*MS&T 2008 Pittsburgh, Joining Symposium*

# Joining of Zirconium Diboride-Based Ceramic Composites to Metallic Systems for High-Temperature Applications

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## Abstract

Three types of hot-pressed zirconium diboride ($ZrB_2$)-based ultra-high-temperature ceramic composites (UHTCC), $ZrB_2$-SiC (ZS), $ZrB_2$-SiC-C (ZSC), and $ZrB_2$-SCS9-SiC (ZSS), were joined to Cu-clad-Mo using two Ag-Cu brazes (Cusil-ABA and Ticusil, $T_L$~1073-1173ºK) and two Pd-base brazes (Palco and Palni, $T_L$~1493-1513ºK). Scanning Electron Microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) revealed greater chemical interaction in joints made using Pd-base brazes than in joints made using Ag-Cu based active brazes. The degree of densification achieved in hot pressed composites influenced the Knoop hardness of the UHTCC and the hardness distribution across the braze interlayer. The braze region in Pd-base system displayed higher hardness in joints made using fully-dense ZS composites than in joints made using partially-dense ZSS composites and the carbon-containing ZSC composites. Calculations indicate a small negative elastic strain energy and an increase in the UHTCC's fracture stress up to a critical clad layer thickness (~23% per side on Mo substrate) because $\alpha_{\text{Cu-clad-Mo}} < \alpha_{ZS}$ ($\alpha$ = CTE). Above this critical thickness, $\alpha_{\text{Cu-clad-Mo}} > \alpha_{ZS}$, strain energy in the UHTCC is positive, and it increases with increasing clad layer thickness. Empirical projections show a reduction in the effective thermal resistance of the joints and highlight the potential benefits of joining the UHTCC to Cu-clad-Mo.

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## Overview

- Introduction and Background
- Experimental Procedure
  - *Active Metal Brazing*
  - *Characterization (SEM, EDS)*
  - *Hardness behavior*
- Results and Discussion
  - *Ag-Cu based brazes*
  - *Pd based brazes*
  - *Strain energy calculations*
  - *Estimation of joint conductance*
- Concluding Remarks
- Acknowledgment

## Introduction and Background

- **$ZrB_2$ has high melting point (~3493 K), good oxidation resistance and low density (6,090 kg.m$^{-3}$).**
- **$ZrB_2$-based UHTCC have potential to operate at 2150-2770 K in applications such as nose cap and sharp leading edges of space vehicles.**
- **High-temperature strength, fracture toughness, oxidation resistance, and thermal shock resistance reported in the literature. However, scant work on joining of $ZrB_2$-based UHTCC to metallic systems has been reported.**
  - **Muolo et al, *Proc. 9th International Symposium on Materials in a Space Environment*, June 2003.**
  - **Singh and Asthana, *Mater. Sci. Eng. A,* 460-461 153-162 (2007).**
  - **Singh and Asthana, *Int. J. Applied Ceramic Technology (in press, 2008).***

## Objective

- **Utilize active metal brazing approach to join three $ZrB_2$-based ultra high temperature ceramic composites (UHTCC) to Cu-clad-Mo using two Pd-base brazes ($T_L$~1492-1511 K) and two AgCuTi brazes ($T_L$~1073-1173 K).**
- **Characterize the joint microstructure, composition, and microhardness distribution across the joint interface.**
- **Estimate the residual stress and effective thermal resistance in the joint.**

# Challenges in Joining of $ZrB_2$-Based Ultra High Temperature Ceramic Composites

- **Wettability:** **flow and spreading characteristics.**

***Pd-base brazes:***

**- No wettability data for Pd on $ZrB_2$.**
**- θ of Co (~39º) and Ni (~42º) at 1773 K indicates wetting.**
***- Pd-base brazes may also wet $ZrB_2$.***

***Ag-Cu brazes:***

**- Cu wets $ZrB_2$ (θ~80º at 1413 K).**
**- Ag does not wet $ZrB_2$ (θ~114º at 1373 K).**
**- Ti, Zr, or Hf in Ag improve the wetting (θ~20-80º).**
***- Cusil-ABA (1.75% Ti) and Ticusil (4.5% Ti) shall wet $ZrB_2$.***

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# Challenges in Joining of $ZrB_2$-Based Ultra High Temperature Composites

- **Thermoelastic incompatibility:** **thermal expansion mismatch.**

**- CTE of $ZrB_2$-based UHTCC ~$7.5\times10^{-6}$/K.**
**- CTE of Cu-clad-Mo ~ $5.6\text{-}11.6\times10^{-6}$/K for 5 to 40% clad thickness.**

**- Thermal strain, $\Delta\alpha\Delta T$, can be decreased by controlling the clad layer thickness.**

**- Copper as a cladding on Mo shall serve as a stress-absorbing layer.**

# Experimental Procedure

## - Materials -

- **Braze alloys: Palni, Palco, Cusil-ABA and Ticusil**
  ***Morgan Advanced Ceramics, Hayward, CA.***

