Active Metal Brazing and Characterization of Brazed Joints in C-C and C-SiC Composites to Copper-Clad-Molybdenum System

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Abstract

Carbon/carbon composites with CVI and resin-derived matrices, and C/SiC composites reinforced with T-300 carbon fibers in a CVI SiC matrix were joined to Cu-clad Mo using two Ag-Cu braze alloys, Cusil-ABA (1.75% Ti) and Ticusil (4.5% Ti). The brazed joints revealed good interfacial bonding, preferential precipitation of Ti at the composite/braze interface, and a tendency toward delamination in resin-derived C/C composite. Extensive braze penetration of the inter-fiber channels in the CVI C/C composites was observed. The Knoop microhardness (HK) distribution across the C/C joints indicated sharp gradients at the interface, and a higher hardness in Ticusil than in Cusil-ABA. For the C/SiC composite to Cu-clad-Mo joints, the effect of composite surface preparation revealed that ground samples did not crack whereas un-ground samples cracked. Calculated strain energy in brazed joints in both systems is comparable to the strain energy in a number of other ceramic/metal systems. Theoretical predictions of the effective thermal resistance suggest that such joined systems may be promising for thermal management applications.

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Outline

- Introduction and Background
- Experimental Procedure
  - *Active Metal Brazing*
  - *Characterization (SEM, EDS)*
  - *Hardness behavior*
- Results and Discussion
  - *C-C to Metal System*
  - *C-SiC to Metal System*
- Concluding Remarks
- Acknowledgment

Introduction and Background

- C-C and C-SiC composites possess good high temperature strength, creep resistance, high thermal conductivity, and low CTE.
- These properties make them suitable for a wide variety of aerospace and ground based applications. Some of these applications include; nose cap and leading edges of re-entry vehicles, aircraft brakes, rocket nozzle components, shrouds, engine flaps, and flame holders of jet engines.
- High conductivity C-C composites are also being developed and utilized for thermal management applications.

Joining of C-C and C-SiC Composites

- Joining and integration is an enabling technology for the manufacturing and application of advanced CMC components.
- Integration of C-C and C-SiC composite sub-elements to metals in components and systems requires the development and validation of innovative joining concepts and technologies.
- Joining of C-C composites to Titanium and Nickel base alloys using active brazes has been developed and reported.

<u>Challenges:</u>

- Poor wettability of ceramics and composites: poor flow and spreading characteristics.
- Thermoelastic incompatibility: large thermal expansion mismatch and residual stresses.

Objective

- Utilize active metal brazing to bond CVI and resin-dervied C-C composites and CVI C-SiC composites to Cu-clad-Mo using two Silver-Copper based active metal braze alloys: Cusil-ABA and Ticusil.
- Characterize the joint microstructure, composition, and microhardness distribution across the joint interface.
- Estimate the residual stress and effective thermal resistance in the joint.

Experimental Procedure - Materials -

- Carbon-Carbon composites
  - *Goodrich Corp., Santa Fe, CA and C-CAT, Inc., Fort Worth, TX*
- Cu-clad-Mo plates (Cu-Mo-Cu ratio: 13%-74%-13%)
  - *H.C. Starck, Inc., Newton, MA*
- C-SiC composites (CVI C-SiC)
  - *GE Power Systems Composites, Newark, DE.*
- Braze alloys (powders), Cusil-ABA and Ticusil
  - *Morgan Advanced Ceramics, Hayward, CA.*

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Composition and Properties of Braze Alloys and Substrate Materials

Composition and Properties of Brazes

Braze (composition, %)	T_L, °C	T_S, °C	E, GPa	YS, MPa	UTS, MPa	CTE, ×10^{-6} C^{-1}	% El.	K, W/m.K
Cusil-ABA® (63Ag-35.3Cu-1.75Ti)	815	780	83	271	346	18.5	42	180
Ticusil® (68.8Ag-26.7Cu-4.5Ti)	900	780	85	292	339	18.5	28	219

