Robust Joining Technology for Solid Oxide Fuel Cells Applications

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Recently, there has been a great deal of interest in research, development, and commercialization of solid oxide fuel cells. Joining and sealing are critical issues that will need to be addressed before SOFCs can truly perform as expected. Ceramics and metals can be difficult to join together, especially when the joint must withstand up to 900°C operating temperature of the SOFCs. The goal of the present study is to find the most suitable braze material for joining of yttria stabilized zirconia (YSZ) to stainless steels. A number of commercially available braze materials TiCuSil, TiCuNi, Copper-ABA, Gold-ABA, and Gold-ABA-V have been evaluated. The oxidation behavior of the braze materials and steel substrates in air was also examined through thermogravimetric analysis. The microstructure and composition of the brazed regions have been examined by optical and scanning electron microscopy and EDS analysis. Effect of braze composition and processing conditions on the interfacial microstructure and composition of the joint regions will be presented.

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Overview

- **Introduction and Background**
- **Objectives**
- **Active Metal Brazes**
  - *Thermal properties*
  - *Oxidation in Air*
  - *Characterization of oxidized specimens*
- **Experimental Procedures**
- **Results and Discussion**
  - *Microstructural Characterization (SEM, Optical)*
  - *Energy Dispersive Spectroscopy (EDS) Analysis*
- **Summary and Conclusions**
- **Future Work**

Introduction and Background

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- Solid Oxide Fuel Cells (SOFCs) technology has gained considerable attention and importance in recent years.
- Robust assembly and manufacturing of components is a key issue for their wide scale applications.
- Metal-Ceramic brazing technology has been identified as a key area of concern for successful application of SOFCs.
  - *Seals, current collector plates, interconnects, etc.*
- Recently, there has been a wide variety of activities in this field from various groups worldwide.
- The brazing technology has to be robust and affordable. The brazed joints have to be environmentally durable under operating conditions.

Objectives

- To investigate and optimize active metal brazing of yttria stabilized zirconia (YSZ) to stainless steels.
- Characterize the microstructure and compositions of brazed joints.

Requirements for Brazing Technology for Solid Oxide Fuel Cell Applications

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Technical Issues in Brazing:

- Different classes of materials
- Must withstand a fuel cell environment
  - 700-900°C
  - Oxidizing atmosphere
- Minimal thermal expansion mismatch

Desirable Properties of Brazes:

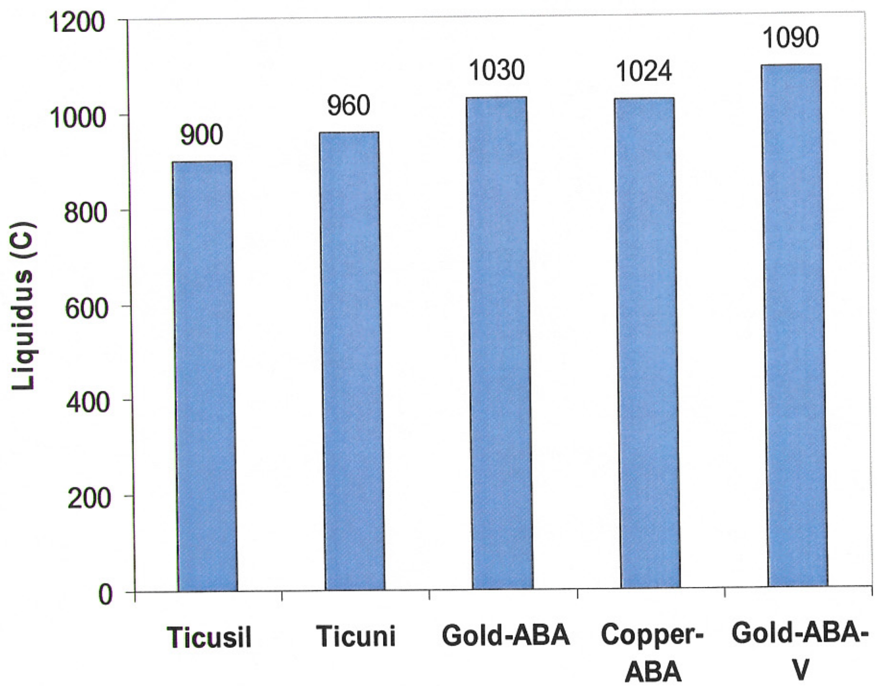
- Liquidus above operating temperature (700-900°C)
- Forms robust joint
- Thermal coefficient of expansion similar to stainless steel and yttria-stablilized zirconia (YSZ)
- Good oxidation resistance
- Economical

Materials and Experimental Procedures

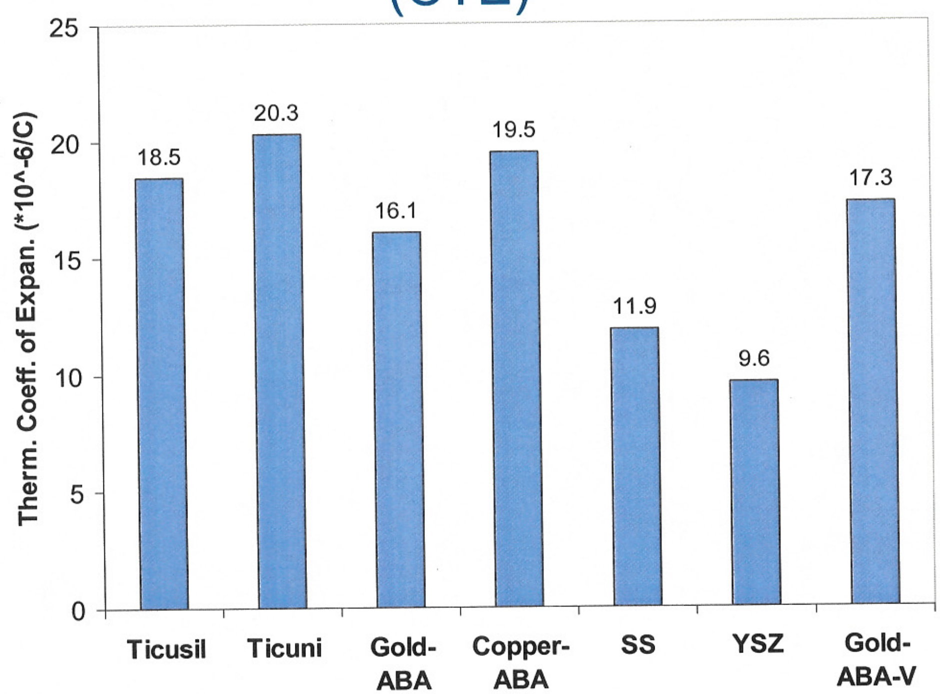
- **Substrate materials**
  - ½" square coupon of yttria-stabilized zirconia (3 and 8 mol%)
  - ½" square coupon of stainless steel (430 and 441)
- **Braze materials** → ***Morgan Advanced Ceramics (Wesgo Metals)***
  - Copper-ABA
  - Gold-ABA
  - Gold-ABA V
  - TiCuNi
  - TiCuSil
- **Experimental procedures**
  - Thermo Gravimetric Analysis in air
  - Furnace brazing in vacuum (10^{-5} Torr)
  - Microstructural Characterization
    - Optical microscopy
    - Scanning Electron Microscopy (SEM)
    - Energy Dispersive Spectroscopy (EDS)

Properties of Active Metal Brazes

Liquidus Temperatures



Coefficients of Thermal Expansion (CTE)



Source: Morgan Advanced Ceramics, Inc.