- **Composites: $ZrB_2$-$SiC_p$ (ZS), $ZrB_2$- SCS9A-$SiC_p$ (ZSS), $ZrB_2$-$SiC_p$-$C_p$ (ZSC)**
  ***Materials and Machines, Inc, Tucson, AZ***
  *(Uni-axially hot-pressed in a graphite die. ZSS made by filament winding, slurry deposition, and hot-pressing)*

- **Cu-clad-Mo plates (Cu-Mo-Cu ratio: 13%-74%-13%)**
  ***H.C. Starck, Inc., Newton, MA.***
  *(Manufactured by rolling a Mo core sandwiched between two Cu layers)*

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# Composition and Properties of Brazes and Substrate Materials

| Braze Composition, (wt %) | Density Kg.m$^{-3}$ | $T_L$, °K | $T_S$, °K | E, GPa | YS, MPa | UTS, MPa | CTE, ×$10^{-6}$ $K^{-1}$ | % El. | K, W/m.K |
|---|---|---|---|---|---|---|---|---|---|
| Cusil-ABA® (63Ag-35.3Cu-1.75Ti) | 18,500 | 1088 | 1053 | 83 | 271 | 346 | 18.5 | 42 | 180 |
| Ticusil® (68.8Ag-26.7Cu-4.5Ti) | 18,500 | 1173 | 1053 | 85 | 292 | 339 | 18.5 | 28 | 219 |
| Palco® (65Pd-35Co) | - | 1492 | 1492 | -- | 341 | 661 | -- | 43 | 35 |
| Palni® (60Pd-40Ni) | 15,000 | 1511 | 1511 | -- | 772 | 978 | 15 | 23 | 42 |

*E: Young's modulus, YS: yield strength, UTS: tensile strength, CTE: coeff. of thermal expansion, %El: percent elongation, K: thermal conductivity.*

| Composite | Composition |
|---|---|
| $ZrB_2$- SCS9A-SiC (ZSS) | $ZrB_2$ + 20 v/o SiC particles + 35 v/o SCS9A SiC fiber |
| $ZrB_2$-SiC-C (ZSC) | $ZrB_2$ + 14 v/o SiC particles + 30 v/o carbon |
| $ZrB_2$-SiC (ZS) | $ZrB_2$ + 20 v/o SiC particles |

*SCS-9A is a small (~78 µm) diameter SiC fiber from Textron Specialty Materials, Lowell, MA.*

# Experimental Procedure

- **Substrates and braze foils cut into 2.54 cm x 1.25 cm x 0.25 cm panels and ultrasonically cleaned.**
- **Two braze foils sandwiched between substrates and heated under vacuum (~$10^{-6}$ torr) to 15-20 °C above braze $T_L$. After 5 min. soak, slowly cooled to room temperature.**
- **Brazed joints mounted in epoxy, ground, polished, and examined using optical microscopy and Scanning Electron Microscopy (JEOL JSM-740A) coupled with EDS.**
- **Microhardness (Knoop indenter) on Struers Duramin-A300 machine (200 g load, 10 s). Four-to-six scans across each joint.**

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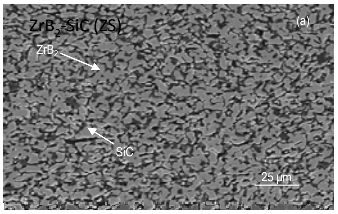
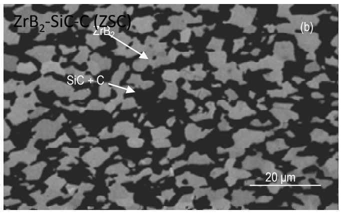
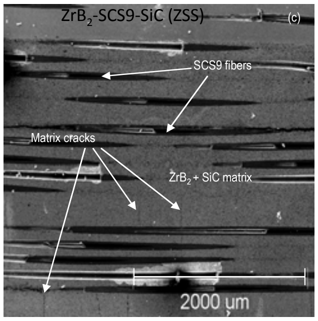
# Microstructure of UHTC Composites







- Equi-axed $ZrB_2$ particles (~6-12 µm dia), tabular/plate-like SiC particles (~3-11 µm × 1.5-3 µm).
- Transverse micro-cracks in ZSS due to CTE mismatch between $ZrB_2$ and SCS9A fiber.

# UHTC Composites-Metal Joints Using Ag-Cu-Ti Active Braze Alloys

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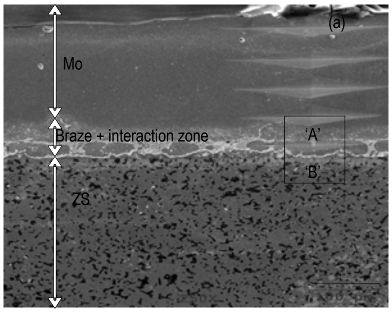
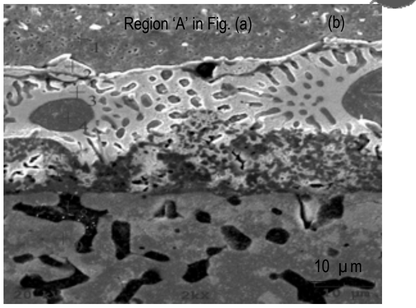
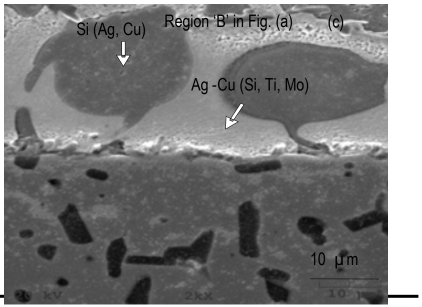
## Microstructure of ZS/Cusil-ABA/Cu-clad-Mo joint

