Joining and Integration of Advanced Carbon-Carbon Composites to Metallic Systems for Thermal Management Applications

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Abstract

Recent research and development activities in joining and integration of carbon-carbon (C/C) composites to metals such as Ti and Cu-clad-Mo for thermal management applications are presented with focus on advanced brazing techniques. A wide variety of carbon-carbon composites with CVI and resin-derived matrices were joined to Ti and Cu-clad Mo using a number of active braze alloys. The brazed joints revealed good interfacial bonding, preferential precipitation of active elements (e.g., Ti) at the composite/braze interface. Extensive braze penetration of the inter-fiber channels in the CVI C/C composites was observed. The chemical and thermomechanical compatibility between C/C and metals at elevated temperatures is assessed. The role of residual stresses and thermal conduction in brazed C/C joints is discussed. Theoretical predictions of the effective thermal resistance suggest that composite-to-metal brazed joints may be promising for lightweight thermal management applications.

Keywords: C/C composite, Cu-clad-Mo, joining, microstructure, thermal management

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Outline

- **Introduction and Background**
- **Technical Challenges**
  - ***Wetting and Reactions***
  - ***Thermal Expansion Mismatch***
  - ***Thermal Resistance of Interface***
- **Experimental Procedure**
  - ***Active Metal Brazing***
  - ***Characterization (SEM, EDS)***
  - ***Hardness behavior***
- **Results and Discussion**
- **Concluding Remarks**

Materials for Thermal Management

- Conventional materials: Cu and Al (K_{Cu} = 400 W/m-K; K_{Al} =205 W/m-K)
- Cu is a better conductor than Al but heavier
  (ρ_{Cu}=8,900 kg.m^{-3}, ρ_{Al}=2,200 kg.m^{-3})
- Cu is less amenable to extrusion (shape limitations)
- Both Cu and Al have high CTE, and their use requires design compromises.

Innovative technologies are needed to seamlessly integrate these materials in systems.

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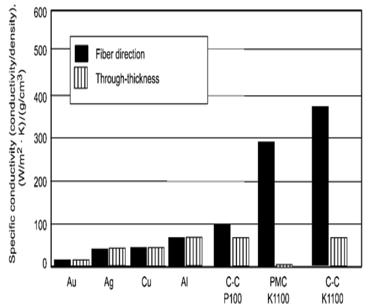
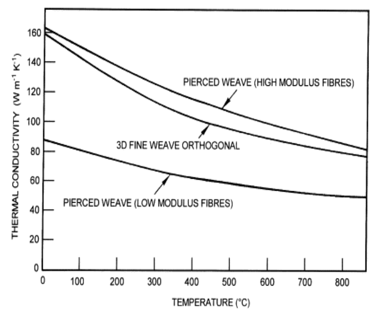
Three Generations of Thermal Management Materials

- <u>First Generation</u>: **high K, low-CTE materials** (**Cu/W**, **Kovar**, **Cu-W**, **Cu-clad-Invar and Cu-clad-Mo**).
  (*Density is compromised!)*
- <u>Second Generation</u>: **SiC/Al**, **E-glass fiber reinforced polymers**, **ceramic- and metal-particle filled polymers**, **C/Cu**, **SiC/Cu**, **C/Al**, **diamond/Cu**, **B/Al**, **BeO/Be**
- <u>Third Generation</u>: **C/C composites**, **C/SiC**, **porous ceramics**, **porous graphite**, **CNT**, **graphene**…

Carbon-Carbon Composites Provide Advantage and Excellent Benefits for Thermal Management

Thermal conductivity of C/C composites strongly depends on the fiber type, architecture, and composite processing technology



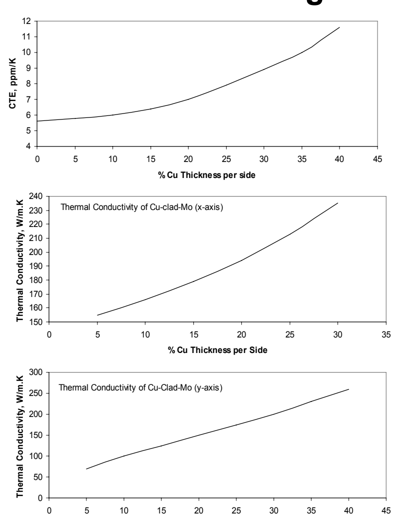


Source: K. Kearns, Composites, ASM Handbook, Vol. 21 (2002) 1067-1070.