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

Composition and Properties of C-SiC Composites

Composite	UTS, MPa	E, GPa	Flexural Strength, MPa	ILSS, MPa	CTE, ×10^{-6}/K	K, W/m.K
CVI C-SiC (42-47% fiber)	350	90-100	500-700	35	3.0[a] 5.0[b]	14.3-20.6[a] 6.5-6.9[b]
LPI C-SiC	250	65	500	10	1.16[a] 4.06[b]	11.3-12.6[a] 5.3-5.5[a]
HiPerComp SiC-SiC (22-24% fiber)	--	285	--	135[c]	3.5[a] 4.07[b]	33.8[a] 24.7[b]

Data used for calculations only.

[a]in-plane value; [b]through-thickness value; [c]from fast fracture strength tests.

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Experimental Procedure

- **Substrates cut into 2.54 cm x 1.25 cm x 0.25 cm plates and ultrasonically cleaned.**
- **3D C-C sectioned along two orthogonal directions to expose fiber plies with different fiber arrangements to evaluate their effect on joining.**
- **Some C-SiC substrates ground using 320#, 400# and 600# grit SiC papers to examine the effect of surface preparation on joining response.**
- **Assembly 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 Field Emission Scanning Electron Microscopy (Hitachi 4700) 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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C-C Composite/Cu-Clad-Mo Joints

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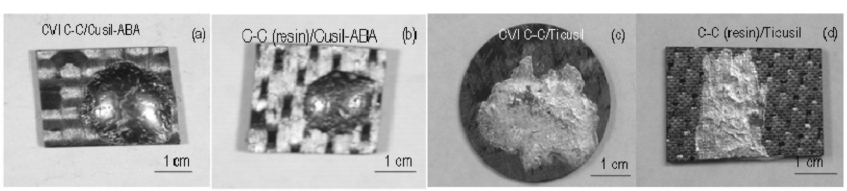
Relative spreading behavior of Cusil-ABA and Ticusil on C-C (tendency to "ball-up" or "spread-out")

Wt. of braze: 0.2 g, contact time: 5 min.
T = 830°C (Cusil-ABA), T = 915°C (Ticusil)



Ticusil (4.5%Ti) exhibited better surface coverage than Cusil-ABA (1.75%Ti). Ti in Ag and Cu is known to decrease the θ (θ < 90°)

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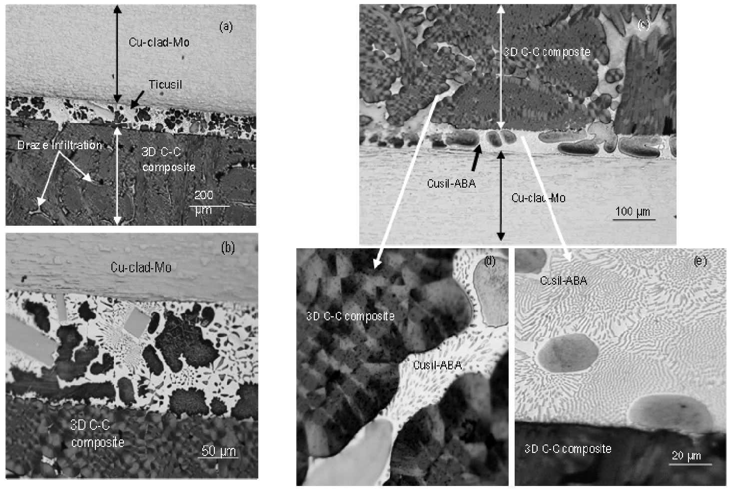
Microstructure of C-C/Cusil-ABA/Cu-clad-Mo Joints



• Braze penetration to several hundred micrometers in 5 min.
• No effect of fiber ply orientation on infiltration.
• Improved wetting by Ti in braze facilitated infiltration.
• No reaction choking and flow cessation from carbide forming reactions.