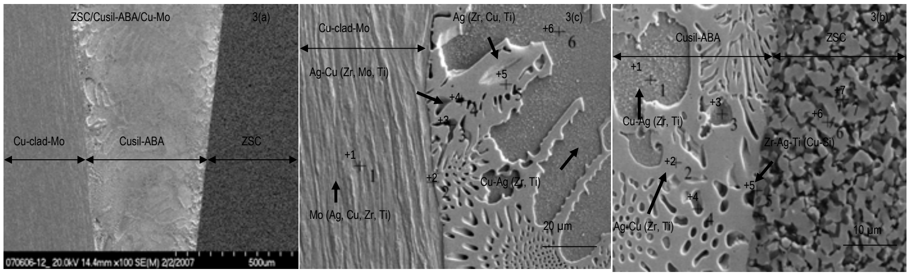




- **Sound joint devoid of imperfections.**
- **Ag-Cu and Si-rich phases decorate the ZS/Cusil-ABA interface**



## Microstructure of ZSC/Cusil-ABA/Cu-clad-Mo joint



- Metal and composite substrates are covered with a Ag-rich phase.
- Relatively large (~19at%) amounts of Ag and Ti at the braze/ZSC Interface.
- Small amounts of Zr and Mo in braze (~4-5at%).

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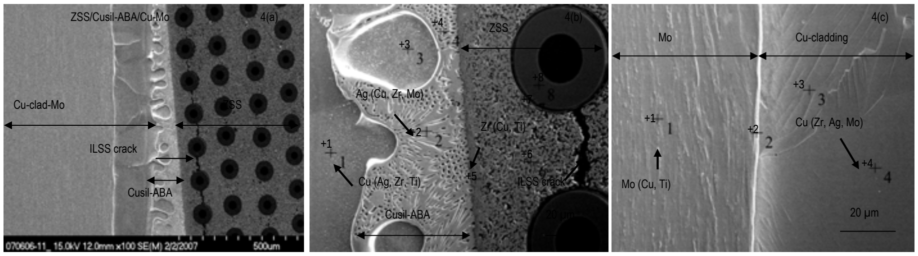
## Microstructure of ZSS/Cusil-ABA/Cu-clad-Mo joint



- Some longitudinal cracking in composite near joint.
- Minute (2-3 atom%) dissolution of Zr in braze.
- Two-phase eutectic structure in braze (Ag- and Cu-rich phases).
- Ag-rich phase deposited onto ZSS.

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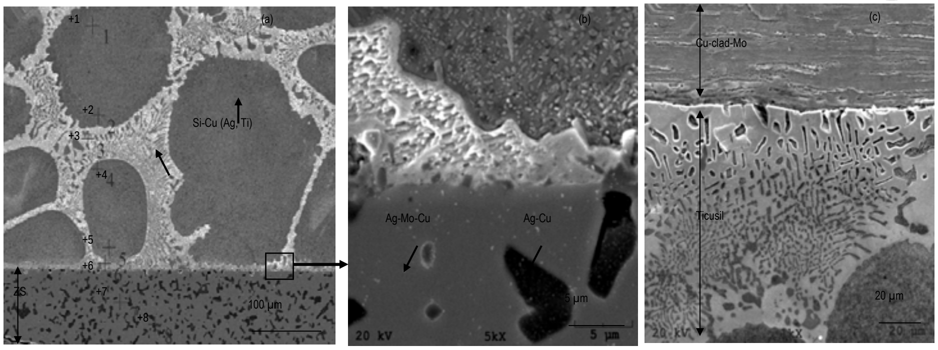
## Microstructure of ZS/Ticusil/Cu-clad-Mo joint



- Sound joint. Ti segregation at interface.
- Extensive Si dissolution in braze.

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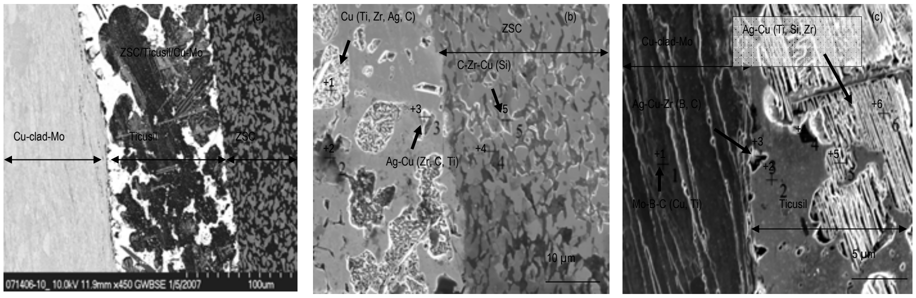
## Microstructure of ZSC/Ticusil/Cu-clad-Mo joint



- Zr dissolution in braze (4-6 at%).
- Cu diffusion in ZSC (4-10 at%).
- C and B dissolution in braze (4-6 at%).