Source: Comprehensive Composite Materials, Vol. 4, 3 (2000).

- **High modulus, high conductivity pitch based carbon fibers can be used to improve the thermal properties of C-C composites.**

Copper-Clad Molybdenum as a Thermal Management Material



(from __Electronic Materials and Processes Handbook__, C.A. Harper, McGraw-Hill, 2003)

- **Copper has excellent thermal conductivity (K for OFHC Cu: 401 W/m.K).**
- **CTE of Cu is high (16.5 ppm/K). Difficulty in joining to ceramic substrates.**
- **Low annealing temperature of Cu causes softening at moderate heat input.**
- **Cladding Mo with Cu lowers CTE and promotes thermoelastic compatibility with ceramics.**
- **Some loss of thermal conductivity (Mo: 138 W/m.K, Cu: 401 W/m.K).**
- **Small weight penalty (density of Cu: 8,900 kg.m^{-3}, density of Mo: 10,280 kg.m^{-3}).**

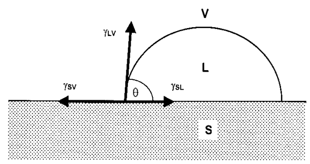
Objective

- Utilize active metal brazing to bond CVI and resin-dervied C-C composites to metals using active braze alloys.
- Characterize the joint microstructure, composition, and microhardness distribution across the joint interface.
- Estimate the residual stress and effective thermal resistance in the joint.

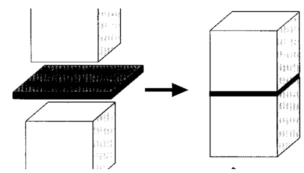
Joining of C-C Composites to Metals

- Joining and integration is an enabling technology for the manufacturing and application of advanced composite components.
- Integration of C-C composite sub-elements to metals in components and systems requires the development and validation of innovative joining concepts and technologies.
- Challenges:
  - Poor wettability of ceramics and composites: poor flow and spreading characteristics.
  - Thermoelastic incompatibility: large thermal expansion mismatch and residual stresses.

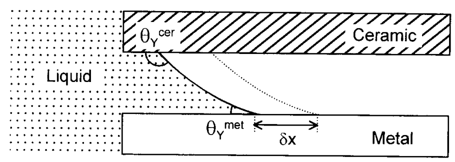
Wettability is Important in Brazing!



Contact angle of braze should be small



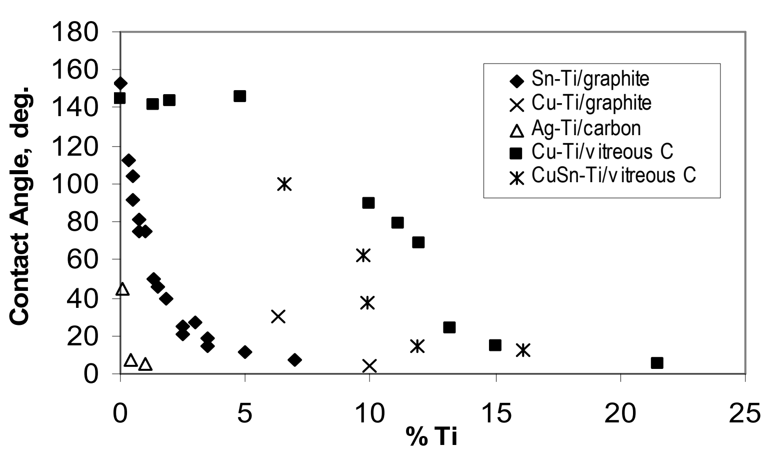
Braze layer melts and spreads between the substrates to form the joint



Ordinary braze alloys wet the metal but not the ceramic!

