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Ceramic-Metal Brazing, From Fundamentals to Applications: A Review of Sandia National Laboratories Brazing Capabilities, Needs, and Opportunities

F. Michael Hosking, John J. Stephens, S. Jill Glass, Justine E. Johannes, Paul Kotula, Neil A. Lapetina, Ron E. Loehman, Tom P. Swiler, Edmund B. Webb III, Charles H. Cadden, T. Oyama, A. P. Tomsia

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Abstract

The purpose of the report is to summarize discussions from a *Ceramic/Metal Brazing: From Fundamentals to Applications* Workshop that was held at Sandia National Laboratories in Albuquerque, NM on April 4, 2001. Brazing experts and users who bridge common areas of research, design, and manufacturing participated in the exercise. External perspectives on the general state of the science and technology for ceramics and metal brazing were given. Other discussions highlighted and critiqued Sandia's brazing research and engineering programs, including the latest advances in braze modeling and materials characterization. The workshop concluded with a facilitated dialogue that identified critical brazing research needs and opportunities.

Keywords

Brazing Science and Technology, Joining, Ceramics, Metal, Interface, Research, Modeling, Characterization

Acknowledgments

The authors would like to acknowledge the program support of Julia Phillips, Mike Cieslak, Duane Dimos, Mark Smith, and Ken Wilson. Cher Porter and Dominique Foley Wilson were responsible for the workshop organization. The authors are particularly indebted to the workshop participants, who contributed to its success. Jim Jellison was especially helpful in facilitating the group discussions. The authors also thank Aaron Hall for his thoughtful review of the manuscript.

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1.0 Introduction

The purpose of the Ceramic/Metal Brazing Workshop that was held at Sandia National Laboratories in Albuquerque, NM on April 4, 2001 was to gather experts from the brazing community to discuss the current state of brazing science and technology at Sandia. This report summarizes the presentations and discussions. The workshop was structured to cover a wide range of topics related to basic and applied research, design, and production. The goal was to identify strategic Science and Technology brazing linkages, needs, opportunities, and potential roadblocks to program growth and Sandia's recognition as a world-class leader in brazing research. The principle outcome of the workshop should be an improved forum for discussing brazing issues, strengthening collaborations and funding, and formalizing future research initiatives.

Introductory remarks by F. M. Hosking reviewed Sandia's investment in ceramic/metal brazing technology (see Figs. 1-8). The critical connections between research, development, and applications were described. Typical Sandia brazing applications include high voltage tubes, thermal batteries, stronglinks, connectors, header feedthroughs, and energy components. To address the different materials and processing issues that go into making reliable braze joints, it is necessary to leverage the multidisciplinary resources at Sandia.

The workshop provided a forum for highlighting Sandia's ceramic-metal brazing programs. Understanding the basic interfacial reactions that occur and how they affect subsequent properties is critical to controlling and optimizing the brazing process. Key research components include fundamental experimentation, applied testing, modeling at different length-scales, and materials characterization. To successfully complete the research-to-applications loop, input and feedback from design and production organizations are necessary.

Non-Sandians were also invited to the workshop to provide an external view on where brazing science and technology is and where it may be going. This included an objective critique of Sandia's brazing research capabilities.

Workshop on Ceramic / Metal Brazing: From Fundamentals to Applications

8:00 - 8:20 a.m.	Badging and Continental Reception
8:20 - 8:30 a.m.	Welcome and Introductions (Julia Phillips)
8:30 - 8:45 a.m.	Workshop Overview / Objectives (Mike Hosking & Ron Loehman)
8:45 - 9:15 a.m.	State of the Science (Tony Tomsia, LBL)
9:15 - 9:45 a.m.	State of the Technology (Toshi Oyama, WESGO Metals)
9:45 - 10:00 a.m.	Sandia Integrated Ceramics Brazing Program (Mike Hosking)
10:00 - 10:15 a.m.	Break
10:15 - 10:35 a.m.	Computational Design Tools & Principles (Justine Johannes)
10:35 - 10:55 a.m.	DP Production Perspective (Neil Lapetina)
10:55 - 11:15 a.m.	Fundamental Wetting and Interfacial Reactions (Ron Loehman)
11:15 -11:35 a.m.	Atomistic/Molecular Braze Interface Modeling (Ed Webb & Tom Swiler)
11:35 - 11:45 a.m.	Morning Wrap-up
11:45 - 1:00 p.m.	Lunch (897/1010-1012)
1:00 - 1:20 p.m.	New Analytical Tools (Paul Kotula)
1:20 - 1:40 p.m.	Development and Production Brazing (John Stephens)
1:40 - 2:45 p.m.	Brazing Science and Technology Needs / Opportunities (All*)
2:45 - 3:00 p.m.	Break
3:00 - 4:00 p.m.	Wrap-up Discussions and Concluding Remarks

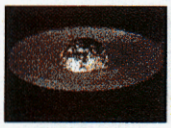
* Discussion facilitated by Jim Jellison

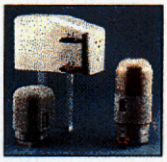
Brazing Science & Technology *Figure 1*

Sandia National Laboratories

Workshop on Ceramic / Metal Brazing: From Fundamentals to Applications

Sandia Supports a Broad Range
<u>of Interdependent Brazing Activities</u>





DEVELOPMENT
(DESIGN)

R <--> D <--> A

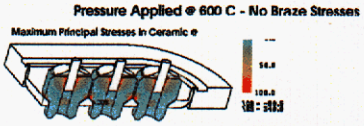
RESEARCH
(BASIC/APPLIED) <--> APPLICATIONS
(PRODUCTION)

Brazing Science & Technology *Figure 2*

Sandia National Laboratories

Typical Ceramics & Metal Brazed Products

- switch tubes
- neutron tubes
- stronglinks
- thermal batteries
- storage containers
- plasma facing components
- feedthrough connectors/headers
- solid oxide fuel cells
- auxiliary power units
- liquid metal thermoelectric cells
- electrochemical potential sensors

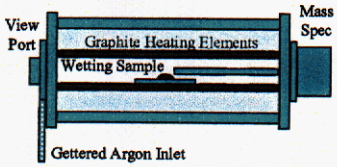


Brazing Science & Technology *Figure 3*

Brazing Research Spans Many Disciplines

Fundamental ⟷ **Applied**

- Ceramics
- Joining
- Characterization
- Computation
- Modeling
- Design
- Development
- Process
- Production



Brazing Science & Technology *Figure 4*

What Are the Issues?

- materials/process selection
- surface conditions
- interfacial reactions
- wetting & flow
- fillet geometry
- microstructures
- hermeticity
- strength/residual stresses
- corrosion/oxidation resistance
- post-processing requirements
- service conditions/reliability

Brazing Science & Technology *Figure 5*

Current S&T Brazing Components

- Experimental Tools (Materials & Process Science Expertise)
- Computational Predictive Tools (Thermal, Fluid Flow, Mechanical, & Interface)
- Analytical Tools (Microstructural & Compositional Characterization)
- Design & Production Feedback (Development, Characterization, Qualification, & Failure Analysis)

Brazing Science & Technology *Figure 6*

Workshop Objectives

- Show S&T program/project linkages
- Validate Ceramics Brazing S&T activities
- Determine Ceramics Brazing S&T needs
- Identify Internal/External Opportunities
- Identify Potential Roadblocks

Brazing Science & Technology *Figure 7*

Workshop Outcome

- Improve Brazing S&T dialog
- Strengthen programmatic linkages & funding
- Formalize a Ceramics Brazing S&T initiative
- Document workshop results in SAND Report

Brazing Science & Technology *Figure 8*

2.0 State of Brazing Science

The state of brazing science was the first technical topic that was discussed (Figs. 9-50). An external perspective was given by Dr. A. P. Tomsia from Lawrence Berkeley National Laboratory on fundamental braze wetting and flow phenomena, focusing on ridge formation, spreading kinetics, reactive wetting, and diffusion processes.

Ceramic-metal adhesion and the effect of chemistry on droplet, fillet, and flaw formation were discussed. One of the critical problems in liquid metal spreading is that the spreading rates are significantly lower than values computed from fundamental principles. This is generally attributed to physical and chemical surface effects, such as roughness, contact angle hysteresis, interface reaction kinetics, and dewetting. Drop transfer experiments were proposed to study these basic advancing and receding spreading effects (Fig. 18).