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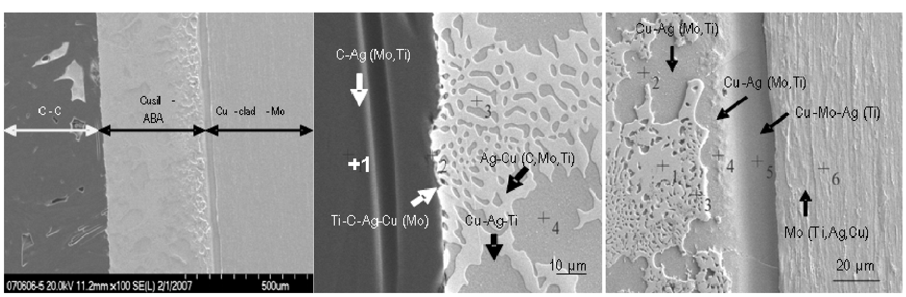
Microstructure of C-C (oriented fibers) composite /Cusil-ABA/ Cu-clad-Mo joint



- **High concentrations of Ti at the C-C/Cusil-ABA interface.**
- **Two-phase eutectic structure of braze (Ag-rich light-grey areas and Cu-rich dark areas).**
- **No melting and solidification of clad layer [M.P. of Cu (1086ºC) > joining temperature].**

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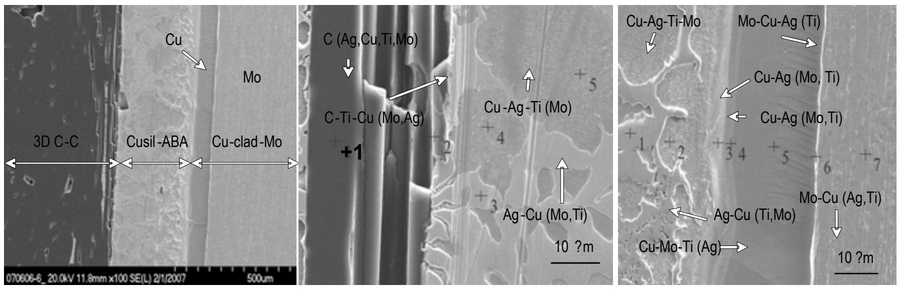
Microstructure of C-C (non-oriented fibers) composite/Cusil-ABA/Cu-clad-Mo joint



- Evidence of Ti segregation on C surface.
- Possible formation of titanium carbide via Ti+C→ TiC (ΔG = -171.18 kJ at 850°C).
- Wettable sub-stoichiometric carbides ($TiC_{0.95}$, $TiC_{0.91}$, $TiC_{0.80}$, $TiC_{0.70}$, $TiC_{0.60}$ and $TiC_{0.48}$) may form.

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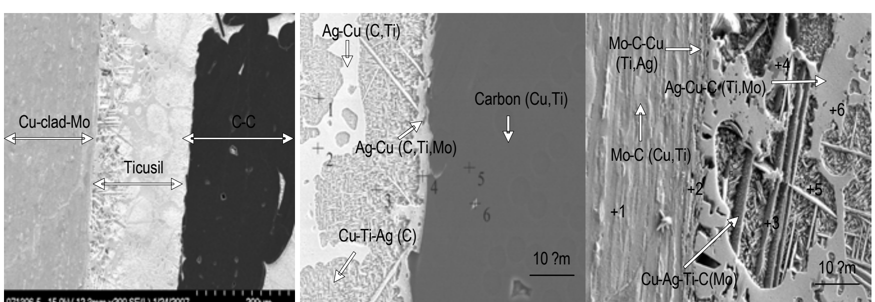
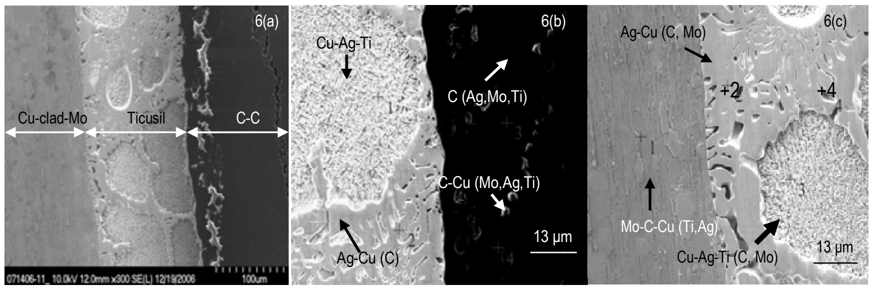
Microstructure of C-C (non-oriented fibers) composite/Ticusil/Cu-clad-Mo joint