# UHTC Composites-Metal Joints Using Pd-Based Braze Alloys

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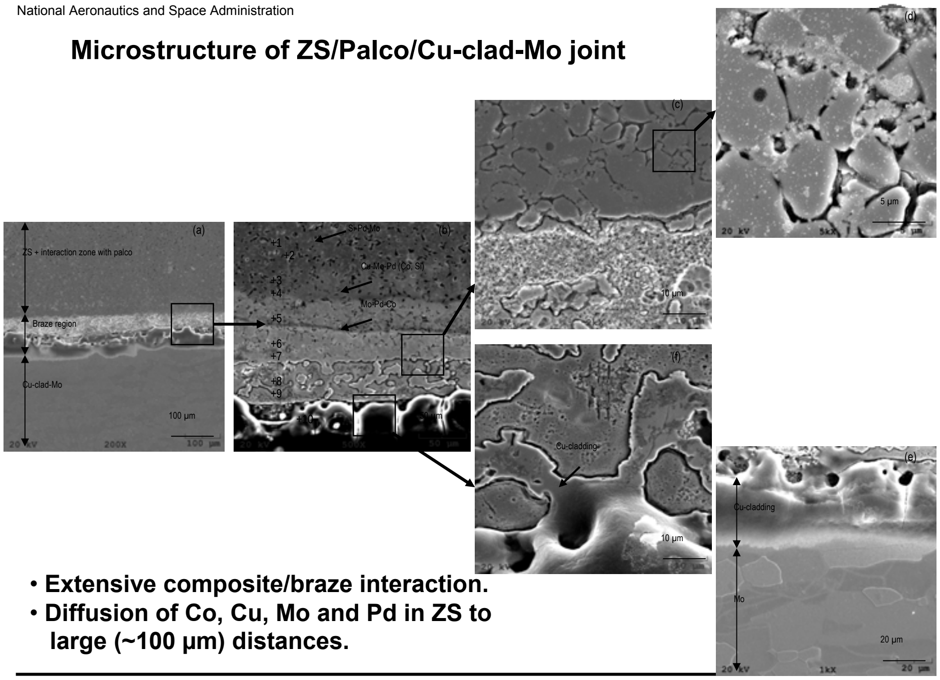
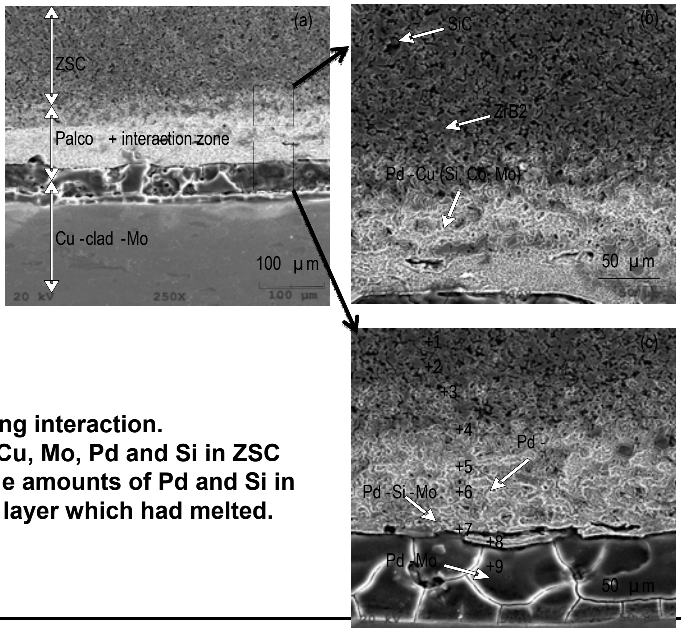
# Microstructure of ZS/Palco/Cu-clad-Mo joint



- Extensive composite/braze interaction.
- Diffusion of Co, Cu, Mo and Pd in ZS to large (~100 µm) distances.

# Microstructure of ZSC/Palco/Cu-clad-Mo joint



- **Strong interaction.**
- **Co, Cu, Mo, Pd and Si in ZSC**
- **Large amounts of Pd and Si in clad layer which had melted.**