Characterization of Braze Materials

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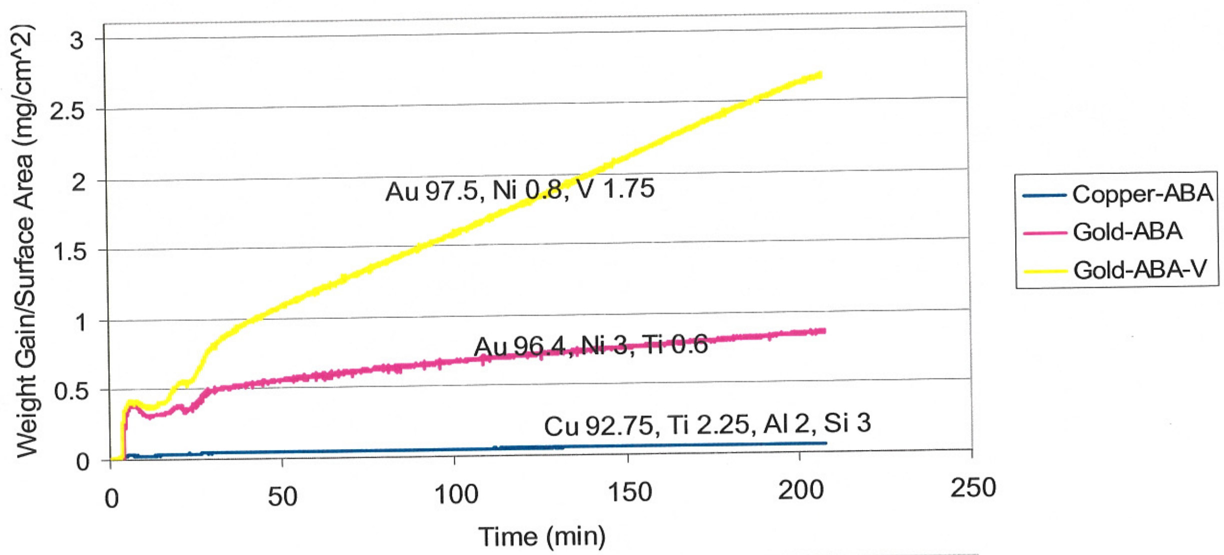
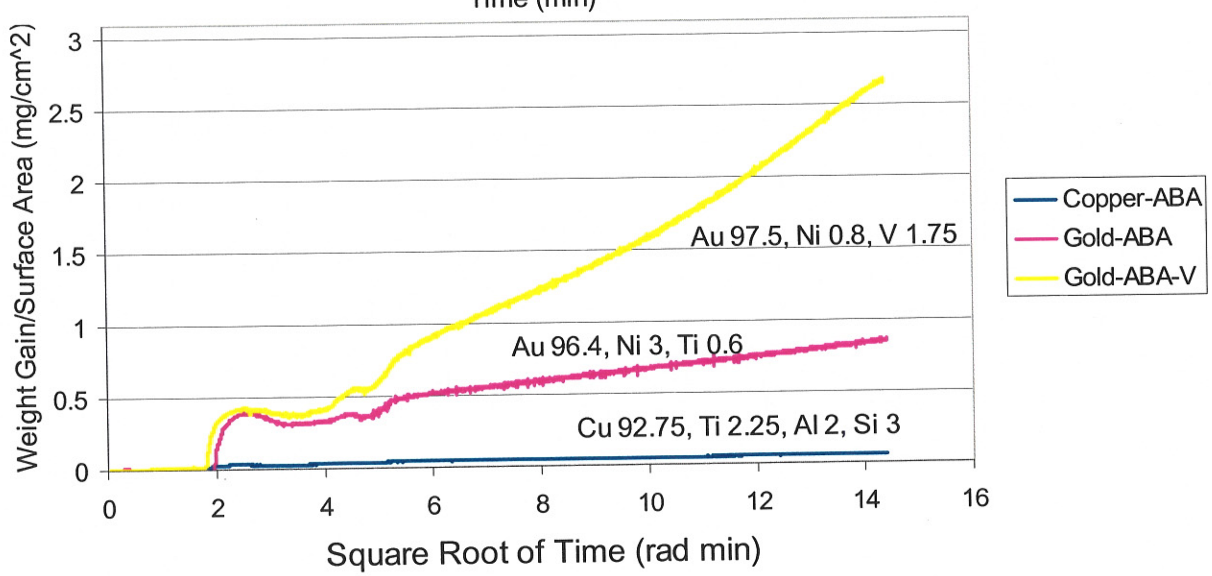
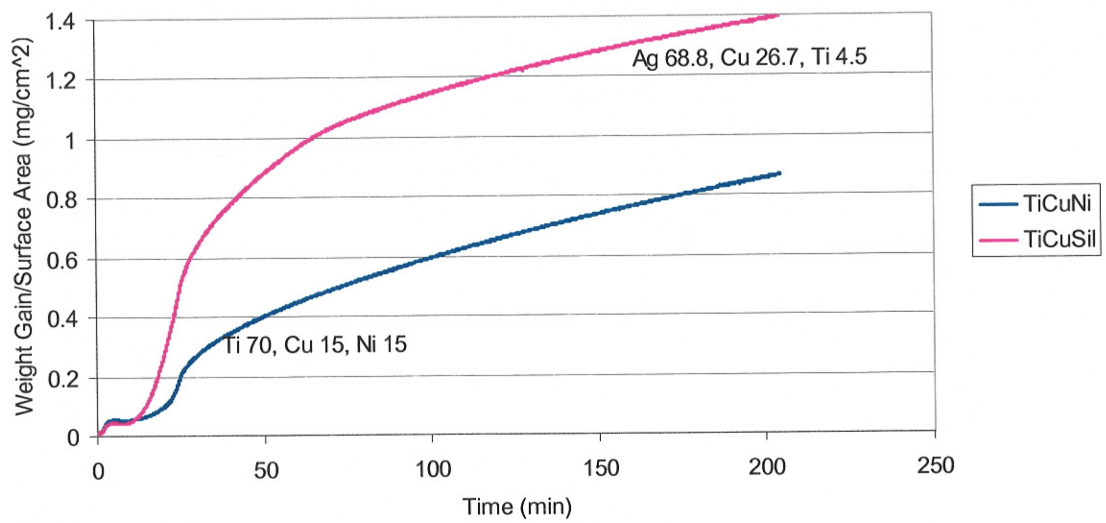
Oxidation Behavior (TGA analysis)
Scanning Electron Microscopy
EDS Analysis

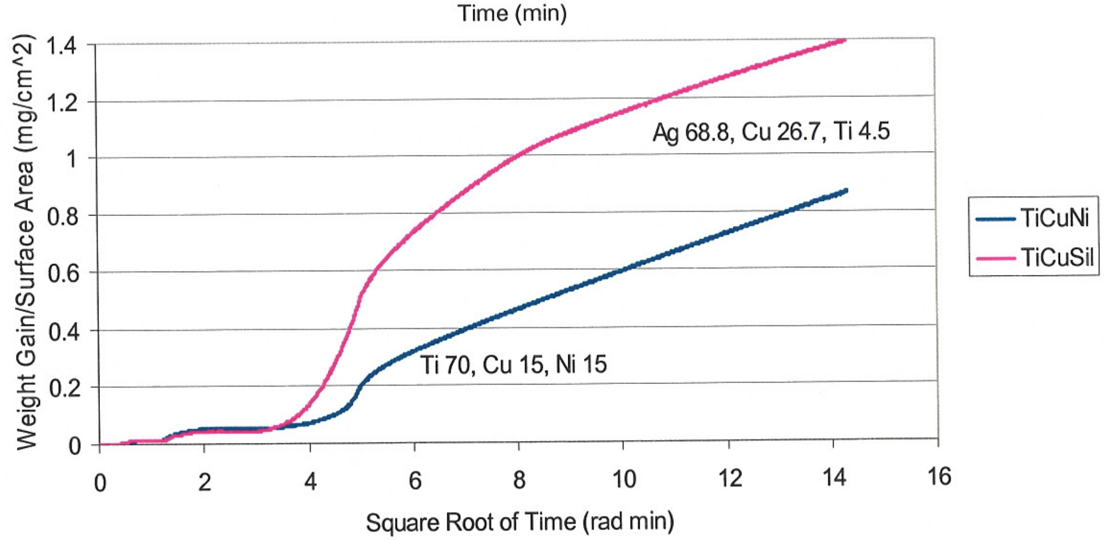
Oxidation Behavior in Air (850°C)





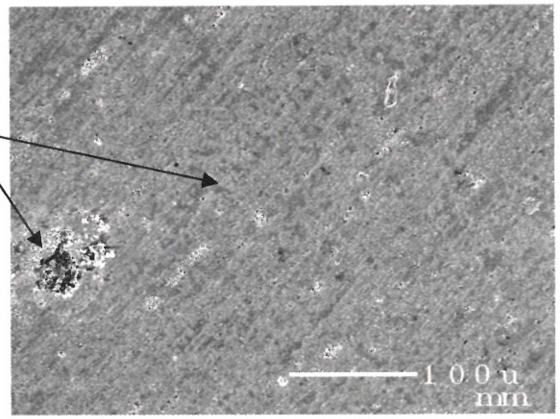
Oxidation Behavior in Air (750°C)



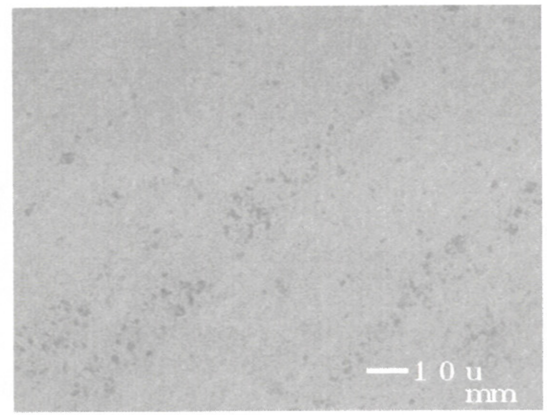


Microstructural Analysis of Copper ABA Foil After Oxidation at 850°C in Air

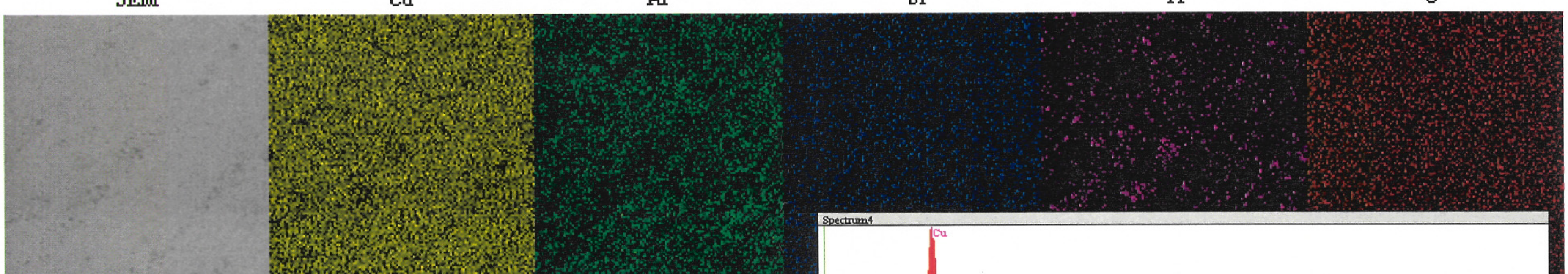
Striations & inclusions in cold worked metal