- Some dissolution of carbon in braze (possibly due to higher temperature of Ticusil).
- Carbon also detected within the Cu-clad-Mo region.

Microstructure of C-C (resin-derived) composite/Ticusil/Cu-clad-Mo joint



- **Cracking within resin-derived C-C composite (low interlaminar shear strength).**
- **Braze displays characteristic two-phase eutectic structure with Ag- and Cu-rich phases.**
- **Preferential precipitation of Ag-rich phase onto both C-C surface and Cu-clad-Mo surface**
- **A small amount of Cu detected within the C-C composite.**

Strain Energy in C-C/Ticusil/Cu-clad-Mo joint

Model Equations

(J.-W. Park, P. F. Mendez and T. W. Eagar, *Acta Mater.*, 2002, 50(5), 883-899)

$$U_{eC} = \frac{\sigma^2{}_{YI}.\Phi.r^3}{E_C}(0.26\Pi_I + 0.54)$$

$$\Phi = 1 - \left(\frac{\alpha_M - \alpha_I}{\alpha_C - \alpha_I}\right)^m$$

$$\Pi_I = \frac{(\alpha_M - \alpha_C)\Delta T E_I}{\sigma_{YI}}$$

U_{eC}:	strain energy
σYI:	yield strength of the braze interlayer
R:	radial distance from the center of the joint
E_C:	elastic modulus of the ceramic
E_I:	elastic modulus of braze
ΔT:	temperature change
α:	CTE of the subscripted phases (M, C, and I)
m:	exponent [m=1 for $\alpha_I > (\alpha_M + \alpha_C)/2$, and m=–1 for $\alpha_I < (\alpha_M + \alpha_C)/2$]

Data for C-C/Ticusil/Cu-clad-Mo Joints

CTE of Cu-clad Mo: ~$5.7\text{x}10^{-6}$/K, CTE of C-C: ~$2.0\text{-}4.0\times10^{-6}$/K over 20-2500°C, CTE of Ticusil: ~ 18.5×10^{-6}/K, E_C = 70 GPa, E_I = 85 GPa, ΔT = 887ºC, σ_{YI} = 292 MPa, m = 1, r ~ 0.63 x 10^{-2} m

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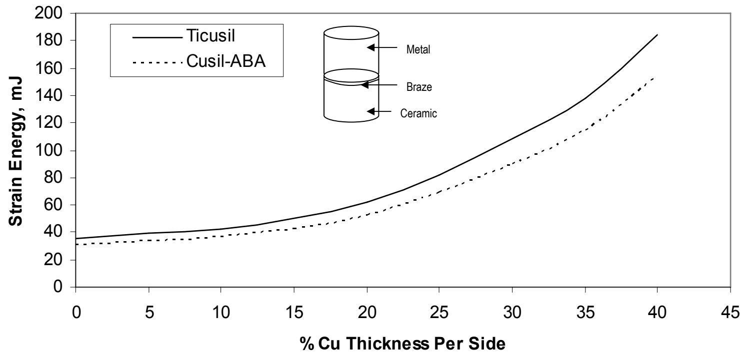
Strain Energy Calculations

Large strain energy → Greater tendency for fracture

(Based on a model due to J.-W. Park, P. F. Mendez and T. W. Eagar, Acta Mater., 2002, 50(5), 883-899)



- **Relatively larger strain energy in C-C/Ticusil/Cu-clad-Mo than in C-C/Cusil-ABA/Cu-clad-Mo.**
- **Ductile braze and Cu cladding prevented failure.**