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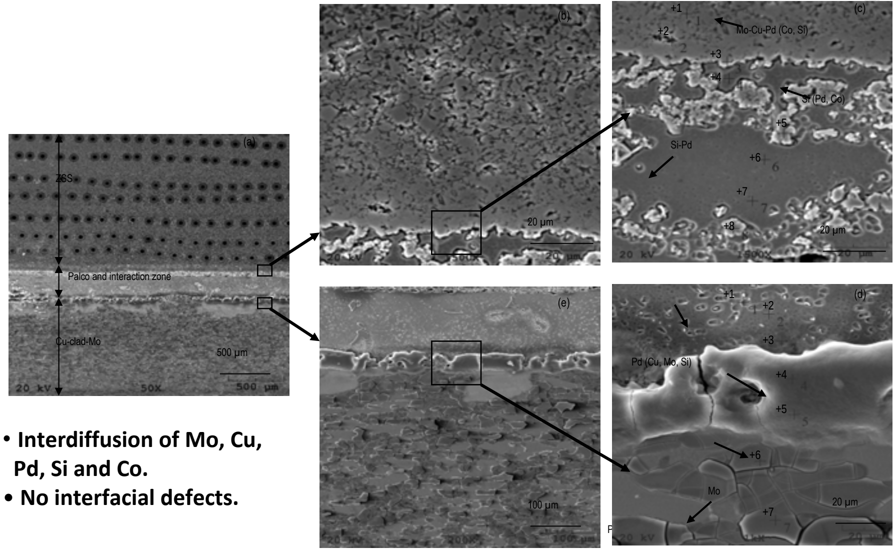
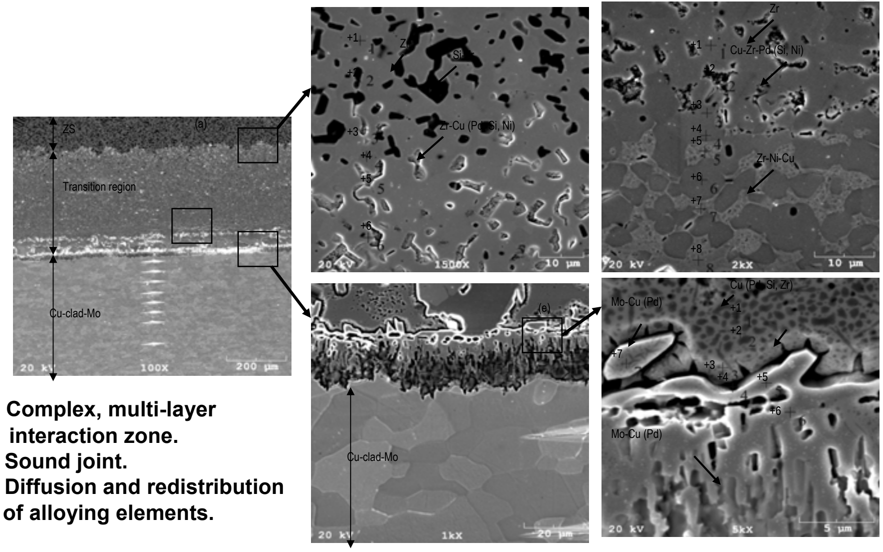
# Microstructure of ZSS/Palco/Cu-clad-Mo Joint Interface

4(a)



- **Interdiffusion of Mo, Cu, Pd, Si and Co.**
- **No interfacial defects.**

# Microstructure of ZS/Palni/Cu-clad-Mo Joint Interface



- Complex, multi-layer interaction zone.
- Sound joint.
- Diffusion and redistribution of alloying elements.

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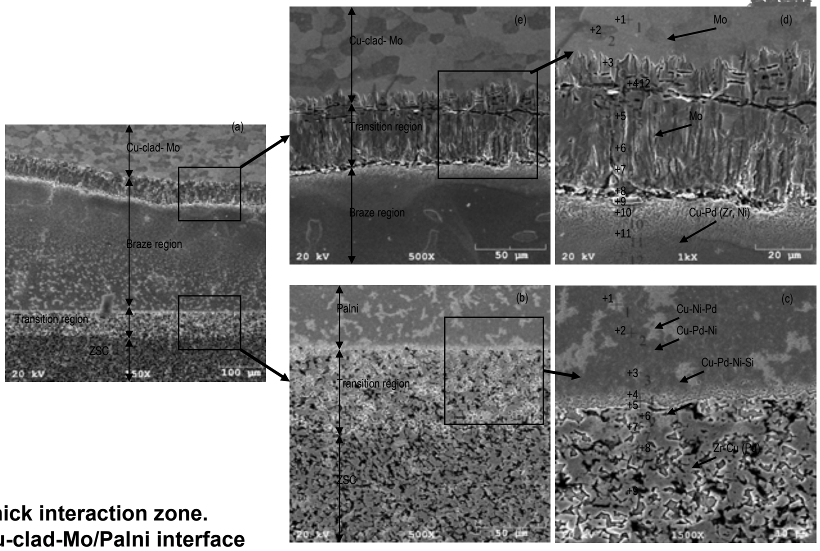
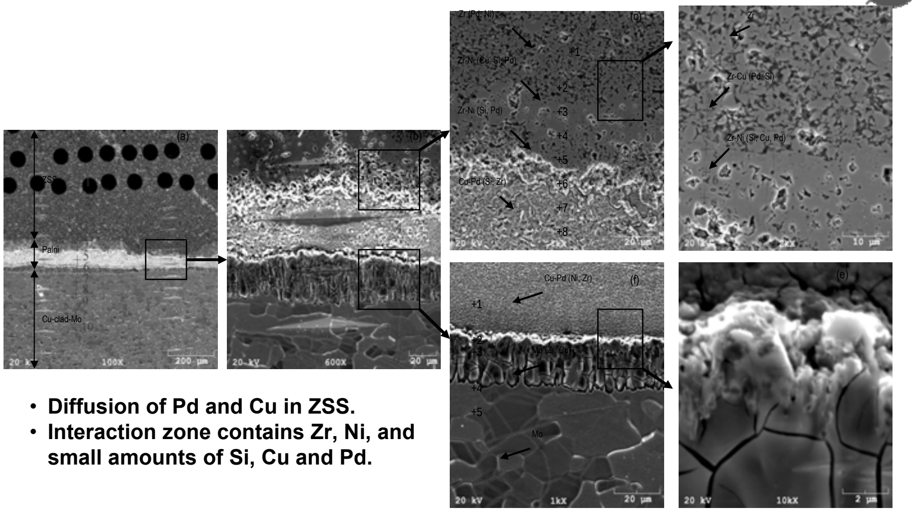
# Microstructure of ZSC/Palni/Cu-clad-Mo Joint Interface