Must use 'active' brazes that wet and bond with both metal and composites

Braze Alloys Containing Active Metal Ti Improve the Wettability with Carbon



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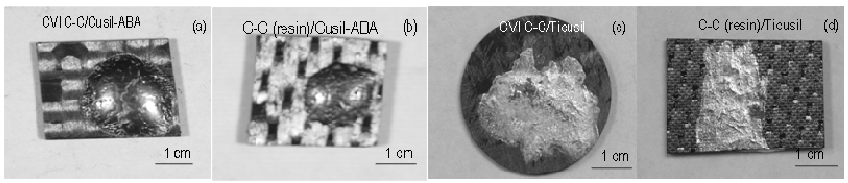
Relative spreading behavior of Cusil-ABA and Ticusil on C-C (tendency to “ball-up” or “spread-out”)

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 ($\theta < 90°$)

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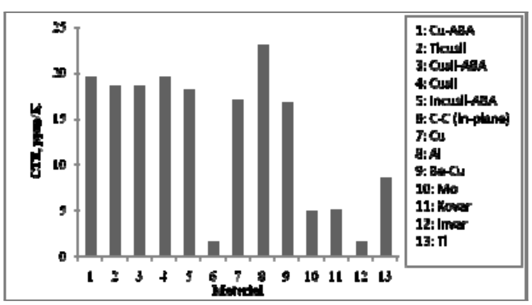
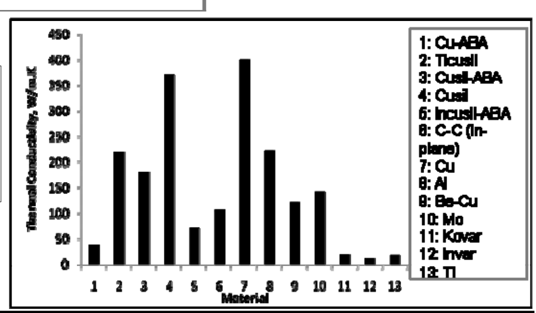
Thermal Properties of Braze and Substrate Materials



A large CTE mismatch between C-C and metallic substrates raises residual stress.



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 $\alpha_I < (\alpha_M + \alpha_C)/2$]

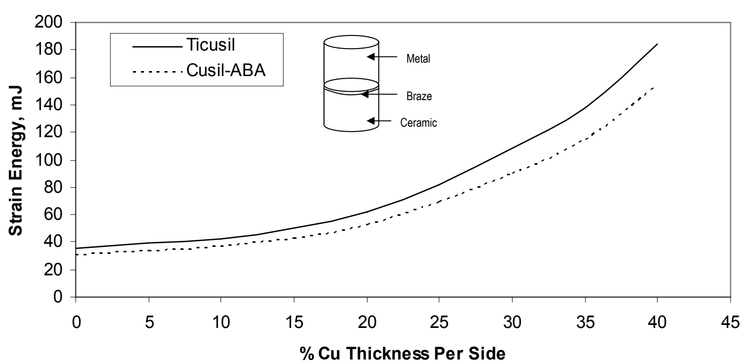
<u>Data for C-C/Ticusil/Cu-clad-Mo Joints</u>

CTE of Cu-clad Mo: ~5.7×10^{-6}/K, CTE of C-C: ~2.0-4.0×10^{-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 ~ 0.63×10^{-2} m

Projection of Strain Energy in C-C/Cu-Clad-Mo Joints

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.**

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)

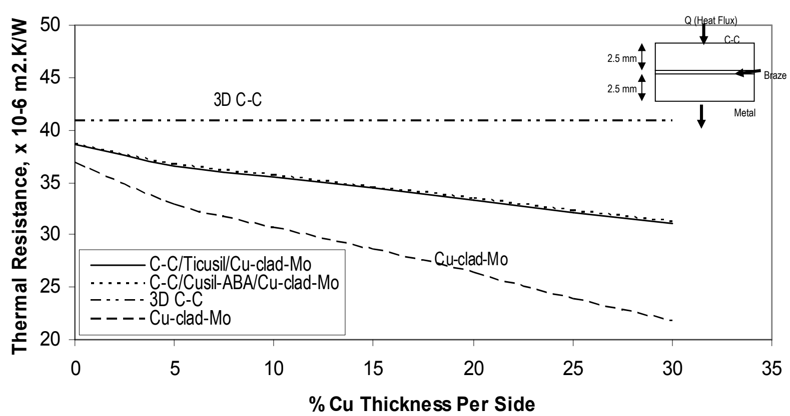
- **R_{eff} of joints depends upon clad layer thickness. R_{eff} is 31.5 to 38.5×10^{-6} m^2.K/W, intermediate between R_{eff} of C-C (= 40.8×10^{-6} m^2.K/W) and R_{eff} of Cu-clad-Mo (= 22.8×10^{-6} m^2.K/W).**
- **An increase in R_{eff} of joints relative to Cu-clad-Mo is compensated by a decrease 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.**