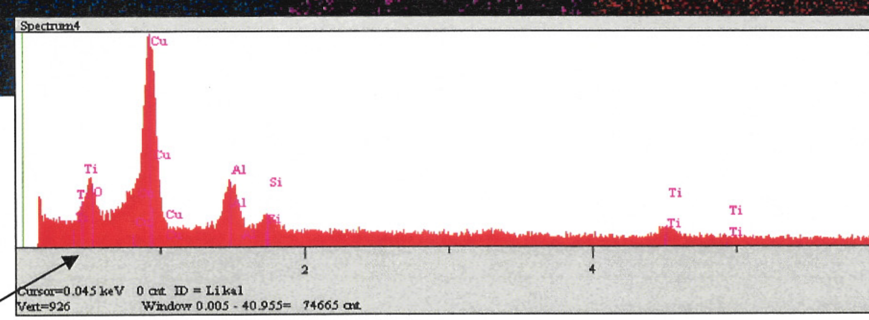
SE image (X 300)



BSE Image (X1000)



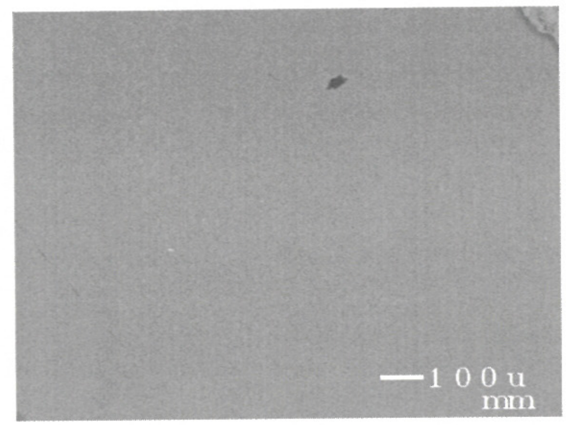
EDS Map Scan of oxide Region:
Oxides→ CuO, Al_2O_3 and trace amt. TiO_2



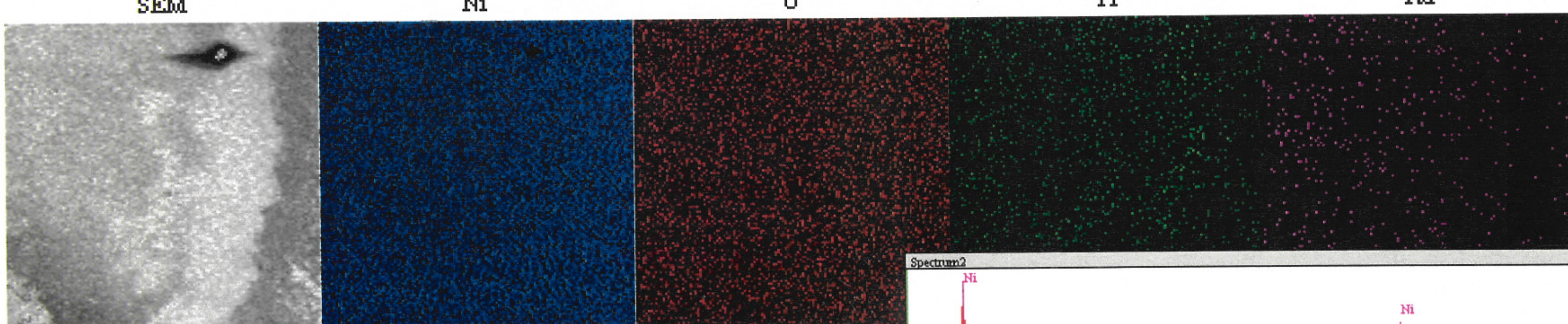
EDS Spectrum of oxide area

Microstructural Analysis of Gold ABA Foil After Oxidation at 850°C in Air

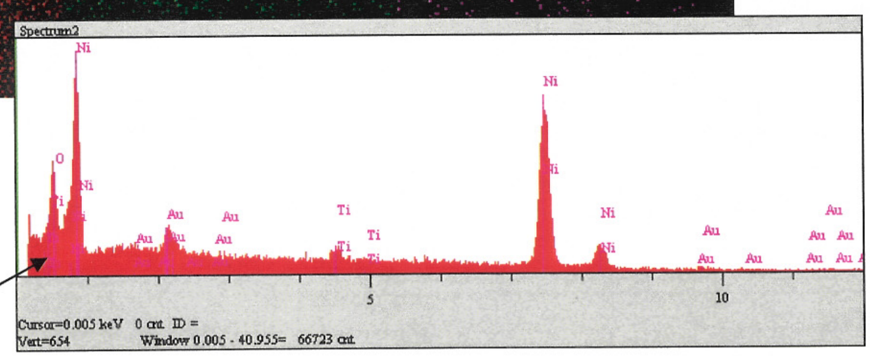
SE image (X 160)



BSE image (X 100)

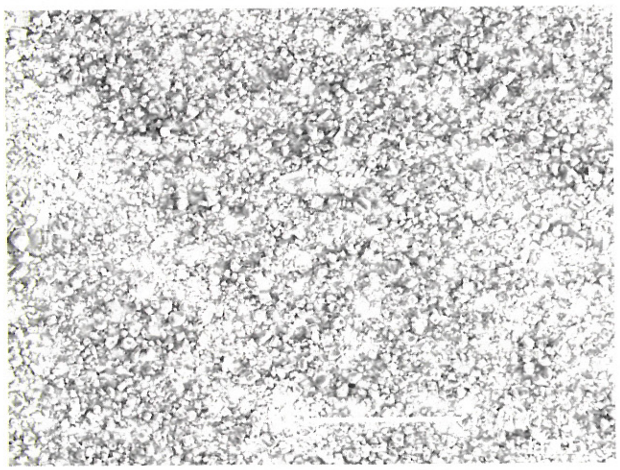


EDS Map Scan of oxide Region:
Oxides→ NiO and trace amts. TiO_2

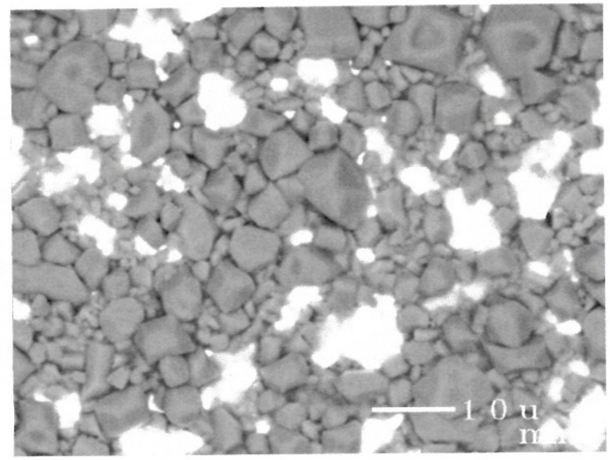


EDS Spectrum of oxide area

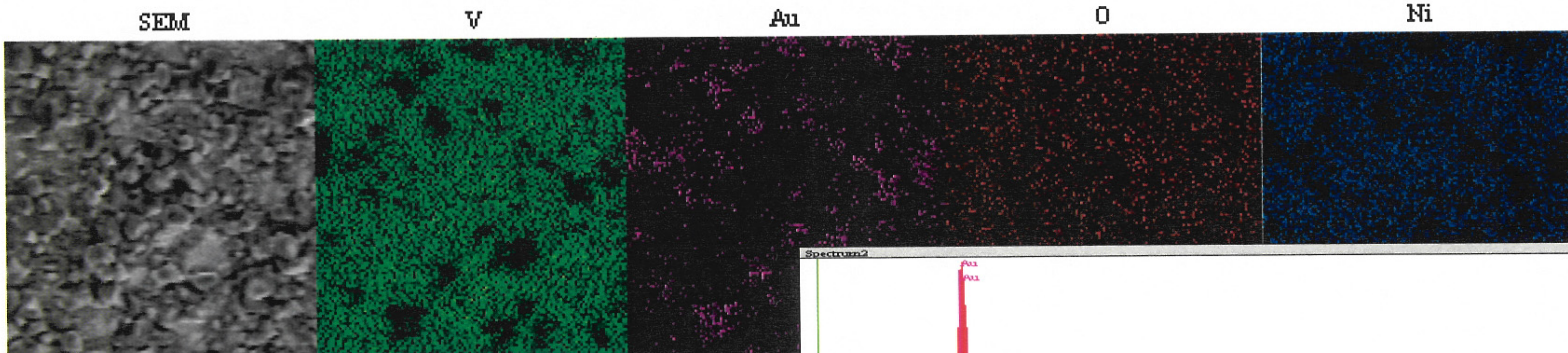
Microstructural Analysis of Gold-ABA-V Foil After Oxidation at 850°C in Air