Tomsia next described the formation of capillary-induced ridges at the leading edge of a spreading droplet, which can eventually pin braze flow. This mechanism is not considered in Young's simple treatment for equilibrium wetting (Fig 20). An example was given where ridges are formed along the metal and solid oxide triple line for liquid metal on polycrystalline alumina (Fig. 21). Atomic force microscopy analysis showed that the ridge profiles were similar to those calculated for stationary and quasi-steady state conditions.

Spreading kinetics depends on the flow regime (Figs. 22-28). Conventional fluid flow occurs if the substrate is rigid and insoluble and no ridge forms (Regime 1). Wetting regimes 2 and 3 are defined by the formation of small or large ridges, respectively, that undercut the spreading liquid droplet. Smaller ridges generally move with the liquid front and approach macroscopic equilibrium wetting (Young's equation), while the larger ridges will inhibit spreading. Regime 4 wetting involves the more complicated case where the liquid metal chemically reacts with the substrate. Finally, different ridge shapes are predicted if surface diffusion is the controlling mechanism.

A four-step sequence for reactive wetting was proposed (Figs. 29-34). Spreading is initially enhanced by adsorption from the supersaturated liquid, with the formation of a ridge under the foot of the liquid front. A reaction product along the liquid-solid interface nucleates and then grows. The liquid front finally detaches or withdraws from the reaction layer.

Other topics that were discussed included the influence of surface and interfacial energy on wetting, grooving and ridging diffusion mechanisms, and grooving kinetics. Surface energy, contact angle, and surface/volume diffusivity data were presented for several metal-alumina systems (Figs. 35-47).

In summary, triple line ridging at the liquid front can control spreading kinetics. Liquid breakaway or attachment affects hysteresis. The relative spreading rates determine ridge and interface morphologies. Optimum wetting occurs with intermediate reactivity. Macroscopic homogenization (i.e., heat flow and reactive element dissolution) can limit spreading velocities. Mass transport is substantially greater for metal/alumina interfaces than for an oxide surface. Interfacial energies are dependent on the partial pressure of oxygen, with transport significantly faster at low values. Diffusion can control transport at grain boundary grooves. Examples were given to demonstrate these conclusions.

Future research was proposed in three critical areas for the science of braze wetting and spreading/flow. The first is metal/ceramic interfacial energetics and kinetics (effect of oxygen partial pressure, impurity adsorption, and interfacial atomic transport). The second is high temperature spreading (oxygen partial pressure, high speed kinetics, equilibrium and nonequilibrium conditions, and reactive spreading). The third is applications (lead-free solders, active metal brazing, semiconductor lighting, biomaterials, piezoelectric ceramics, and fuel cells).

Ceramic-Metal Interfaces
State of the Science

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Berkeley, California, USA
April 4, 2001, Sandia National Laboratory

Materials Sciences Division

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Figure 9

Ceramic-Metal Interfaces
State of the Science

Outline

Ridge Formation

Spreading Kinetics

Reactive Wetting

Diffusion Processes

Figure 10

Wetting

Essential aspect of many industrial processes:

High T

Welding
Brazing
Soldering
Interconnections
Packaging
Composite processing
Liquid phase sintering

Low T

Eye irrigation
Adhesive bonding
Tertiary oil recovery
Application of:
- insecticides
- paints
- detergents
- inks

Figure 11

Ceramic-Metal Adhesion
Effect of Chemistry: Formation

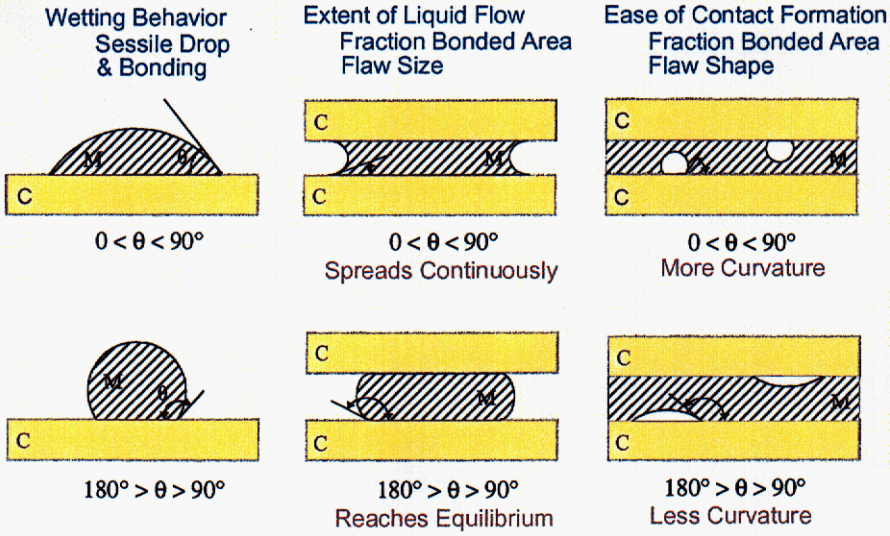


Figure 12

Physics of Spreading

Figure 13

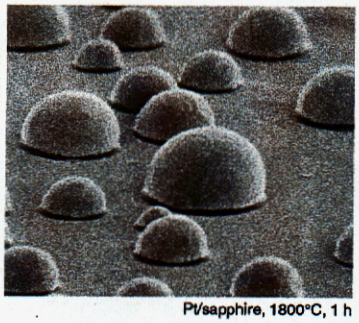
Wetting: an energy probe & kinetics determinant

$$\gamma_{sl}\cos\theta = \gamma_{sv} - \gamma_{lv}$$

1D approximation

$$W_{ad} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}$$

$$W_{ad} = \gamma_{lv}(1 + \cos\theta)$$



Pt/sapphire, 1800°C, 1 h

Wetting of Metals on Al_2O_3

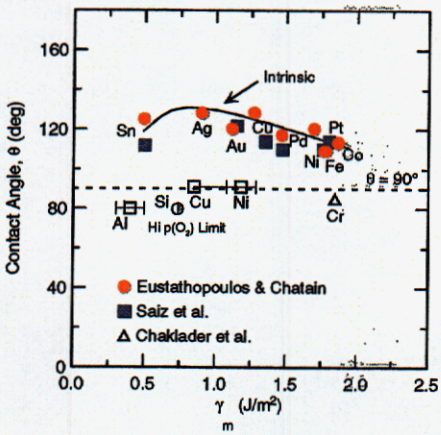
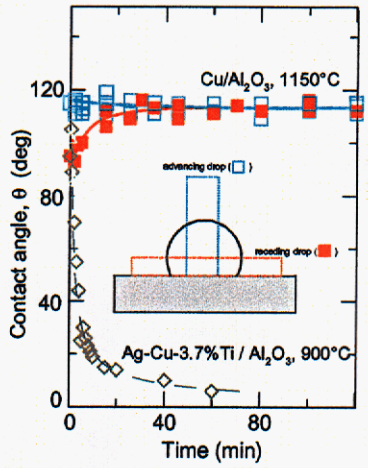


Figure 14

Liquid Metal Spreading



Long standing problems:

- Slow spreading rates
- Hysteresis/Variability
- Mechanism for reactive element enhancement

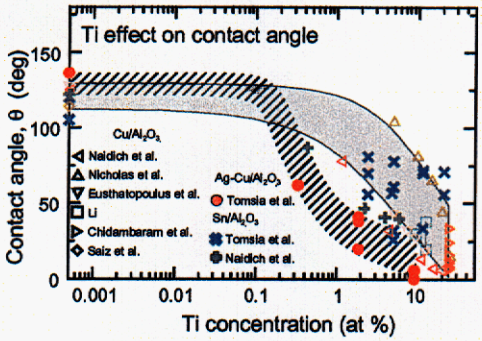
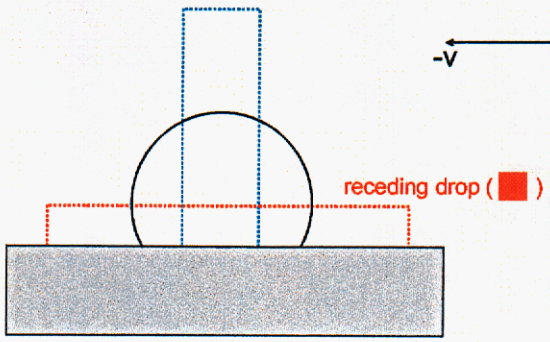