Effective Thermal Resistance of C-C/Cu-clad-Mo 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} depends upon clad layer thickness. It decreases with increasing clad layer thickness. Potential benefit to join C-C to Cu-clad-Mo in thermal management systems.

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.*

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.**
- **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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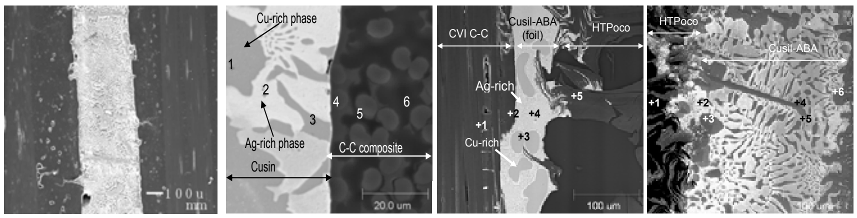
Examples of Brazed Joints of C-C Composite



C-C/Cusil-ABA/C-C C-C/Cusin/Ti C-C/Cusil-ABA/Poco C-C/Cusil-ABA/Poco

Singh et al, Mater. Sci. Eng. A, 452-453, 2007, pp. 699-704
Singh et al, Mater. Sci. Eng. A 498, 2008, 31-36
Singh and Asthana, Composites Sci. & Tech. (in the press);
Singh et al, Mater. Sci. Eng. A, 412, 2005, 123-128;
Morscher et al, Mater. Sci. Eng. A, 418(1-2), 2006, pp 19-24.

Joining of C-C to Ti, Cu-clad-Mo and Ni-base superalloys using a wide variety of braze alloys was demonstrated

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Braze Effectiveness in Joining C-C to Metals

Composite	Metallic Substrate	Braze	Bonding
C-C[1,6]	Ti	Silcoro-75[8], Palcusil-15[8], Cusil	Weak
C-C[2]	Ti	Ticuni, Cu-ABA, Ticusil	Good
C-C[1,6]	Ti and Hastealloy	MBF-20[8], MBF-30[8]	Good (Ti), Fair (Hastealloy)
C-C[3,4,5]	Ti, Cu-clad Mo[9], Inconel 625	Ticusil[7]	Good[4], Fair[5]
C-C[3,4,5]	Cu-clad Mo[9]	Cusil-ABA[7]	Good
C-C[3,4,5]	Ti and Inconel 625	Cusil-ABA[7]	Good

[1]Polished; [2]Not-polished; [3]3-D composite; [4]Oriented fiber at the joint (3-D composite); [5]Non-oriented side at the joint; [6]T-300 C fibers in resin-derived C matrix; [7]Braze paste; [8]Braze foil; [9]H.C. Starck, Inc., MA.

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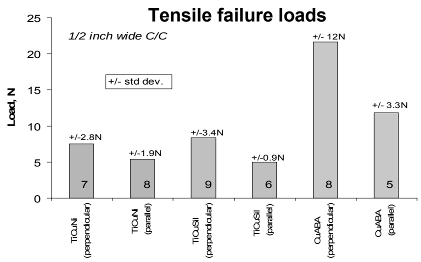
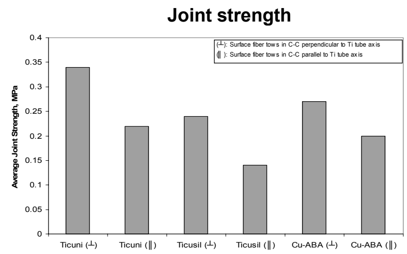
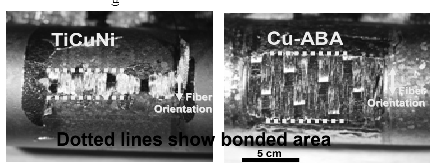
Mechanical Behavior of Brazed C-C plate/Ti-tube Joints