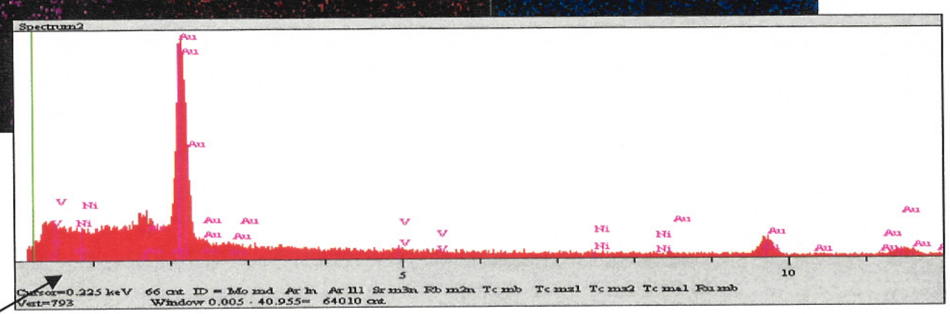
SE image (X 300)



BSE image (X 5200)

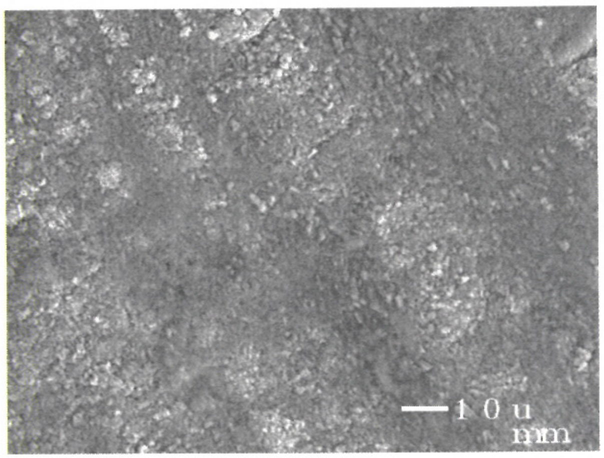


EDS Map Scan of oxide Region:
Oxide→ V_2O_5 and NiO

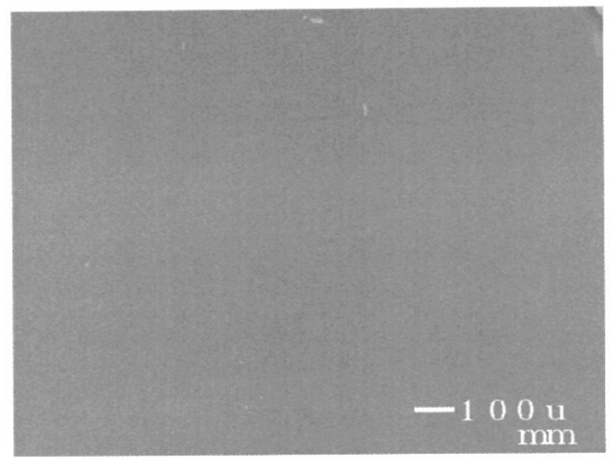


EDS Spectrum of oxide area

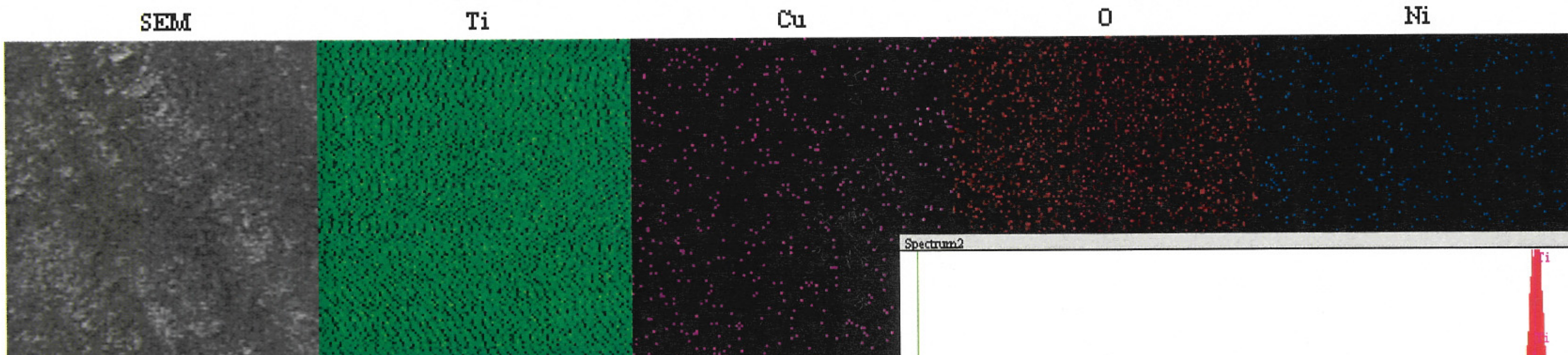
Microstructural Analysis of TiCuNi Foil After Oxidation at 750°C in Air



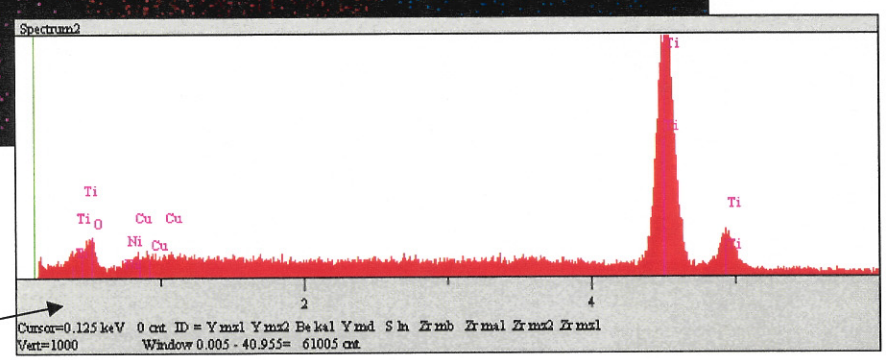
SE image (X 1000)



BSE image (X 85)

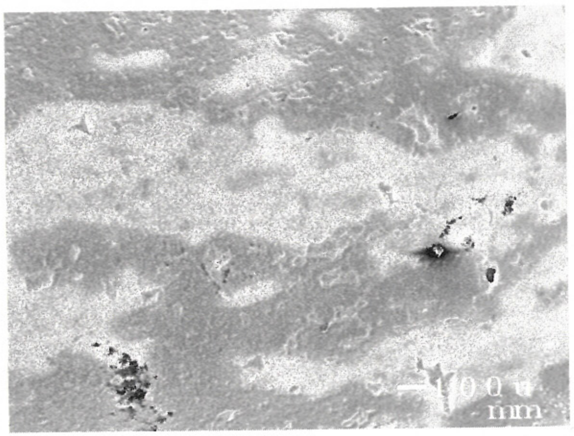


EDS Map Scan of oxide Region:
Oxide→ TiO_2

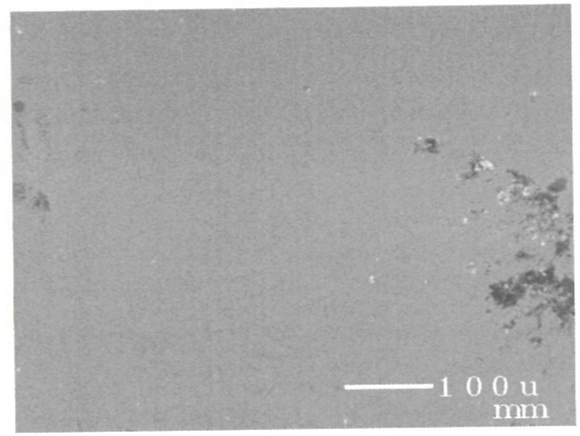


EDS Spectrum of oxide area

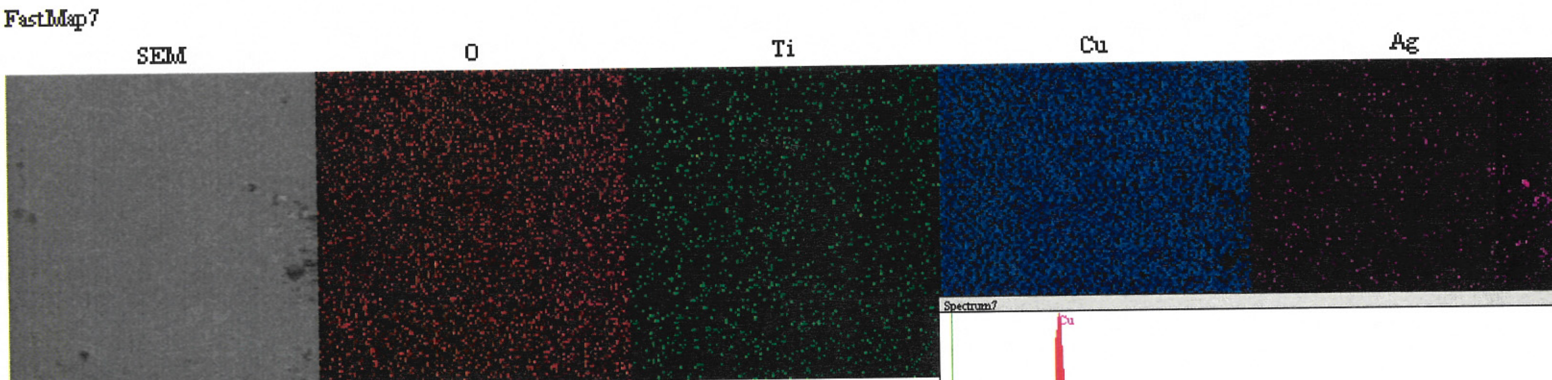
Microstructural Analysis of TiCuSil Foil After Oxidation at 750°C in Air