Figure 15

Wetting & Dewetting



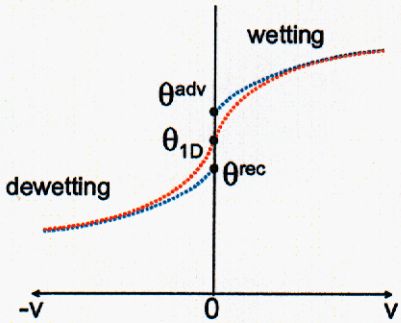


Figure 16

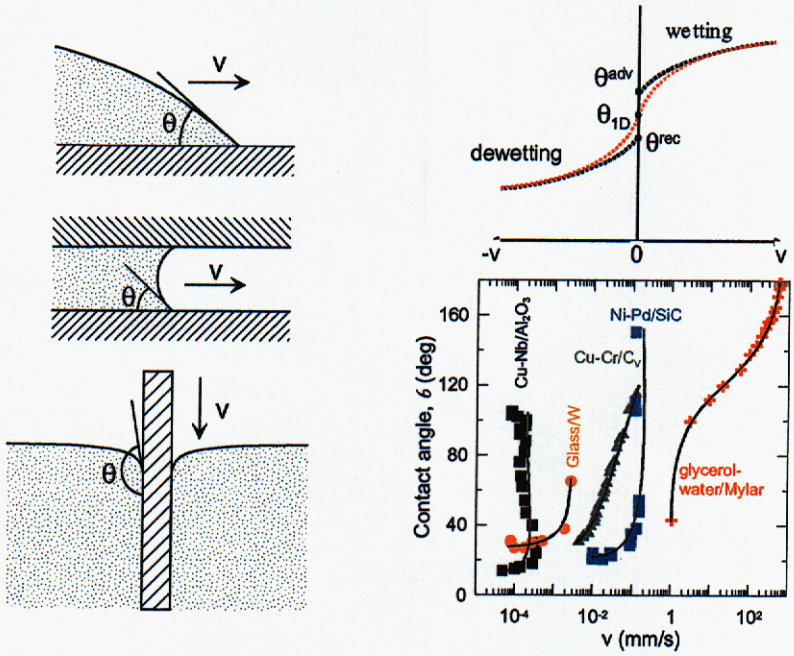
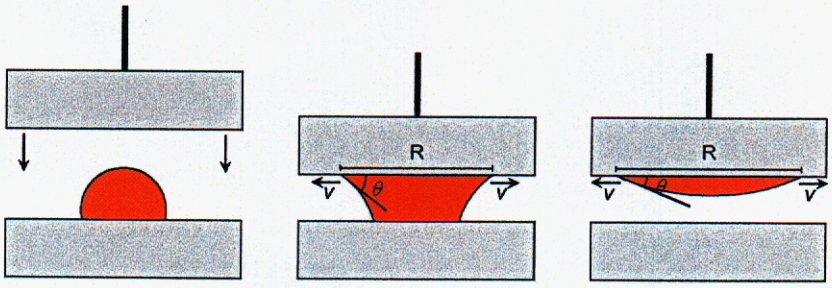


Figure 17

Drop Transfer Experiments



R(t), v(t), θ(t)
$v = f(\theta)$

Figure 18

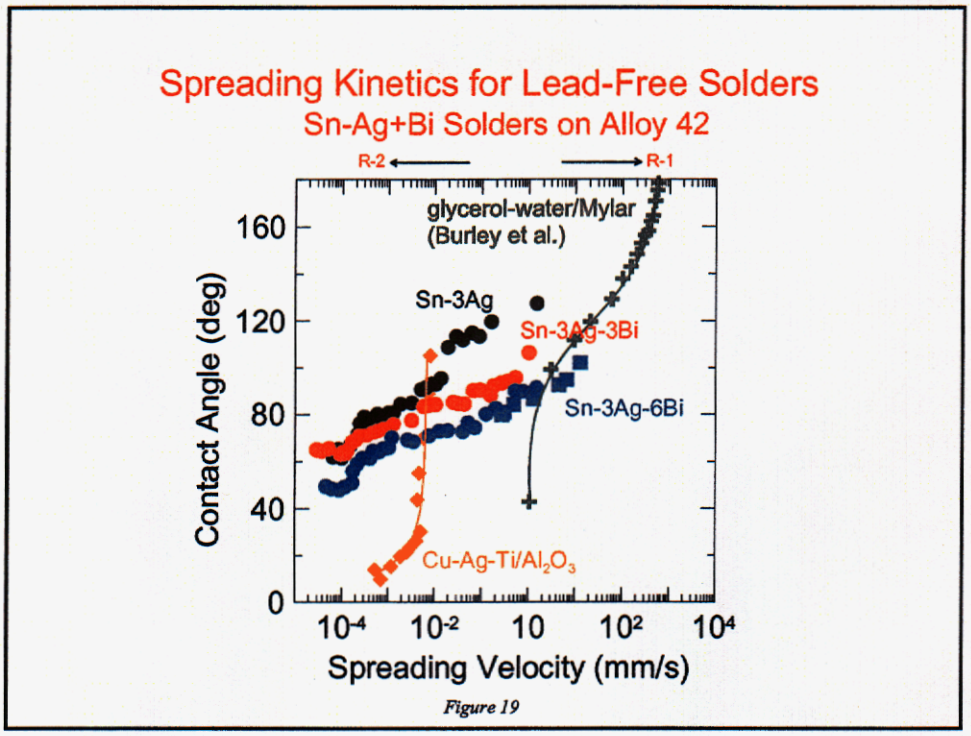


Figure 19

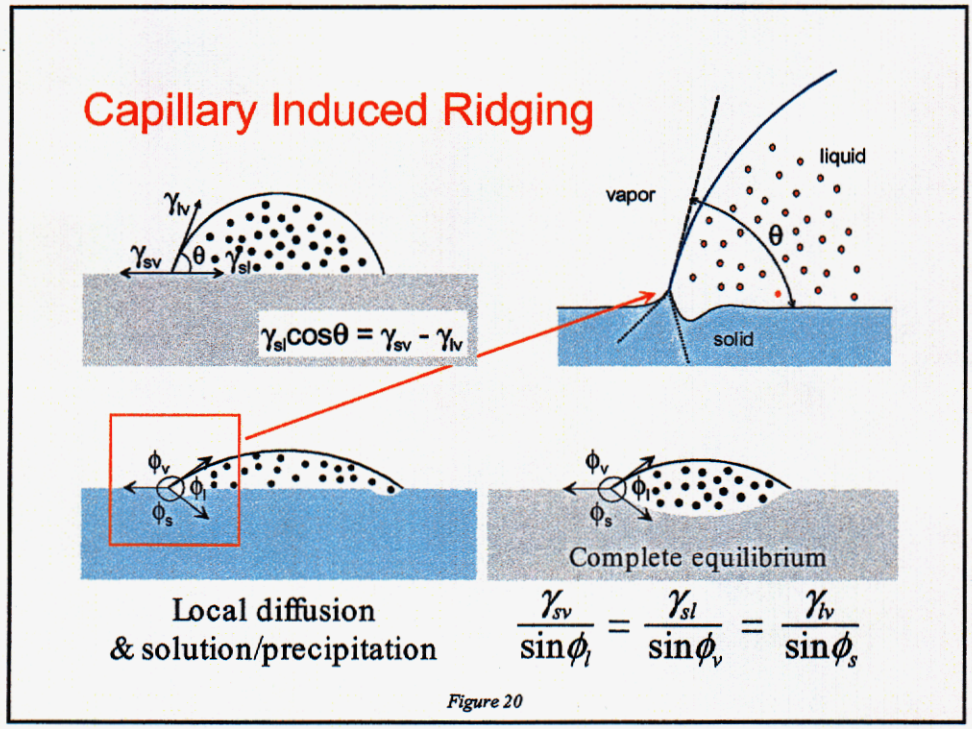
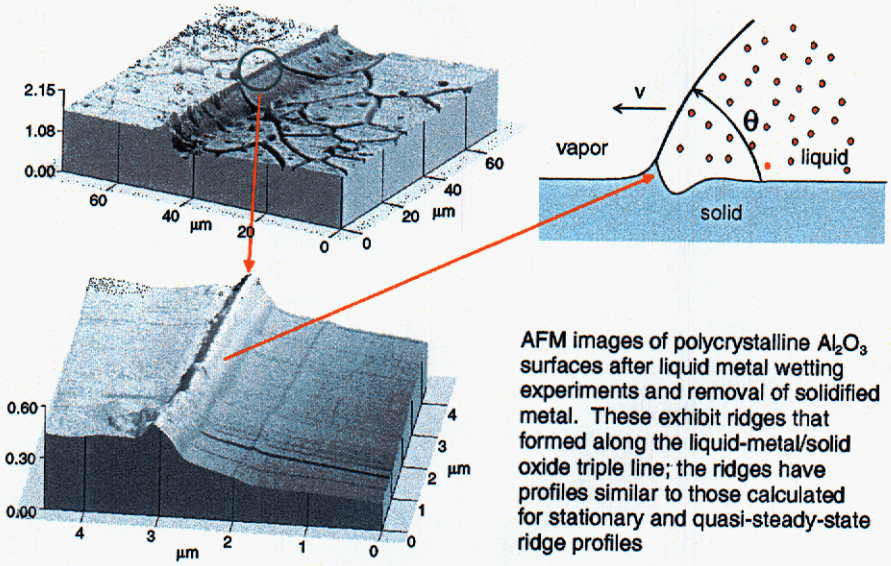


Figure 20

Structure of Triple Junction in HT Wetting Reveals Origin of Hysteresis

Ni/Al_2O_3, 1500°C, 5 min.