- Thick interaction zone.
- Cu-clad-Mo/Palni interface cracked.

# Microstructure of ZSS/Palni/Cu-clad-Mo Joint Interface



- **Diffusion of Pd and Cu in ZSS.**
- **Interaction zone contains Zr, Ni, and small amounts of Si, Cu and Pd.**

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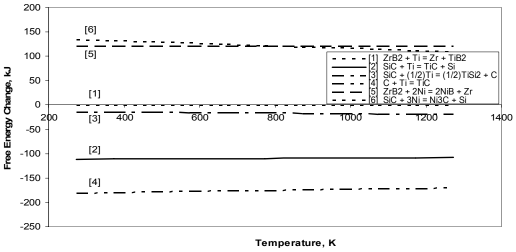
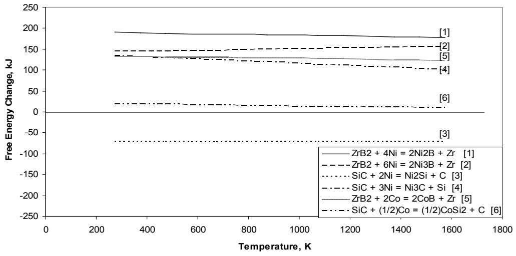
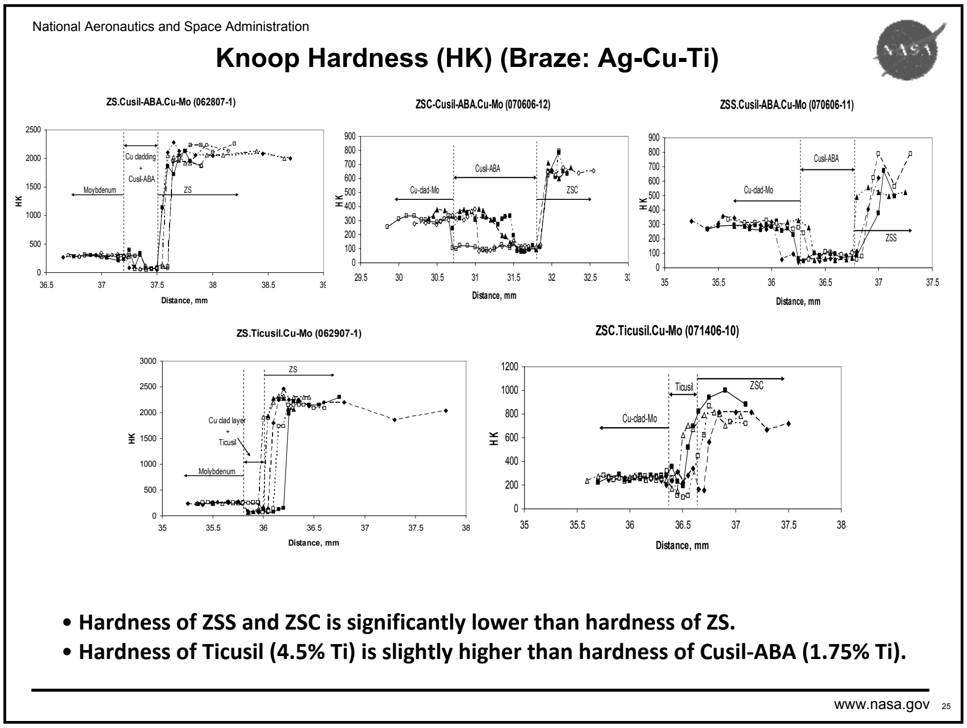
# Free Energy Change for Reaction of $ZrB_2$, SiC and C with Ti and Ni





- **TiC, $Ni_2Si$ and $TiSi_2$ could form from the reaction of SiC with Ti and Ni.**
- **$Pd_3Zr$, $Pd_2Zr$, PdZr, and $PdZr_2$, and CoZr, $Co_2Zr$, and $CoZr_2$ could also form (phase diagram).**



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## Knoop Hardness (HK) (Braze: Ag-Cu-Ti)