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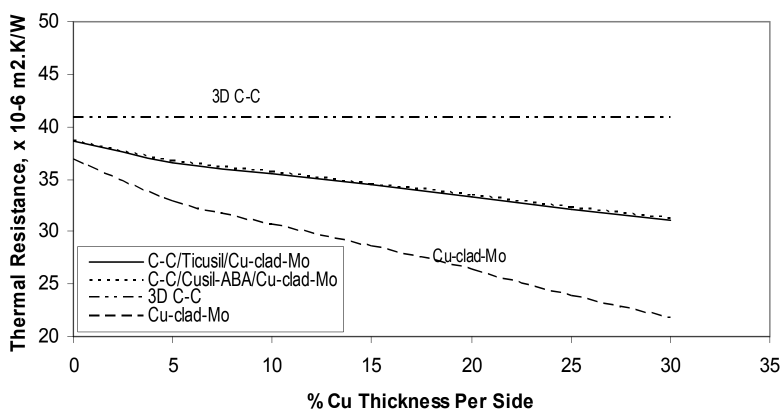
Thermal Resistance of C-C Composite/Cu-clad-Mo Brazed Joints

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

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

($\mathbf{R_{eff}}$: effective thermal resistance, Δx_i: thickness K_i: thermal conductivity)



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Thermal Conduction in Brazed Joint

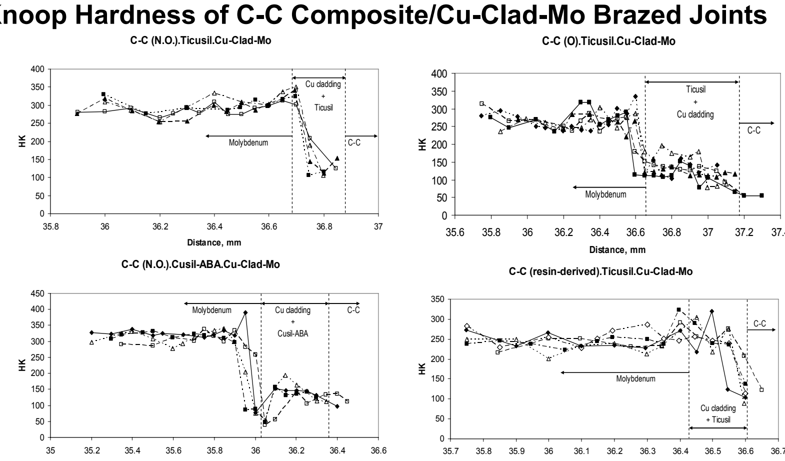
Effective thermal resistance (1-D steady-state conduction)

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

($\mathbf{R_{eff}}$: effective thermal resistance, Δx_i: thickness K_i: thermal conductivity)

- **R_{eff} of joints depends upon clad layer thickness. R_{eff} is 31.5 to 38.5×10^{-6} m^2.K/W, intermediate between R_{eff} of C-C (= 40.8×10^{-6} m^2.K/W) and R_{eff} of Cu-clad-Mo (= 22.8×10^{-6} m^2.K/W).**
- **An increase in R_{eff} of joints relative to Cu-clad-Mo is compensated by a decrease in weight.**
- **Even with the lower conductivity Cusil-ABA braze (K = 180 W/m-K), there will be less than 1% difference in R_{eff} with respect to Ticusil.**
- **Flexibility in selecting brazes to satisfy other criteria (e.g., ductility, wetting etc.).**
- **Potential benefit to join C-C to Cu-clad-Mo in thermal management systems.**

Knoop Hardness of C-C Composite/Cu-Clad-Mo Brazed Joints



- **No effect of fiber ply orientation**
- **No effect of composite type (CVI *vs* resin-derived) on HK within the braze region.**
- **HK of Mo substrate is ~200-330.**
- **HK depends on braze type: Ticusil exhibits slightly higher HK (~85-200) than Cusil-ABA (~50-150).**

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C-SiC Composite/Cu-Clad-Mo Joints