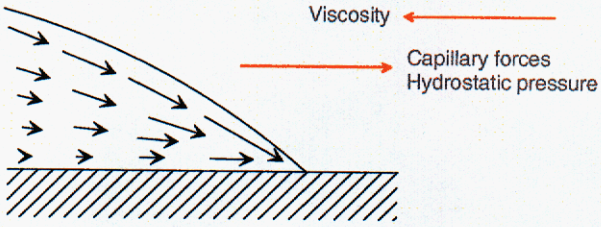


AFM images of polycrystalline Al_2O_3 surfaces after liquid metal wetting experiments and removal of solidified metal. These exhibit ridges that formed along the liquid-metal/solid oxide triple line; the ridges have profiles similar to those calculated for stationary and quasi-steady-state ridge profiles

Figure 21

Regime 1 Fluid Flow

Substrate rigid & insoluble



Equlibrium: Constant Curvature

$t_{cc} = \eta R/\gamma_{lv} \approx 10^{-5}$ s

Spreading velocity: $|v(t)| = k|(\theta - \theta_{1D})^n|$

Release of free energy = friction term

$$\gamma_1(\cos\theta_{1D} - \cos\theta(t)) = 3v\eta l/\theta(t)$$

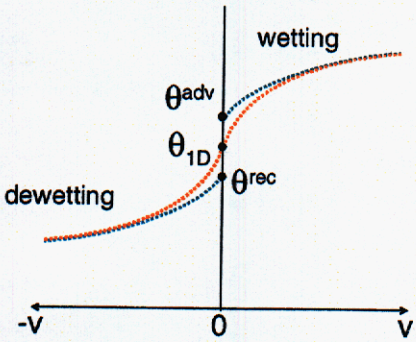
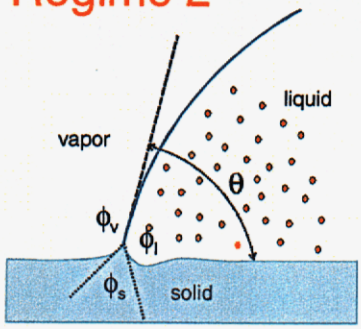


Figure 22

Regime 2



Small Ridge

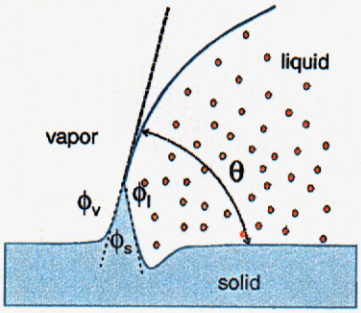
$h/R <<<< 1$ (typically $h/R < 10^{-3}$)

Microscopic 2-D equlibrium

Macroscopic 1-D equilibrium
Constant curvature
$\delta G=0$ in 1-D $\Rightarrow \gamma_{sv}=\gamma_{lv}\cos\theta+\gamma_{ls}$

Requires: ridge carried with liquid front

Regime 3



Big Ridge

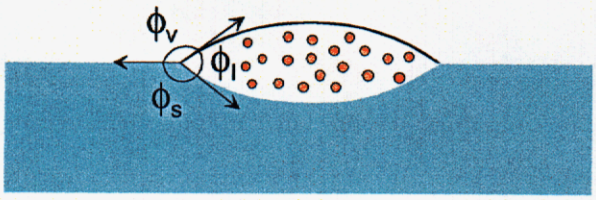
$h/R > 10^{-3}$

Microscopic 2-D equlibrium

Macroscopic $\delta G=0$ in 1-D doesn't apply

Figure 23

Regime 4



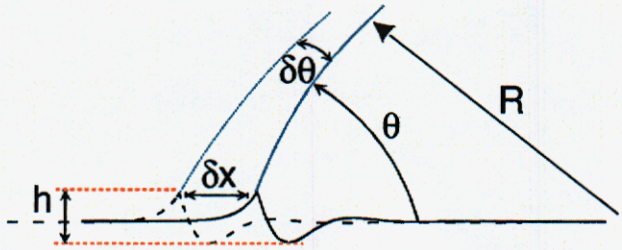
$$\frac{\gamma_{sv}}{\sin\phi_l} = \frac{\gamma_{sl}}{\sin\phi_v} = \frac{\gamma_{lv}}{\sin\phi_s}$$

Full 2-D equilibrium

Figure 24

Expected Shape of a Ridge & Associated Undercutting

Equivalent to Mullins treatment of grain boundary grooving



Microscopic 2D equilibrium

$h/R < 0.1$

$v_{\parallel} = dx/dt \qquad v_{\perp} = dh/dt$

$v_{\parallel} / v_{\perp}$

Figure 25

If no ridge, capillary forces drive liquid toward constant curvature shape and θ towards θ_{1D}

Small ridge same as no ridge

When a ridge is present:

$$\left(\frac{\partial G}{\partial m_+}\right)=0 \quad \left(\frac{\partial G}{\partial m_-}\right)=0 \quad \left(\frac{\partial G}{\partial \theta}\right)=0 \qquad \text{If } 2D = \phi_1$$

Total variation of surface energy can be written as:

$$dG = \left(\frac{\partial G}{\partial r}\right)_h dr + \left(\frac{\partial G}{\partial h}\right)_r dh \le 0$$

The variations from the 1D value as h grows:

$$(\Delta\theta)^2 \le \frac{1}{f(\theta_{1D})}\frac{h}{V^{1/2}} \qquad \text{If at } \theta = \theta_{1D}$$

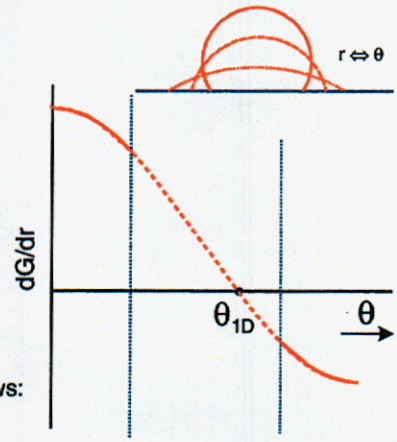
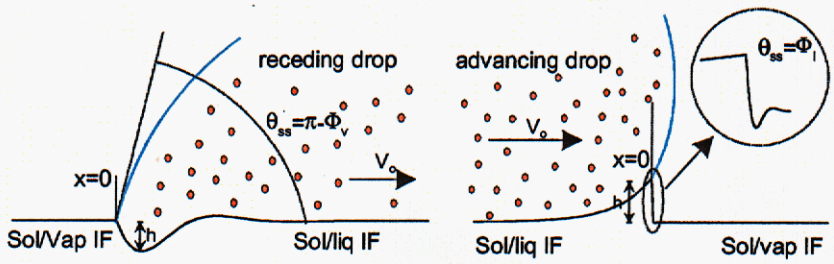


Figure 26

Surface Diffusion Control

Steady state solutions

If surface diffusion coefficient is much larger for the solid/liquid IF (D_{sl}>>D_{sv}) different shapes predicted for receding and advancing drop

