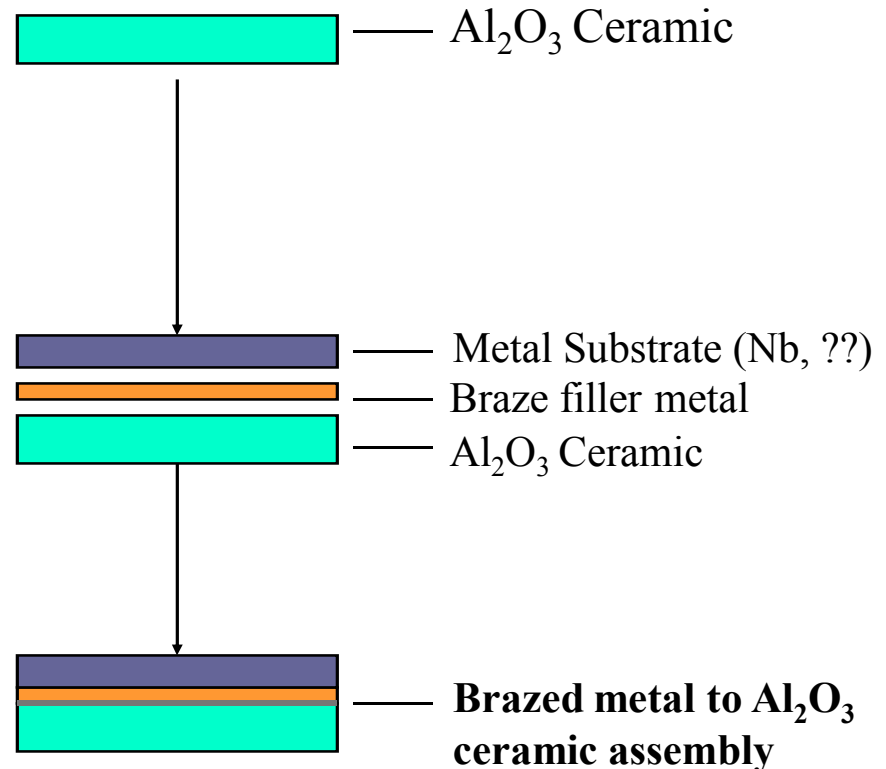
# Direct Brazing

## Advantages

- Ease of use
- Inexpensive
- Variety of filler metal schemes & temperature ranges
- No specialized metallization equipment or processes required
- Easily brazed using standard filler metals

## Disadvantages

- Requires specialized equipment/atmosphere control
- Not usable with all joint designs





# Direct Brazing

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## ASTM-F19 Tensile Button Test Results

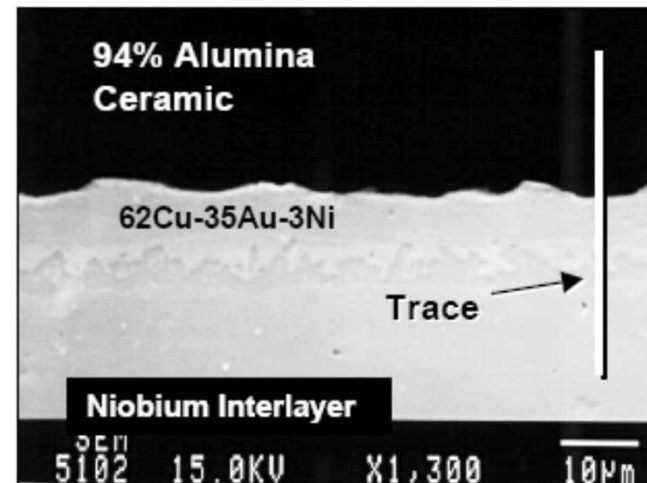
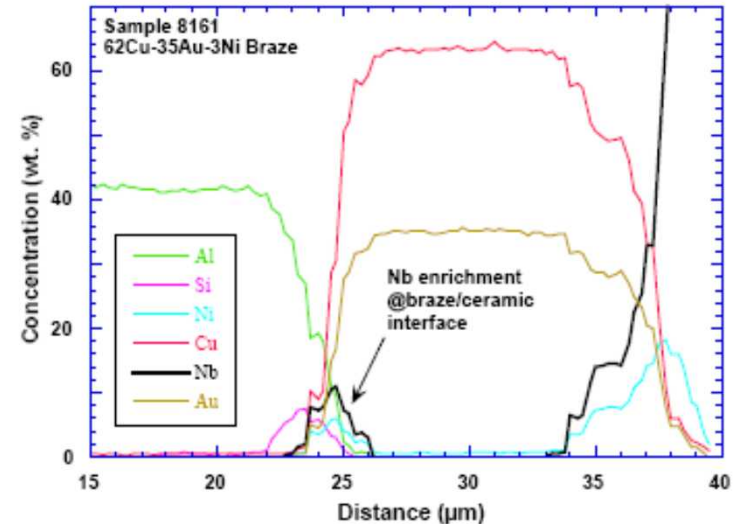
| Filler Metal  | Non-metal Substrate | Metal Substrate | Brazing Temperature | Furnace Atmosphere | Tensile Strength |
|---------------|---------------------|-----------------|---------------------|--------------------|------------------|
| 62Cu-35Au-3Ni | 94% Alumina         | Niobium         | 1058°C/3 min        | Vacuum             | 8.8ksi ±1.0ksi   |
| 92Au-8Pd      | 94% Alumina         | Niobium         | 1270°C/4 min        | Vacuum             | 12.8ksi ±1.8ksi  |
| 50Au-50Cu     | 94% Alumina         | Niobium         | 1000°C/3 min        | Vacuum             | 8.8ksi ±0.8ksi   |
|               |                     |                 |                     |                    |                  |

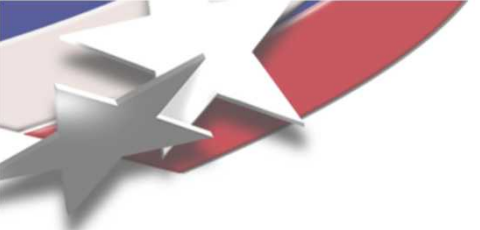
# Direct Brazing

## Requirement for successful braze joints:

- 1) Sufficient solubility of the metal member within the liquid braze alloy.
- 2) An "active" element within the metal member of the brazement.

This example shows how Niobium provides the "active" element to react with alumina ceramic.





# Summary

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- **Variety of methods can be used to make hermetic, strong metal to ceramic brazed assemblies.**
- **The use of conventional filler metals may be used when the ceramic surface is pre-metallized.**
- **A limited set of conventional filler metals form sufficient bond strength when used in conjunction with specific base metal combinations such as niobium and titanium.**
- **Active braze filler metals can be used as a replacement system for most metal to ceramic brazed assemblies with no loss of mechanical properties.**
- **Active and direct brazing techniques work best with butt or lap-style braze joint geometries.**



# Acknowledgements

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- **Mike Hosking**
- **Paul Vianco**
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- **Bonnie McKenzie**
- **Tom Crenshaw**