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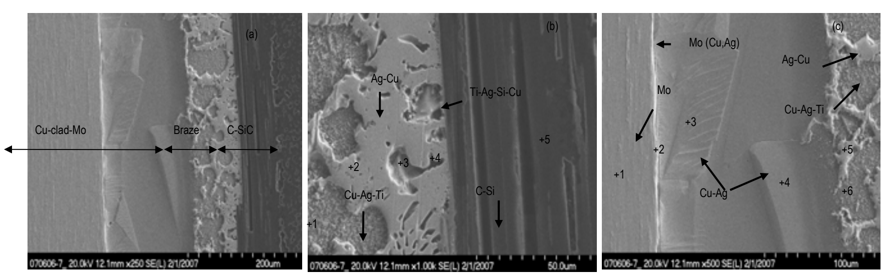
Microstructure of C-SiC (ground)/Cusil-ABA/Cu-Clad-Mo Joint



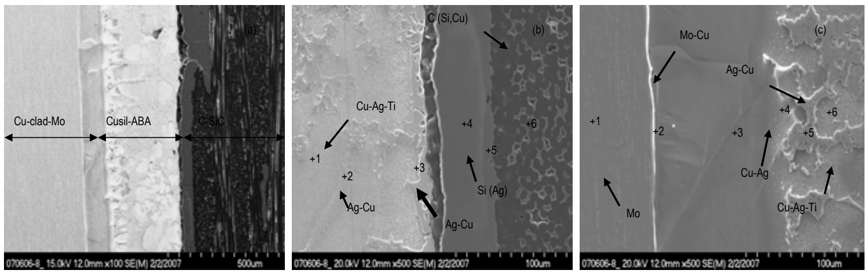
• Intimate physical contact at CMC/braze and braze/Cu-clad-Mo interfaces.

• The C-SiC/Cusil-ABA interface is enriched in Ti (45.8 atom %) and Si (9.6 atom %).

• Braze matrix displays two-phase eutectic structure comprised of Cu(Ag) and Ag(Cu) phases.

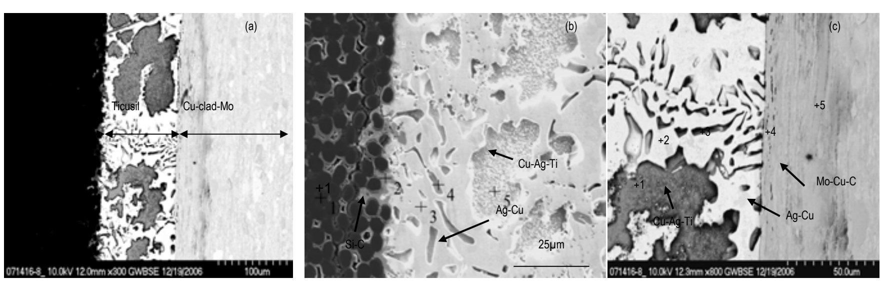
• Little indication of diffusion between braze and Cu-clad-Mo. No melting of clad layer occurred.

Microstructure of C-SiC (as received)/Cusil-ABA/Cu-Clad-Mo Joint



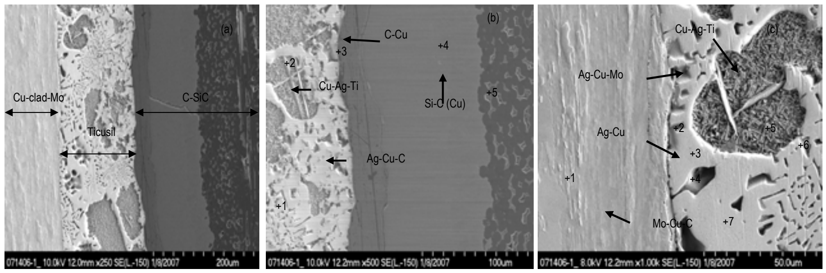
- Cracked C-SiC/braze interface. Cracking occurred due to residual stresses from CTE mismatch.