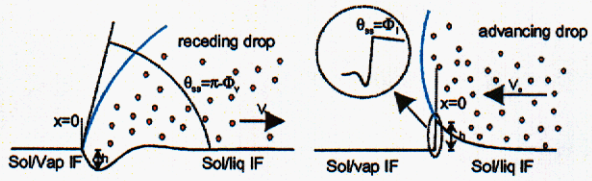


$$v_{ss}^{rec} = B_{sl} e^{\frac{\pi}{6\sqrt{3}}} \left[\frac{2y_{sl}'(0)}{h\sqrt{3}} \right]^3 \qquad v_{ss}^{adv} = B_{sv} \left[\frac{y_{sv}'(0)}{h} \right]^3$$

$$B_{si} = \frac{\omega D_{si} \gamma_{si} \Omega}{kT}$$

Figure 27

Theory of Ridging Controlled Spreading



Key elements:
- Breakaway condition
- Steady state velocities
- Quasi stationary velocity
- ⇒ Behavior diagram

Rationale for when:
- γ's from Young equation OK
- $\gamma_m(\theta - \theta_{1D})$ ~ driving force

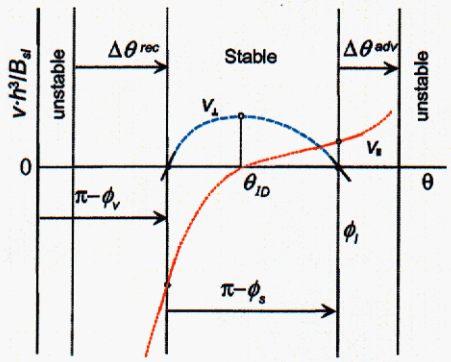


Figure 28

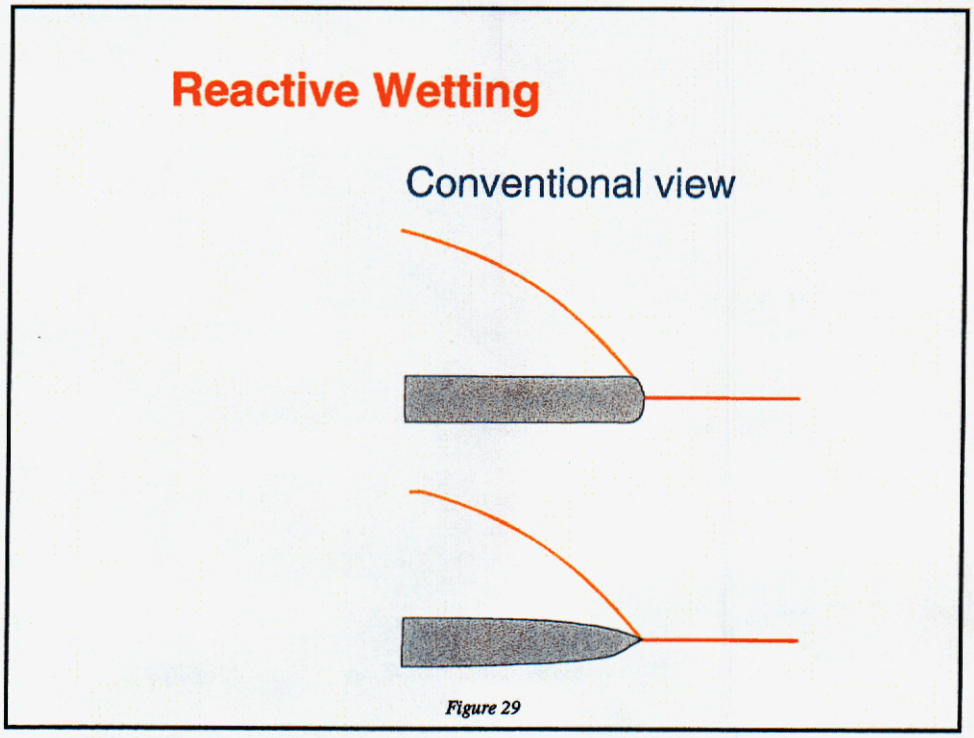


Figure 29

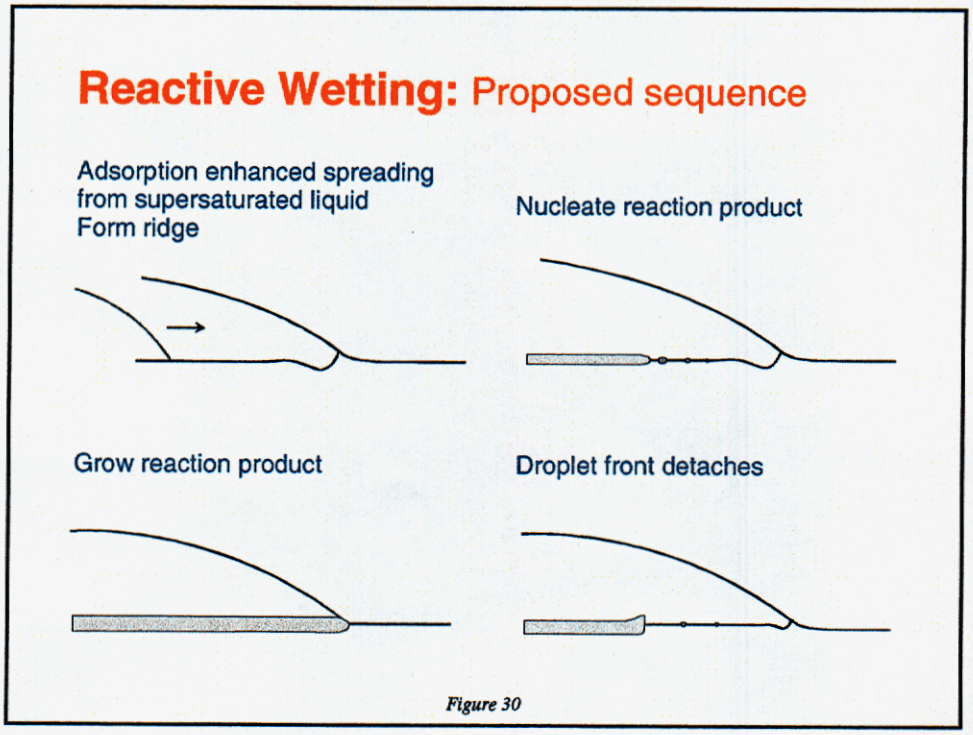
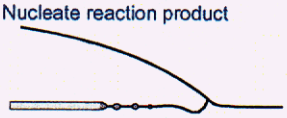


Figure 30

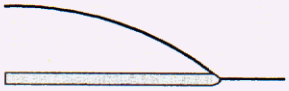
Reactive Wetting – Competitive Mechanisms

Adsorption enhanced spreading
from supersaturated liquid
Form ridge

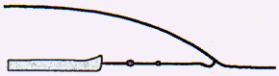
Nucleate reaction product



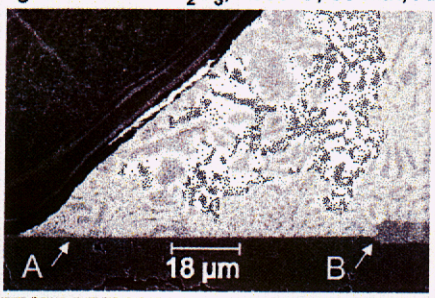
Grow reaction product

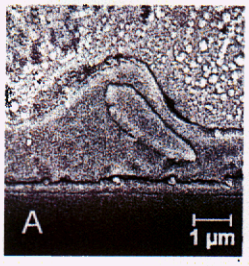


Liquid front detaches



Ag-Cu-1.9% Ti/Al_2O_3, 1000°C, 60 min, Ar





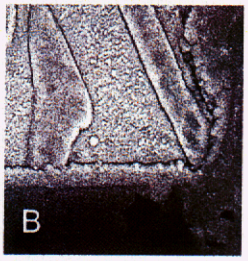


Figure 31

Diffusion at C/M Interfaces

Free Al_2O_3 surface

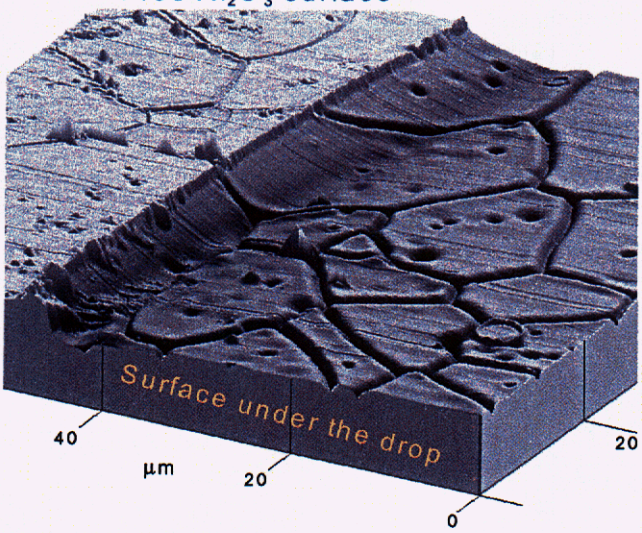


Figure 32

AFM image of an alumina substrate after removal of Ni drop (melted 60 min/1773 K)