Fracture surface of joints
(fiber tows in surface ply were perpendicular to tube axis)

Fracture always occurred within surface ply and not within braze (good chemical bonding)

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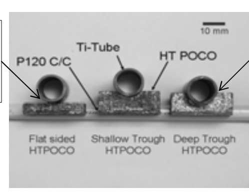
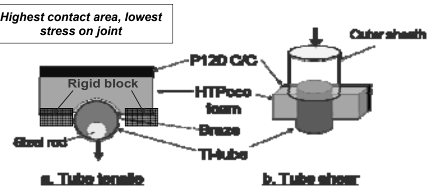
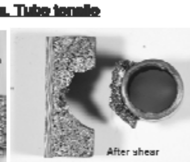
Failure Behavior of Ti-Tube/Poco/P120 C-C Joint

Lowest contact area, highest stress on joint

Highest contact area, lowest stress on joint

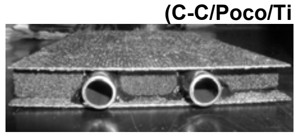


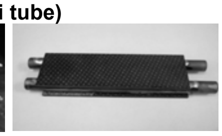




Fracture always occurred within Poco foam!

Light-weight space radiator sub-element
(C-C/Poco/Ti tube)





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C-C Composite/Cu-Clad-Mo Joints

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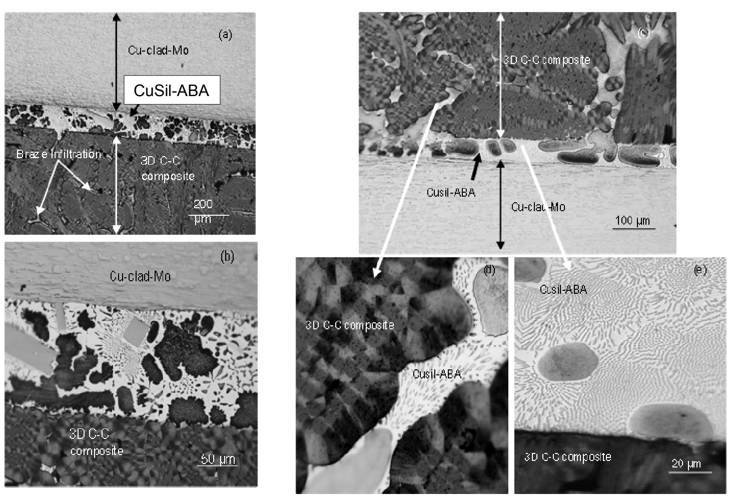
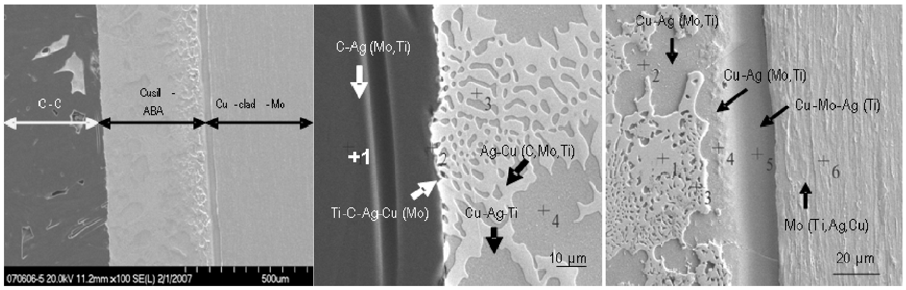
Microstructure of C-C/Cusil-ABA/Cu-clad-Mo Joints



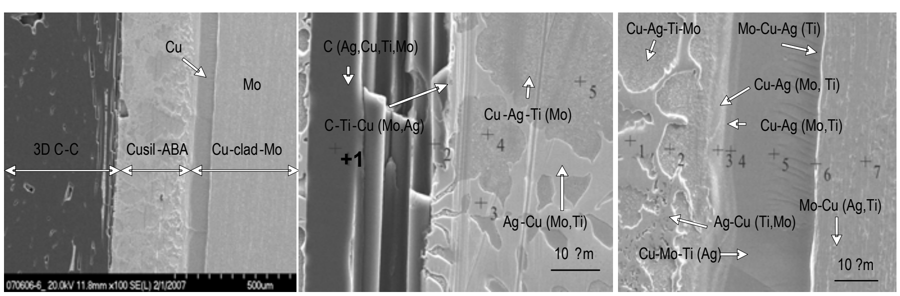
• Braze penetration to several hundred micrometers in 5 min.
• No effect of fiber ply orientation on infiltration.
• Improved wetting by Ti in braze facilitated infiltration.
• No reaction choking and flow cessation from carbide forming reactions.