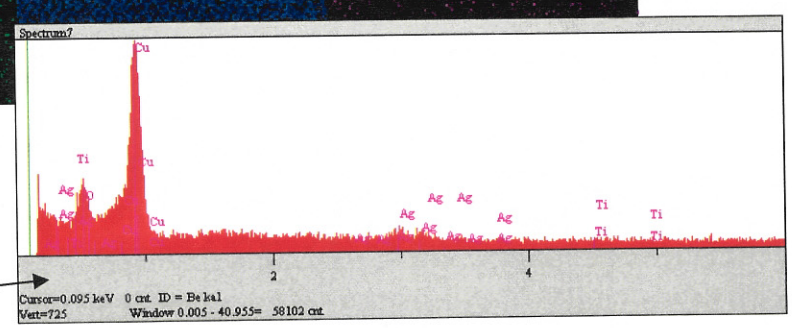
SE image (X 65)



BSE image (X 200)



EDS Map Scan of oxide Region:
Oxides→ CuO and TiO_2



EDS Spectrum of oxide area

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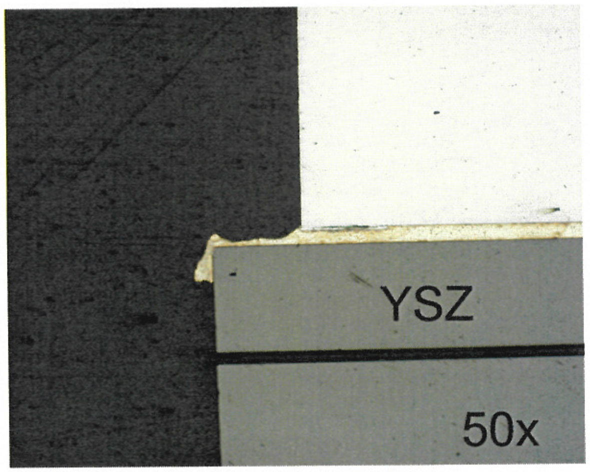
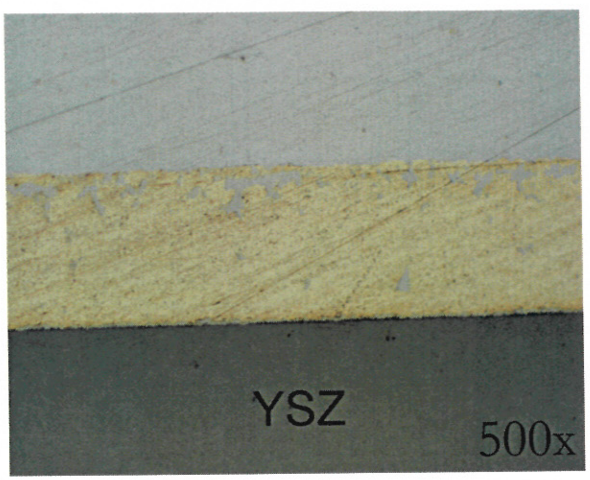
Optical Microscopy
SEM and EDS Analysis

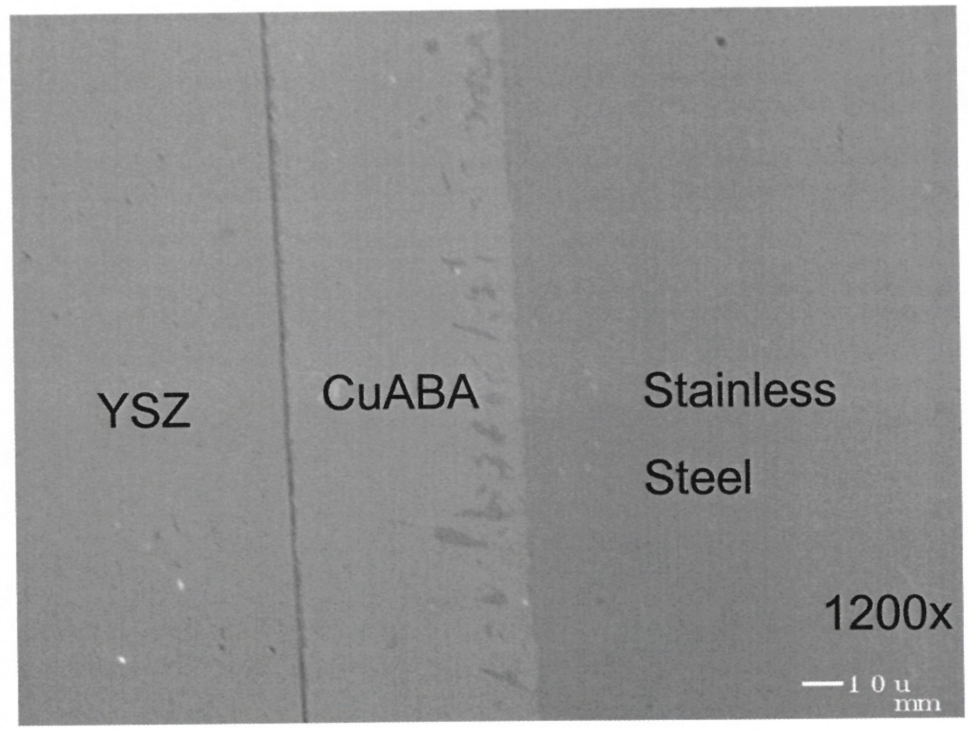
Copper-ABA Microscopy

Optical



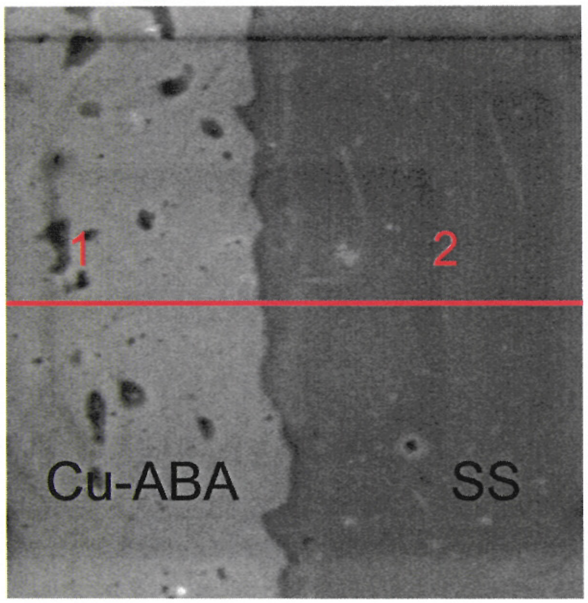


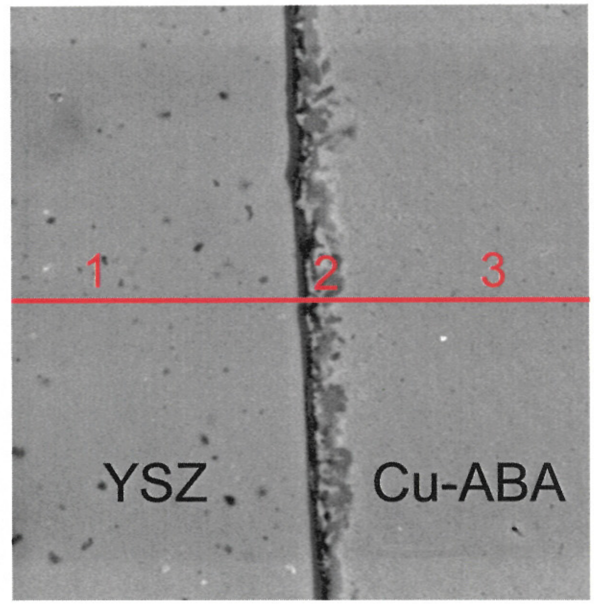
SEM



Copper-ABA EDS

Original Composition of Cu-ABA: 92.75% Cu, 3% Si, 2.25% Ti, 2% Al





Compositions:

1. 80%Cu, 6%Ti, 5%Si, 3%Fe, 3%Al, 2%Cr
2. 64%Fe, 19%Cr, 8%Al, 8%Si, 1%Ti

Al, Si, & Ti diffuses into the SS while the Fe & Cr migrate into the Cu-ABA

Compositions:

1. 85%Zr, 14%Y
2. 29%Ti, 29%Zr, 16%Al, 14%Si, 12%Y
3. 60%Cu, 13%Zr, 12%Y, 8%Al, 3% Si, 4%Ti

The interface is made up mostly of Ti & Zr. Zr & Y diffuse through the interface into the Cu-ABA. No traces of Cu-ABA constituents within the YSZ.