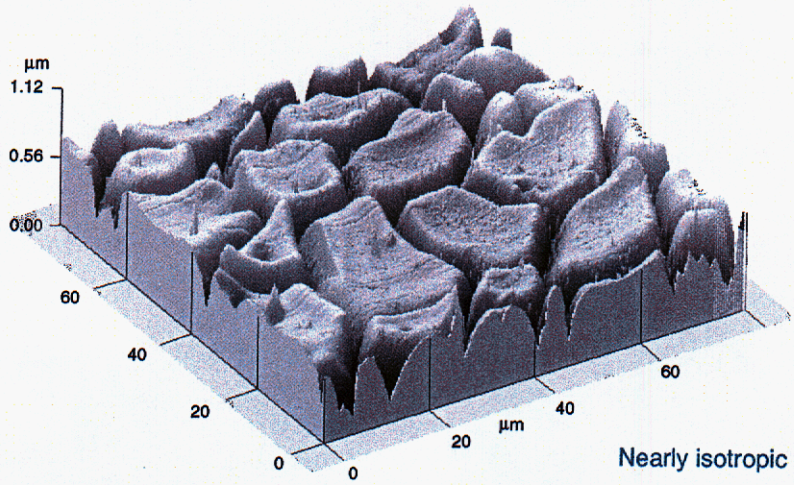


Figure 33

AFM image of an alumina substrate after removal of Al drop (melted 15 min/1773 K)

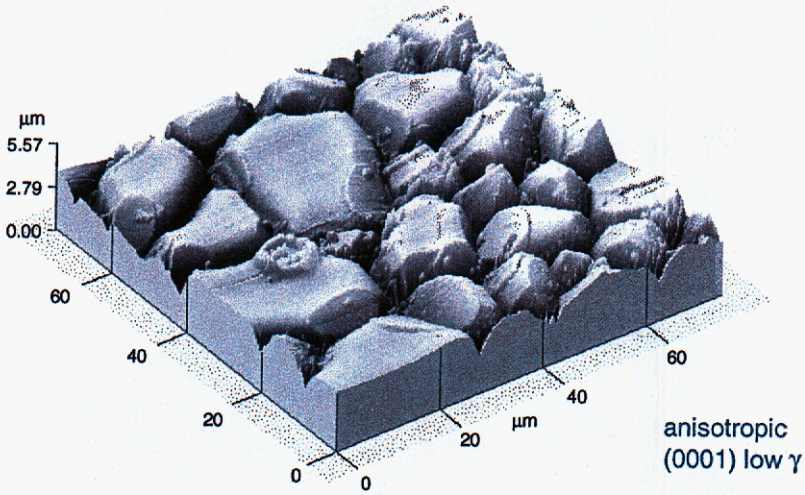


Figure 34

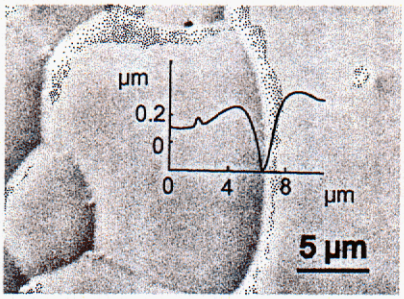
Wetting: An Energy Probe & Kinetics Determinant

$\gamma_{sl}\cos\theta = \gamma_{sv} - \gamma_{lv}$

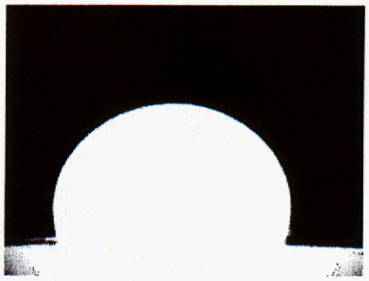
1D approximation

$W_{ad} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}$

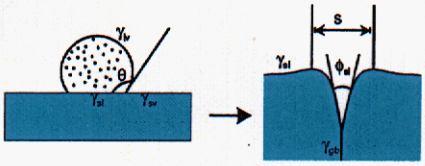
$W_{ad} = \gamma_{lv}(1 + \cos\theta)$



Ni/sapphire, 60 min, 1500°C



Ni on Alumina, 1500°C



$\gamma_{gb}=2\gamma_{sl}\cos(\phi_{sl}/2)$

$\gamma_{gb}=2\gamma_{sv}\cos(\phi_{sv}/2)$

Figure 35

Surface Energy of Cu vs. $p(O_2)$

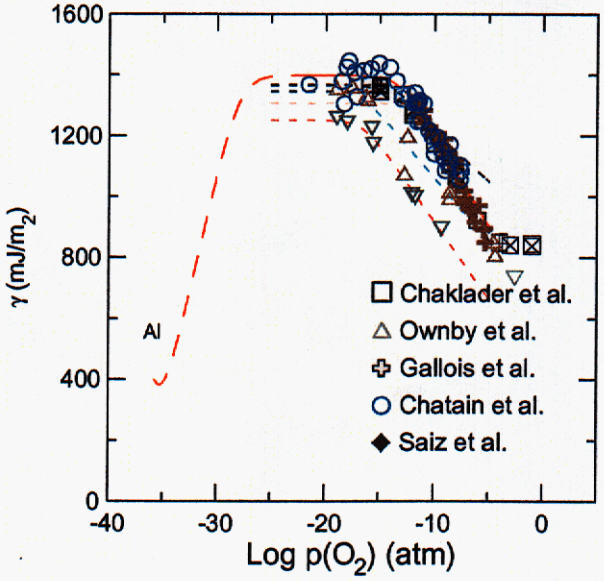


Figure 36

Wetting & Interfacial Energies

Cu-Al_2O_3

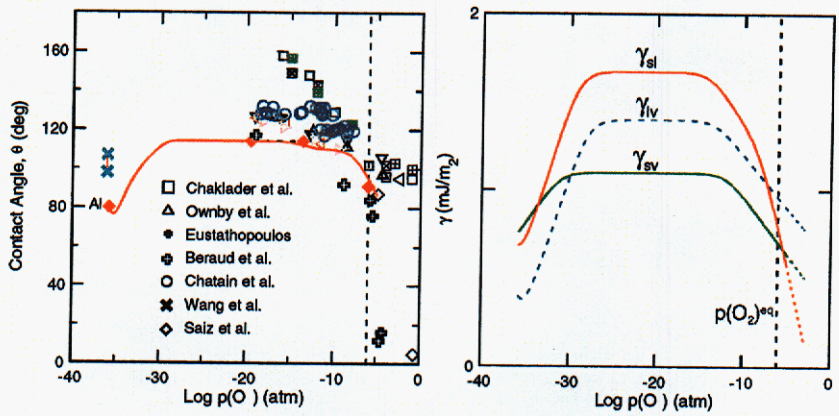


Figure 37

Interfacial Energies - $p(O_2)$ Dependence Established

System		θ	ϕ^l	ϕ^v	γ_{lv} (J/m²)	γ_{sl} (J/m²)	γ_{sv} (J/m²)	γ_{gb} (J/m²)
Al/Al_2O_3	1500°C	70°	93°	107°	≥0.3 [15]	≥0.65	≥0.76	≥0.90
Al/Al_2O_3	1500°C	80° [15]	93°	107°	≤0.74 [31]	≤0.81	≤0.95	≤1.12
Ni/Al_2O_3	"Plateau"	114°	142°	108° [3,4]	1.9 [26]	1.73	1.0	1.13