Microstructure of C-SiC (ground)/Ticusil/Cu-Clad-Mo Joint



- Good braze/composite interaction and defect-free joint.
- Large quantities of Ti (18.6 atom%), Mo (36.4 at%) and Ag (45 at%) within C-SiC (point 1, Fig. b).
- Ti segregation at interface (point 2, Fig. b). Si diffusion to ~15-20 µm in braze (point 4, Fig. b).
- Two-phase eutectic structure with Ag-rich phase deposited on C-SiC and Cu-clad-Mo surfaces.
- No melting of Cu clad layer.

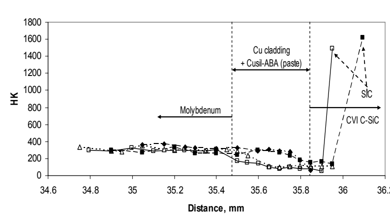
Microstructure of C-SiC (as received)/Ticusil/Cu-Clad-Mo Joint



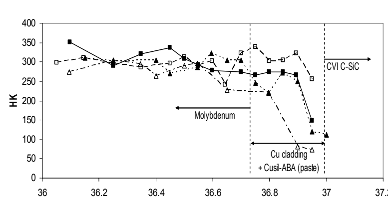
- Defect-free joint with CVI SiC layer on composite intact.
- Higher thermal strain ($\Delta\alpha\Delta T$) in Ticusil joints than Cusil-ABA joints ($\Delta T_{Ticusil} > \Delta T_{Cusil\text{-}ABA}$) is compensated by better wetting and bonding in Ticusil due to its higher Ti content (4.5% Ti).
- Cu detected to ~100 µm distance within the composite (points 4 and 5, Fig. b). Ag-rich phase preferentially precipitated on C-SiC and Cu-clad-Mo.

Knoop Hardness (HK) Distribution Across the Interface

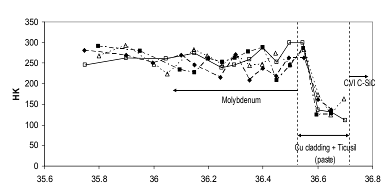
CVI C-SiC (unground).Cusil-ABA.Cu-Clad-Mo



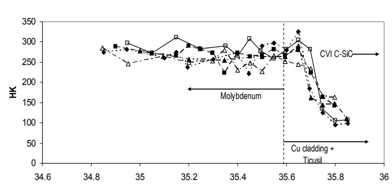
CVI C-SiC (ground).Cusil-ABA.Cu-Clad-Mo



CVI C-SiC (unground).Ticusil.Cu-Clad-Mo

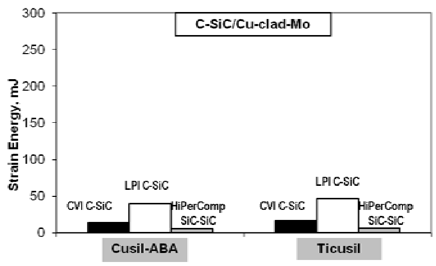


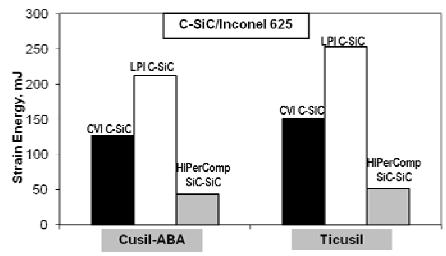
CVI C-SiC (ground).Ticusil.Cu-Clad-Mo



- No effect of grinding on hardness profiles.
- The braze regions display lower hardness than the Mo substrate except in C-SiC/Ti joint.
- The hardness of composite depends upon the path traversed by indenter. The hardness rose to 1,500 - 2,000 HK when SiC matrix regions were encountered by the indenter between C fibers.