Gold-ABA Microscopy

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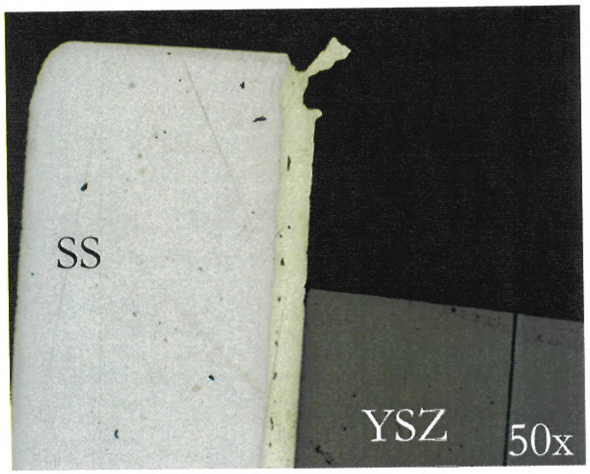
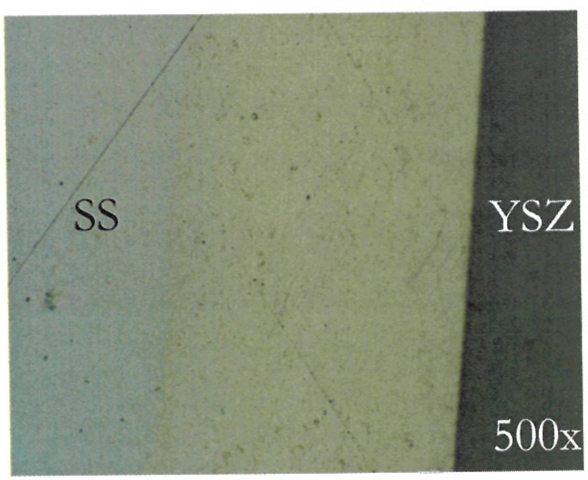
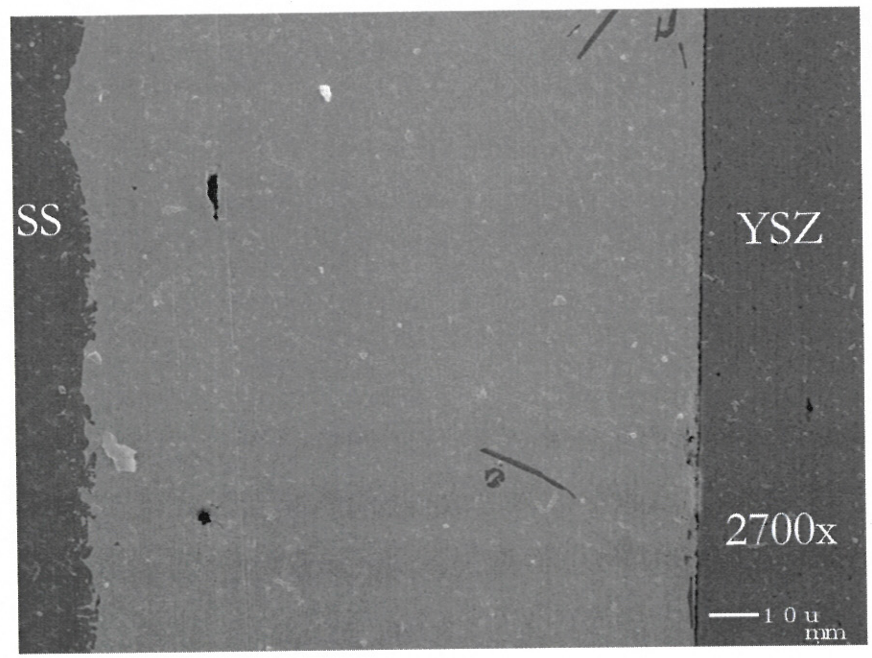
Optical



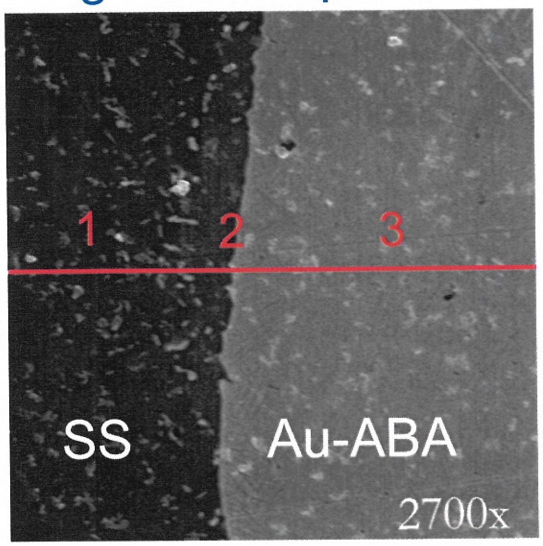


SEM



Gold-ABA EDS

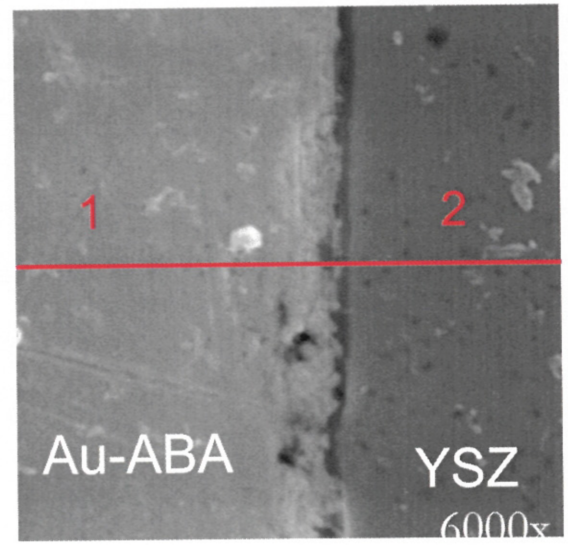
Original Composition of Gold-ABA: 96.4% Au, 3% Ni, 0.6% Ti



Compositions:

1. 71%Fe, 29%Cr
2. 87%Fe, 13%Cr
3. 83% Au, 4%Ni, 9%Fe, 4%Cr

Fe & Cr both migrate into the Au-ABA



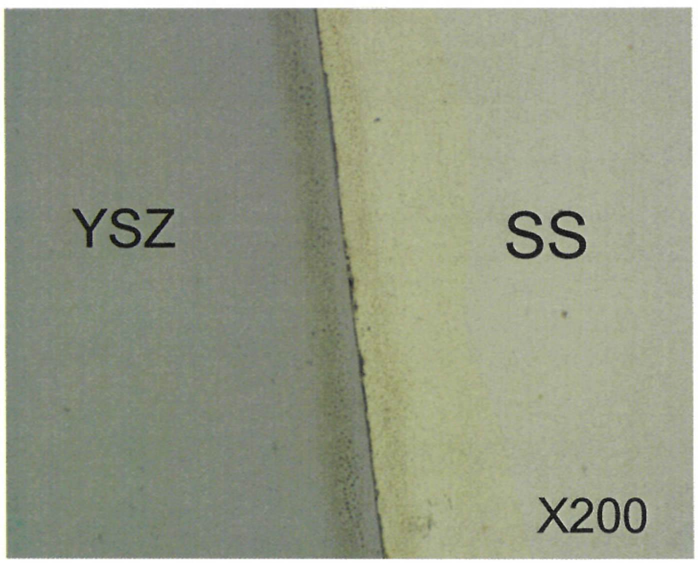
Compositions:

1. 88%Au, 8%Ni, 2%Ti, 1%Y, 1%Zr
2. 90%Zr, 10%Y

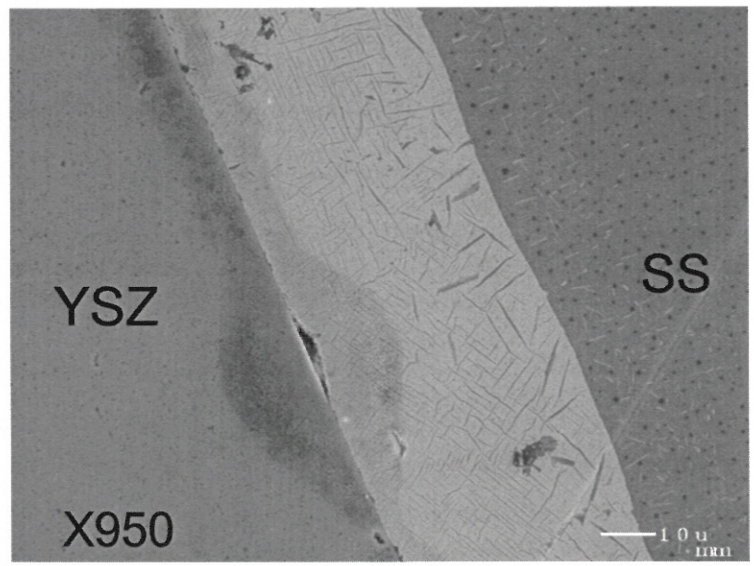
Diffusion of Zr & Y into the Au-ABA

Gold ABA-V Microscopy

Optical Images

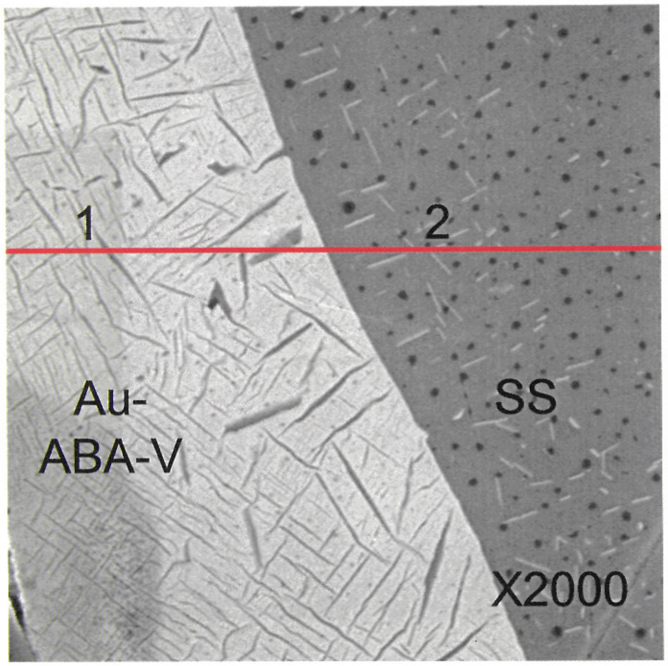


SEM



Gold ABA-V EDS

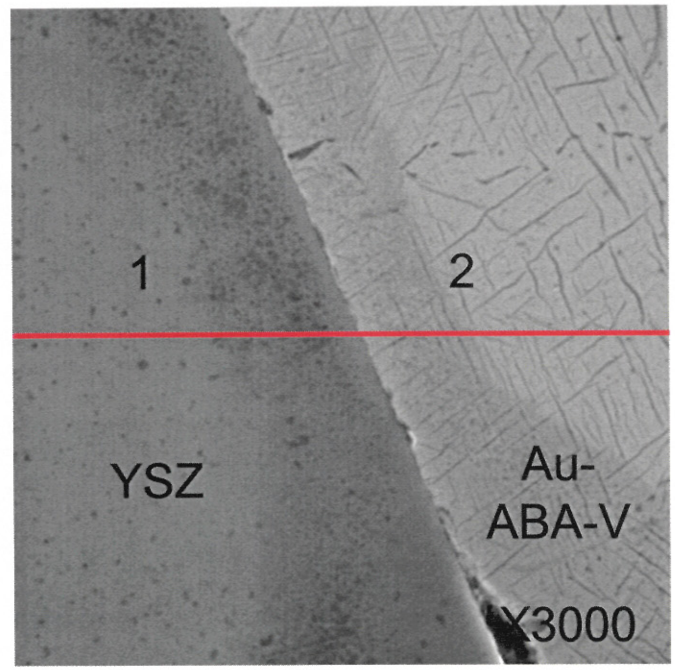
Original Composition of Gold ABA-V: 97.5% Au, 1.75% V, 0.8% Ni



Composition:

1. **78%Au, 6%Cr, 7%Fe, 5%V, 4%Ni**
2. **80%Fe, 17%cr, 3%V**

Fe & Cr migrate into Au-ABA-V
while V diffuses into SS



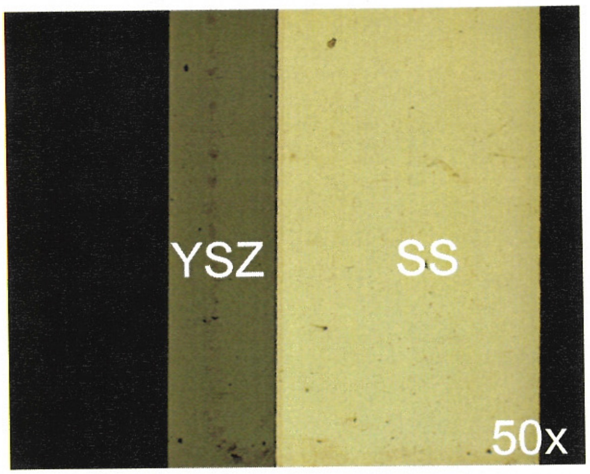
Composition:

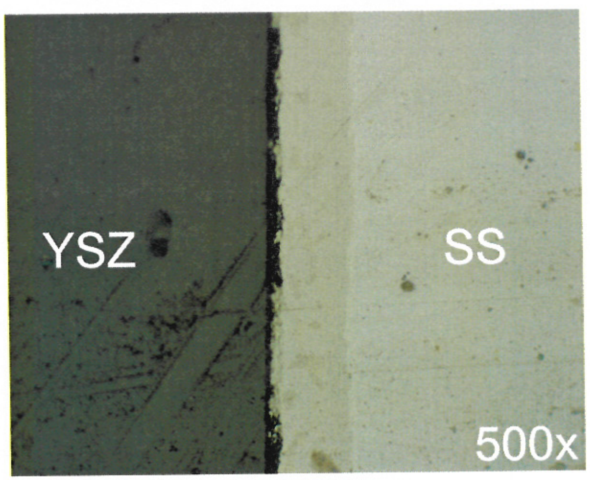
1. **85%Zr, 10%Y, 5%V**
2. **92%Au, 4%Ni, 3%V, 1%Y**

V also migrates into the YSZ
while Y diffuses into Au-ABA-V

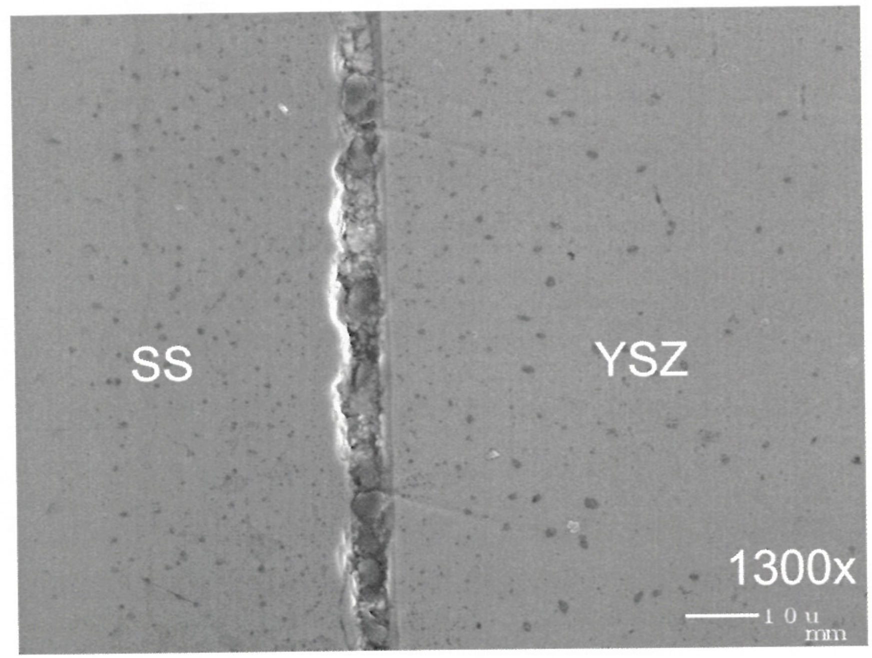
TiCuNi Microscopy

Optical





SEM



TiCuNi EDS

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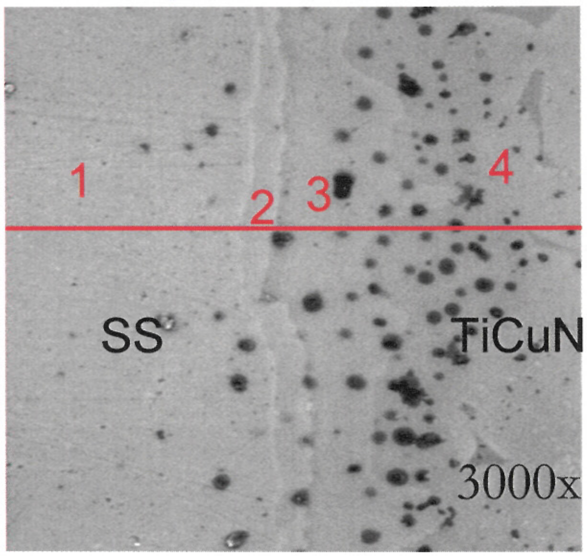
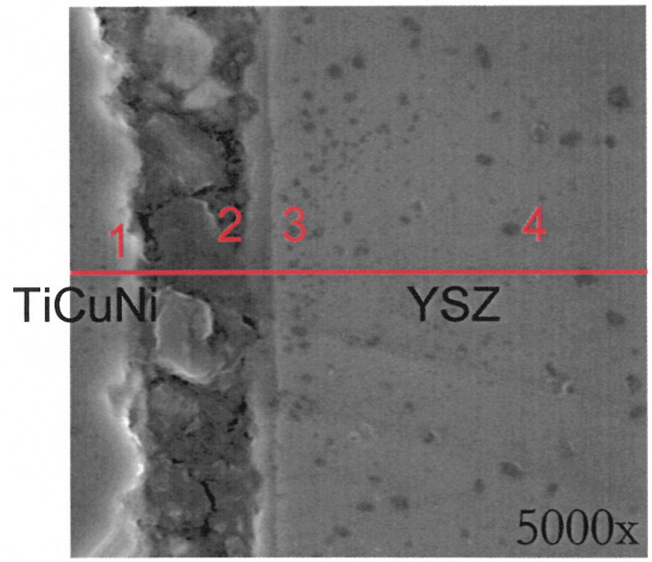
Original Composition of TiCuNi: 70% Ti, 15% Cu, 15% Ni



Composition:

1. 78%Fe, 20%Cr, 2%Ti
2. 61%Fe, 25%Ti, 14%Cr
3. 32%Ti, 23%Ni, 21% Cu, 17%Fe, 8%Cr
4. 44%Ti, 24%Cu, 15%Ni, 10%Fe, 6%Cr

The TiCuNi & SS completely diffuse into one another. If is very difficult to determine the interface.