Theory for $p(O_2)$ dependence based on mutual adsorption

First set of energies for range of $p(O_2)$

W_{ad} increased 5x in 20 years

E. Saiz, R. M. Cannon & A. P. Tomsia, *Acta Mater*, 99

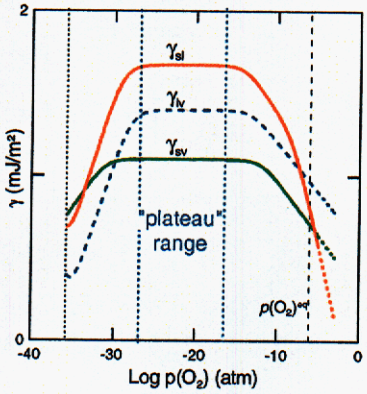
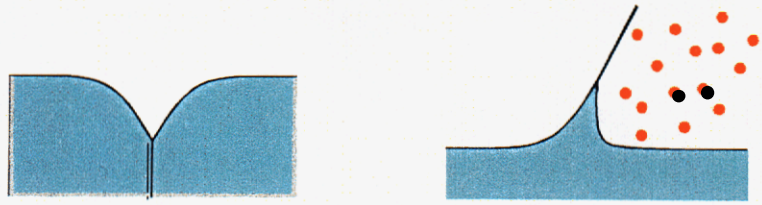
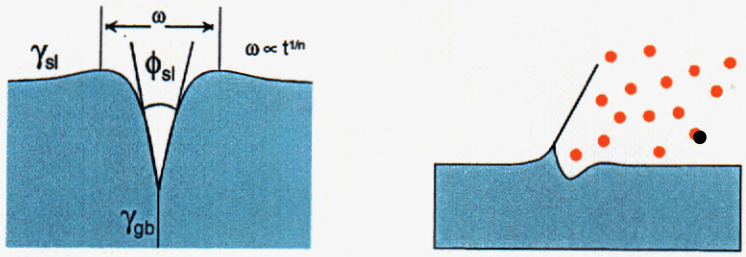


Figure 38

Grooving and Ridging Mechanisms



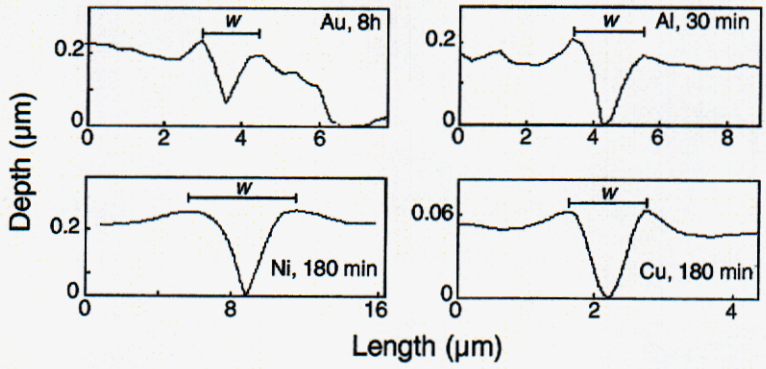
Interfacial reaction controls



Diffusion controls

Figure 39

AFM Profiles of GB Grooves



The groove shapes indicate that mass transport is controlled by diffusion

Figure 40

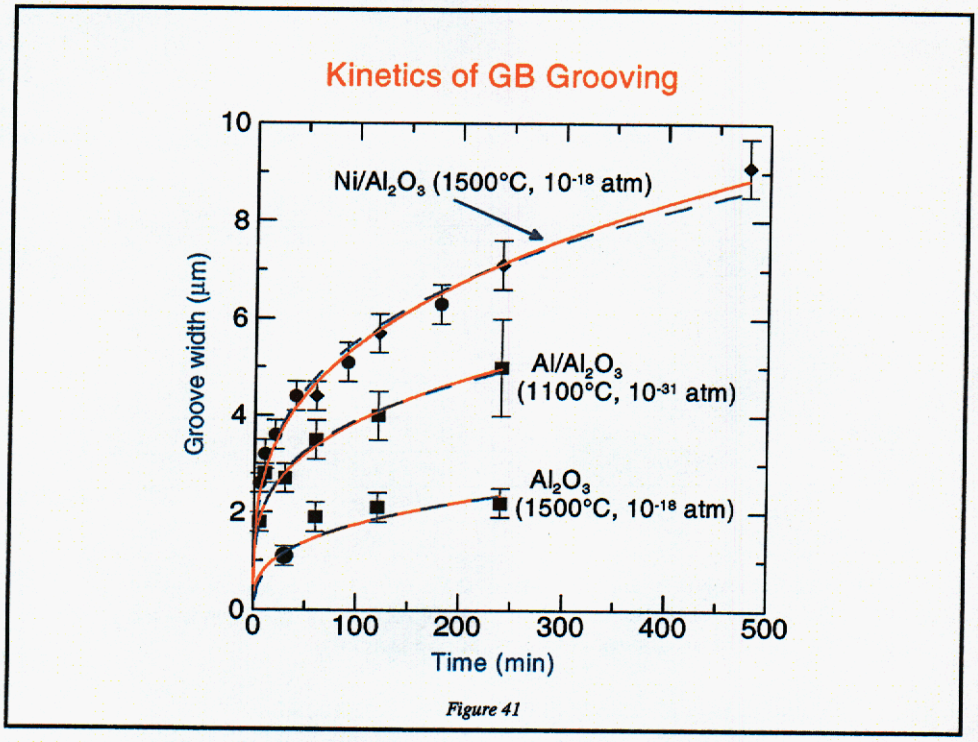


Figure 41

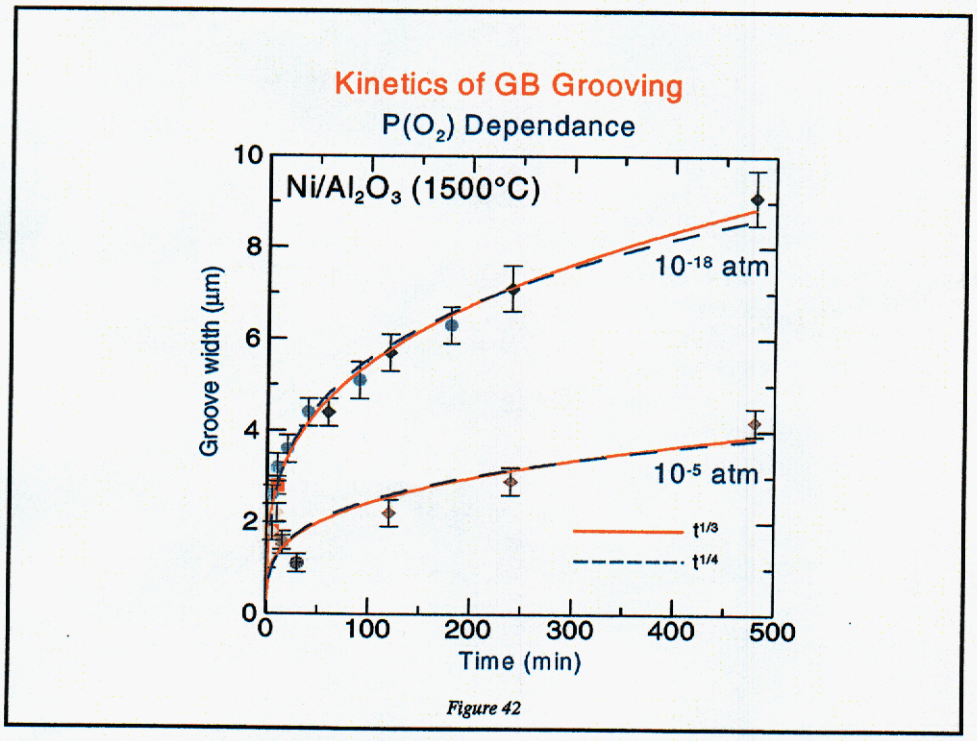


Figure 42

Surface and Volume Diffusivities

System	pO_2 (Pa)	T (K)	Surface Diffusion		Volume Diffusion		Combined		
			$\omega \times D_i$ ($m^3 \cdot s$)	w_0 (nm)	$x \times D_v$ ($m^2 \cdot s$)	w_0 (nm)	$\omega \times D_i$ ($m^3 \cdot s$)	$x \times D_v$ ($m^2 \cdot s$)	w_0 (nm)
Al_2O_3*	10^{-10}	1873	4.6×10^{-21}	0					
Al_2O_3 (Ni)*	10^{-10}	1773	2.0×10^{-22}	0					
Al_2O_3 (Ni)	1	1773	4.2×10^{-23}	0					
Al_2O_3 (Al)	10^{-17}	1773	2.6×10^{-18}	2688					
Ni/Al_2O_3*	10^{-10}	1773	4.4×10^{-19}	-795	1.1×10^{-13}	525	8.4×10^{-22}	5.9×10^{-14}	220
Ni/Al_2O_3	1	1773	3.0×10^{-20}	-39	1.6×10^{-14}	25	7.6×10^{-23}	8.6×10^{-15}	0
Au/Al_2O_3*	10^{4}	1373	1.8×10^{-24}	195	3.5×10^{-18}	385			
Cu/Al_2O_3*	10^{-10}	1423	2.8×10^{-22}	0	7.8×10^{-16}	0			
Al/Al_2O_3	10^{-26}	1373	1.1×10^{-19}	-162	5.0×10^{-14}	630	4.1×10^{-20}	6.6×10^{-16}	0

Calculated surface and volume diffusivities at the M/Al_2O_3 interfaces as well as on the Al_2O_3 surface outside the metal drop (denoted $Al_2O_3(M)$). The * denotes those interfaces expected to be stoichiometric (with no adsorption).