- **Hardness of ZSS and ZSC is significantly lower than hardness of ZS.**
- **Hardness of Ticusil (4.5% Ti) is slightly higher than hardness of Cusil-ABA (1.75% Ti).**

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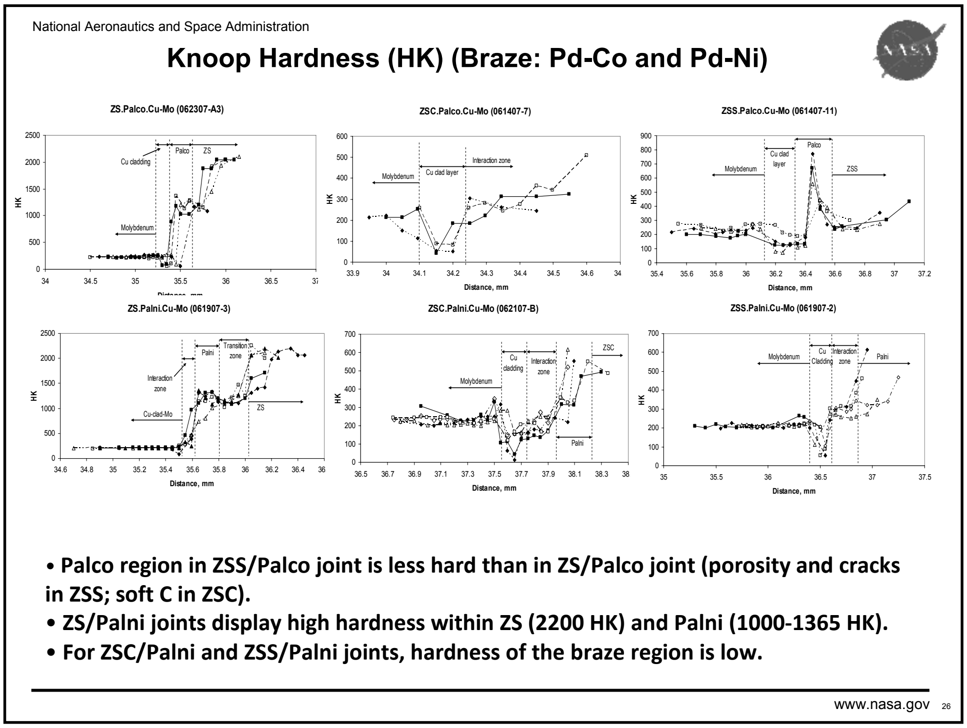

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## Knoop Hardness (HK) (Braze: Pd-Co and Pd-Ni)

- **Palco region in ZSS/Palco joint is less hard than in ZS/Palco joint (porosity and cracks in ZSS; soft C in ZSC).**
- **ZS/Palni joints display high hardness within ZS (2200 HK) and Palni (1000-1365 HK).**
- **For ZSC/Palni and ZSS/Palni joints, hardness of the braze region is low.**

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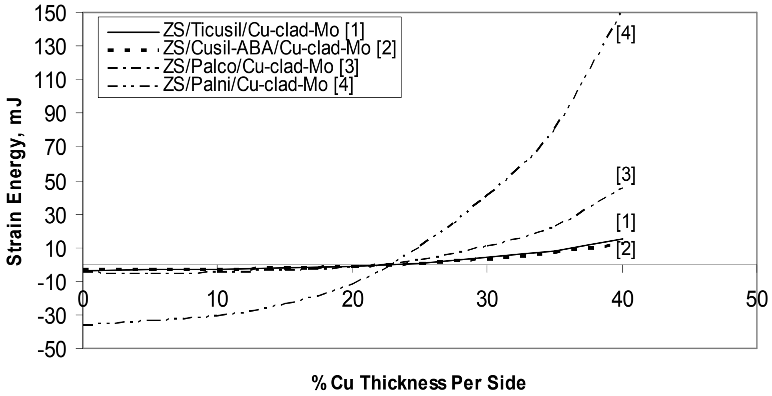
## Strain Energy in ZS/Cu-clad-Mo Joints vs Clad Layer Thickness



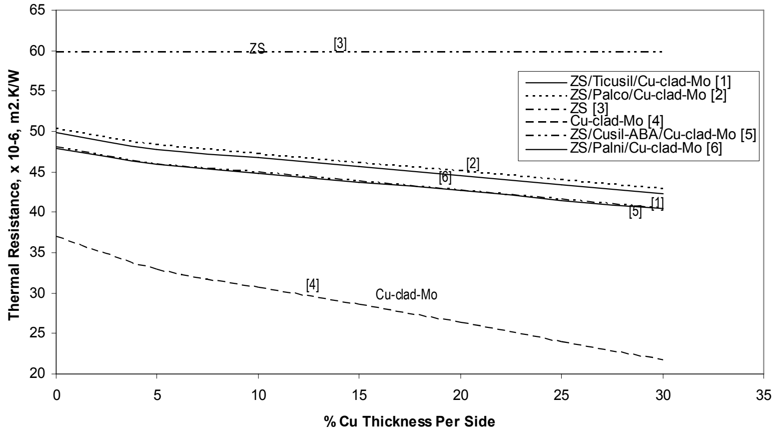
- Strain energy ($U_{eC}$) is negative up to ~23% thickness; above this, $U_{eC} > 0$, and increases with increasing thickness ($U_{eC} < 0$ means increased fracture stress).
- Increase in $U_{eC}$ is largest for Palni and smallest for Cusil-ABA, and inversely related to the yield strength of braze.
- Palni is not recommended for thick cladding (but has highest temperature capability).
- There is a small (max. ~15%) difference in $U_{eC}$ for Ticusil and Cusil-ABA joints.