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].

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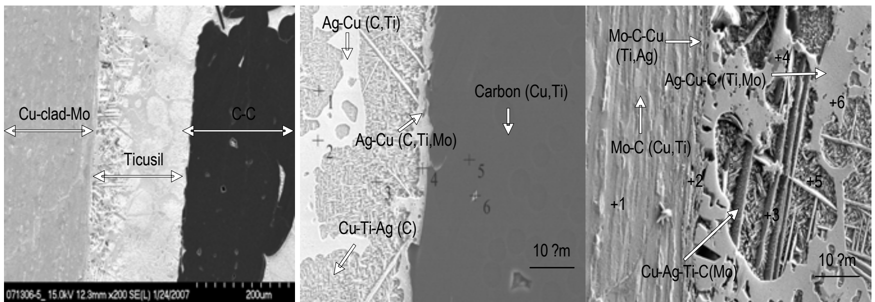
Microstructure of C-C (non-oriented fibers) composite/Ticusil/Cu-clad-Mo joint



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

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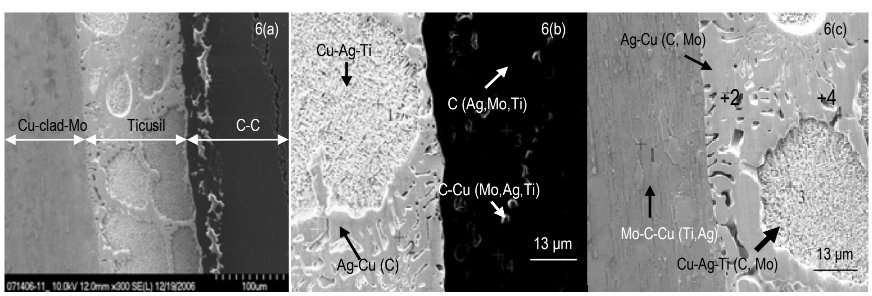
Microstructure of C-C (resin-derived) composite/Ticusil/Cu-clad-Mo joint



- 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.

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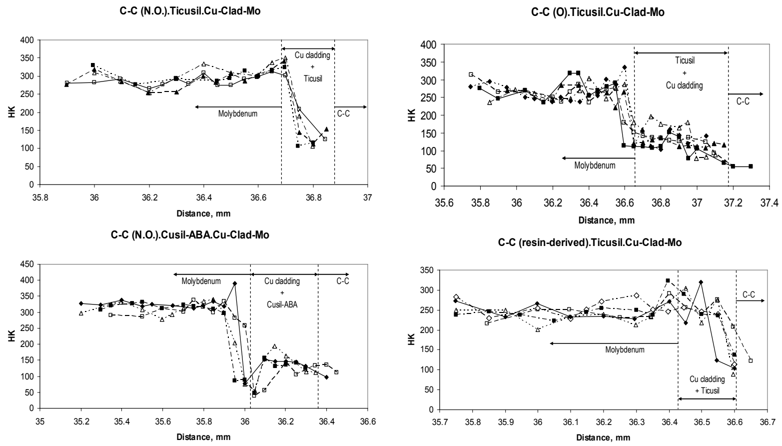
Knoop Hardness of C-C Composite/Cu-Clad-Mo Brazed Joints



- 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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Concluding Remarks

- Active metal brazing can be successfully utilized for the integration of carbon-carbon composites to metallic systems.
- However, significant efforts are needed in developing joint design methodologies, understanding the size effects, and thermomechanical performance of integrated systems in service environments.
- Global efforts on standardization of integrated component testing are required. In addition, development of life prediction models for integrated components is also needed.