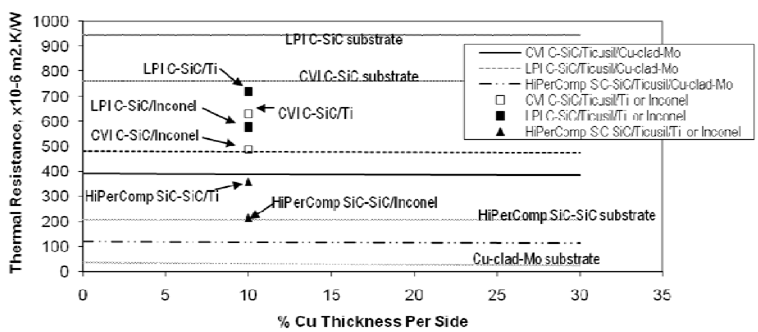
Strain Energy in C-SiC Composites Joined to Cu-Clad-Mo





- C-SiC/Cu-clad-Mo joints display low strain energy (small tendency to fracture).
- HiPerComp SiC-SiC is a better candidate for joining to Cu-clad-Mo than CVI C-SiC and LPI C-SiC.
- Strain energy is slightly lower for Cusil-ABA than Ticusil. The greater ductility and smaller %Ti of Cusil-ABA reduce strain energy but higher Ti content of Ticusil promotes braze flow.
- A tradeoff between chemically enhanced wetting and thermoelastic compatibility probably exists.

Effective thermal resistance (R_{eff}) of joints and substrates



- Thermal resistance of Cusil-ABA and Ticusil joints differ by less than 1%. This suggests flexibility in selecting braze composition to satisfy other criteria.
- R_{eff} decreases as clad layer thickness increases; maximum decrease is less than 7% at 30% clad thickness.
- Different C-SiC composites exhibit different levels of drop in thermal resistance when joined to Cu-clad-Mo; the lowest thermal resistance is achieved for the HiPerComp SiC-SiC composite.

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Composite Surface Preparation, Thermal Strain and Joint Integrity

Joint	$\Delta\alpha\Delta T$	Surface Preparation	Joint Integrity
C-SiC/Cusil-ABA/Cu-clad-Mo	1.944×10^{-3}	Ground	No crack
C-SiC/Cusil-ABA/Cu-clad-Mo	1.944×10^{-3}	Not Ground	Cracked
C-SiC/Ticusil/Cu-clad-Mo	2.148×10^{-3}	Ground	No crack
C-SiC/Ticusil/Cu-clad-Mo	2.148×10^{-3}	Not Ground	No crack

$\Delta\alpha\Delta T$ values are calculated using the following data: $\alpha_{Cu\text{-}clad\text{-}Mo} = 6.4\times10^{-6}$/K (15% Cu [22]), $\Delta T_{Cusil\text{-}ABA} = 810°C$, $\Delta T_{Ticusil} = 895°C$.

- **Surface preparation had a greater effect on joint integrity in Cusil-ABA joints than Ticusil joints.**
- **The higher Ti content of Ticusil led to stronger bonding that presumably offset the negative effect of a slightly larger thermal strain.**

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Concluding Remarks

- **C-C composites displayed sound bonding with Cu-clad-Mo and Ti segregation at interface. Braze infiltrated the inter-fiber channels in CVI C-C.**
- **Chemical degradation of C-C was minimal. Delamination occurred in resin-derived C-C due to its low inter-laminar shear strength.**
- **Sharp hardness gradients developed at Cu-clad-Mo/braze interface. Hardness was somewhat higher within Ticusil than Cusil-ABA regions of joints.**
- **C-C/Cu-clad-Mo joints have lower thermal resistance compared to C-C.**
- **C-SiC surface preparation influenced joint integrity in Cusil-ABA joints more than in Ticusil joints. The higher Ti content of Ticusil led to stronger bonding that offset the negative effect of a larger thermal strain.**
- **Ti and Si enrichment occurred at C-SiC/braze interface. Grinding did not influence hardness profiles.**
- **Strain energy and thermal resistance depend upon C-SiC type. HiPerComp joints exhibit smaller strain energy and thermal resistance than CVI C-SiC and LPI C-SiC joints.**

Acknowledgement

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