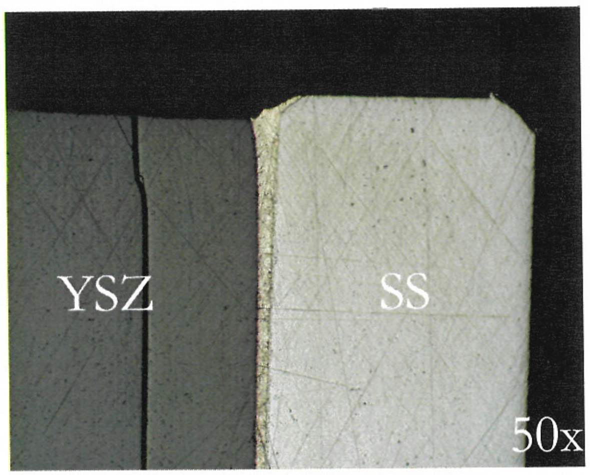
Composition:

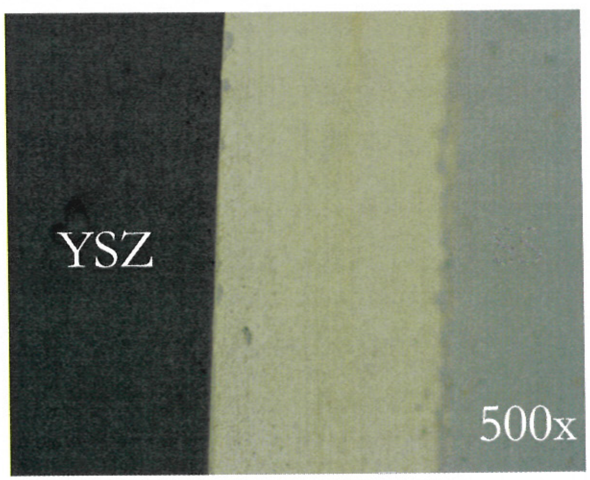
1. 56%Ti, 23%Ni, 11%Fe, 6%Cu, 3%Zr, 1%Y
2. 47%Zr, 31%Ti, 22%Y
3. 71%Ti, 29%Zr
4. 93%Zr, 7%Y

Cracking occurs along the YSZ & TiCuNi interface.

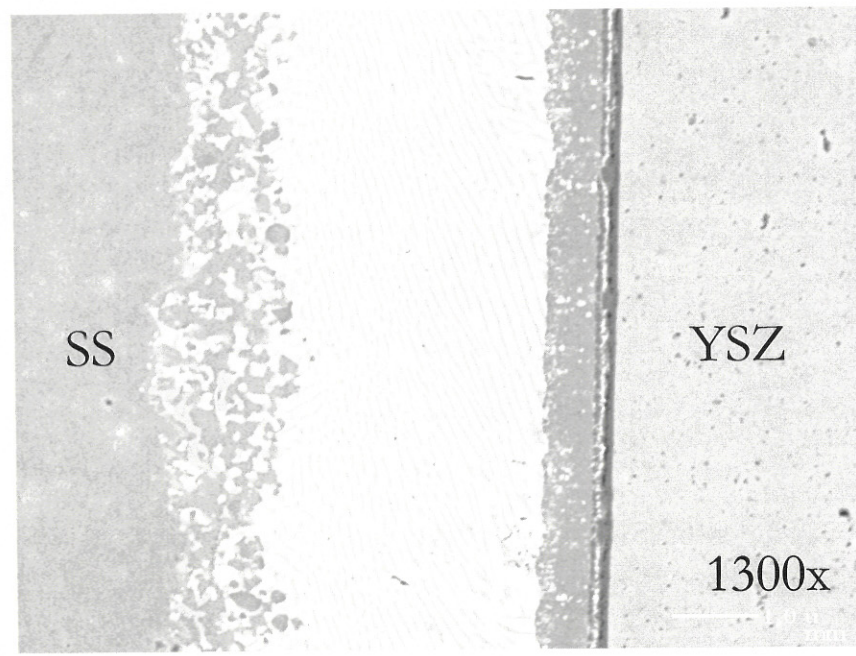
TiCuSil Microscopy

Optical





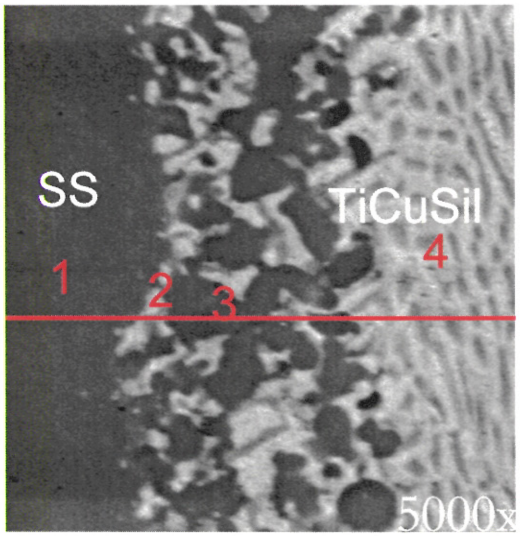
SEM



TiCuSil EDS

QSS Group, Inc.

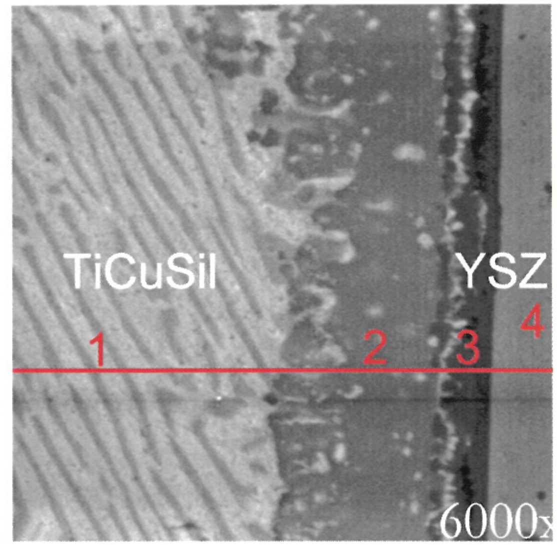
Original Composition of TiCuSil: 68.8% Ag, 26.7% Cu, 4.5% Ti



Composition:

1. **61%Fe, 27%Cr, 7%Ag, 5%Ti**
2. **45%Cu, 30%Ag, 10%Fe, 8%Ti, 7%Cr**
3. **51%Fe, 21%Ti, 16%Cr, 12%Ag**
4. **51%Ag, 22%Cu, 10%Fe, 9%Cr, 8%Ti**

TiCuSil interacts well with both the YSZ and the SS. The SS & TiCuSil are interdiffused along the interface.



Composition:

1. **60%Ag, 28%Cu, 6%Ti, 3%Zr, 3%Y**
2. **52%Ti, 23%Cu, 13%Ag, 8%Zr, 4%Y**
3. **78%Ti, 14%Zr, 8%Ag**
4. **80%Zr, 17%Ag, 3%Y**

There is a build up of Ti along the interface. The Ti removes oxygen from the YSZ creating the dark region.

Summary

	Liquidus	Oxidation Rate	CTE	Interaction	Cost
Copper ABA	high	low	possible issue	Good	moderate
Gold ABA	high	low	close to substrates	Good	high
Gold ABA-V	high	high	close to substrates	Good	high
TiCuNi	low	low	possible issue	YSZ issue	low
TiCuSil	low	high	close to substrates	Good	low

Conclusion/Future Work

- **Conclusions**
  - All the active metal brazes show good bonding with the YSZ & SS substrates
  - Application conditions & cost could be used as selection criteria

- **Future Work**
  - Mechanical testing of brazed joints at room and high temperatures
  - Thermal cycling and testing in a fuel cell-like environment

Acknowledgements

- Dr. Linus Thomas-Ogbuji
- John Setlock
- Richard Dacek
- Larry Huse and Mark Jester
- Jeanie Petko