## Estimation of Thermal Resistance of ZS/Cu-clad-Mo Joints vs Clad Layer Thickness

**Effective thermal resistance (1-D steady-state conduction)**

$$R_{eff} = \Sigma(\Delta x_i/K_i)$$

**($R_{eff}$: effective thermal resistance, $\Delta x_i$: thickness $K_i$: thermal conductivity)**



## Estimation of Thermal Conduction in Brazed Joints

**Effective thermal resistance (1-D steady-state conduction)**

$$R_{eff} = \Sigma(\Delta x_i/K_i)$$

**($R_{eff}$: effective thermal resistance, $\Delta x_i$: thickness $K_i$: thermal conductivity)**

- **$R_{eff}$ decreases with increasing clad layer thickness (e.g., by ~15% when thickness increases from 0 to 30%).**
- **The values of $R_{eff}$ for Ticusil and Cusil-ABA joints are nearly identical.**
- **Because of its miniscule thickness, braze layer makes a negligible contribution to $R_{eff}$.**
- **Small changes in $R_{eff}$ accompany greater changes in strain energy when clad layer thickness is changed (flexibility in selecting thickness for low CTE mismatch without detriment to thermal conduction).**
- **Potential benefit to join UHTCC to Cu-clad-Mo to enhance heat dissipation.**

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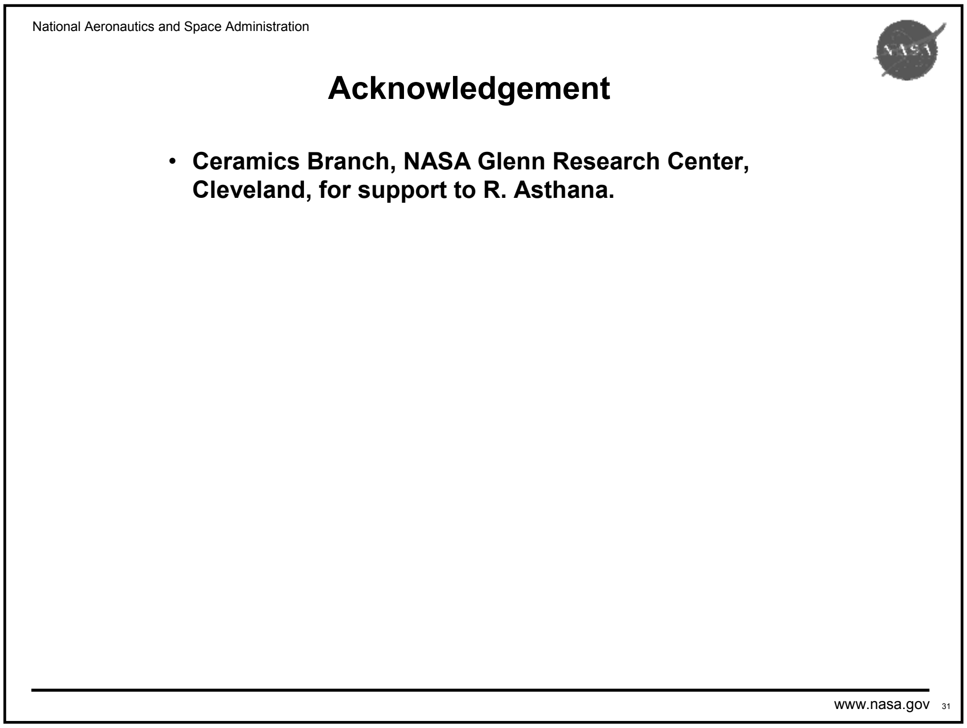
## Concluding Remarks

- **Three hot-pressed $ZrB_2$-based UHTCC were joined to Cu-clad-Mo using AgCuTi brazes ($T_L$~1073-1173 K) and Pd-based brazes ($T_L$~1493-1513 K).**
- **More extensive interaction occurred in Pd-based braze alloy joints than in AgCuTi-based joints.**
- **Pd-braze region displayed higher hardness in joints made using ZS than ZSS or ZSC.**
- **Joints reveal negative strain energy up to ~23% clad layer thickness. Above 23% thickness, strain energy is positive, and increases with thickness.**
- **Projected reductions in the thermal resistance highlight the benefits of joining the UHTCC to Cu-clad-Mo.**



## Acknowledgement

- Ceramics Branch, NASA Glenn Research Center, Cleveland, for support to R. Asthana.