Figure 43

Interfacial Kinetics

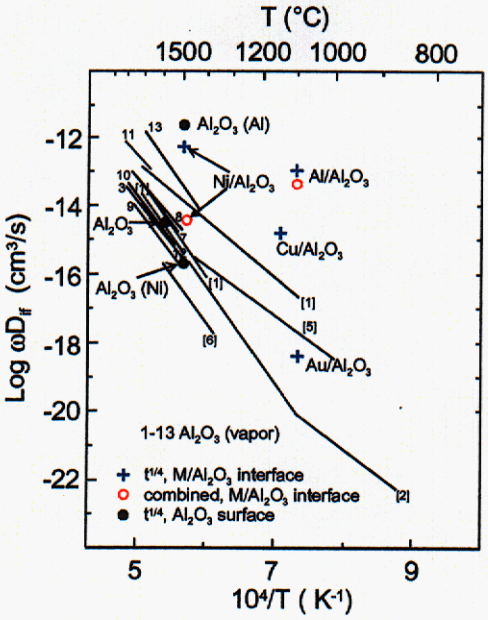
Transport from GB grooving

First data for liquid M/Al_2O_3 interfaces

Transport for noble metals via liquid

Very fast in ultra low $p(O_2)$

Slower in high $p(O_2)$



E. Saiz, A. P. Tomsia & R. M. Cannon

Figure 44

Liquid Metal and Al_2O_3 Surface Diffusivities

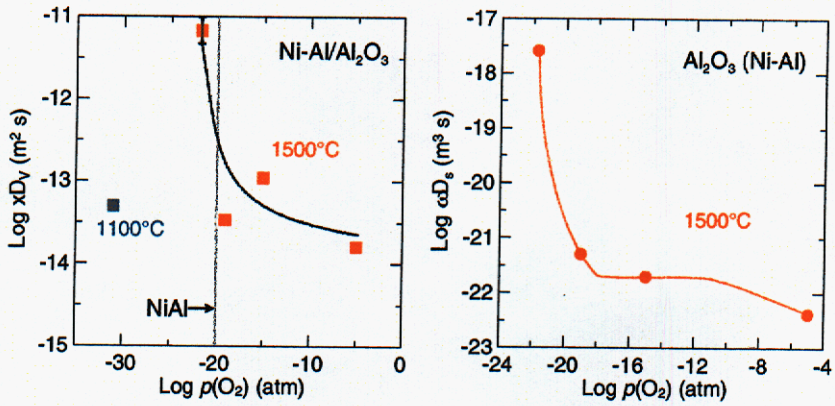


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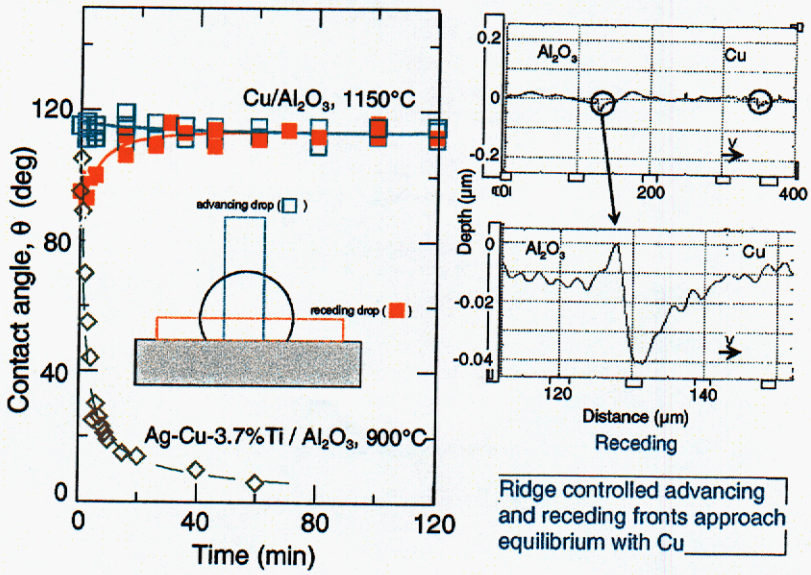
Figure 45



Ridge controlled advancing and receding fronts approach equilibrium with Cu

Figure 46

Cu/Al_2O_3, 1150°C

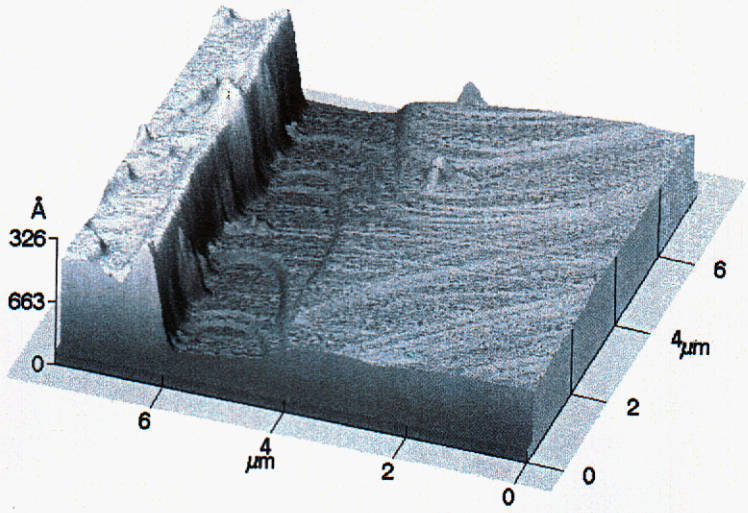


Figure 47

Conclusions: Ridging and Reactive Wetting

Triple line ridging can control spreading kinetics.
Regime 2: approach macroscopic Young eq.
Breakaway/attachment affects hysteresis

Divide reactive wetting process into steps.
- Spreading & adsorption
- Spreading & ridging
- Nucleate reaction product
- Grow reaction product

Relative rates dictate morphology.

Adsorption type dictates interface metastability:
- Monolayer - metastable till nucleation
- Multilayer – vanishing nucleation barrier

Optimum wetting from intermediate reactivity

Macroscopic homogenization can limit velocities
- Heat flow
- Dissolution of reactive element

Figure 48

Conclusions: Diffusion Processes

Ni/Al_2O_3 and Cu/Al_2O_3 interfaces more isotropic than are Al_2O_3 surfaces

Al/Al_2O_3 interface and Al_2O_3 with Al vapor are highly faceted

Data and models for $p(O_2)$ dependence of interfacial energies

Shape of interfacial GB grooves suggests that for Cu and Ni (at 1.05 $T_{m\text{-metal}}$), diffusion controls transport

Time evolution for grooves under Ni on Al_2O_3 more consistent with control by diffusion through the liquid

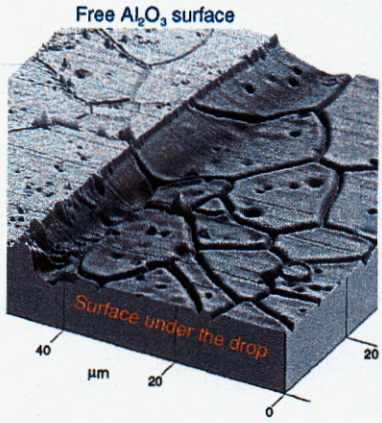
Mass transport is one to five orders of magnitude faster for metal/Al_2O_3 interfaces than on oxide surface

Transport for interface and alumina surface several orders of magnitude faster at low $p(O_2)$

Au on Al_2O_3 exhibits large $p(O_2)$ effect on transport rates

Figure 49

Future: Wetting & Spreading



Metal/ceramic IF energetics and kinetics
- Effect of $p(O_2)$
- Effect of impurity adsorption
- Interfacial atomic transport

High temperature spreading
- Effect of $p(O_2)$
- Kinetics - high speed
- Equilibrium and nonequilibrium
- Reactive spreading

Applications
- Lead-free solders
- Semiconductor lighting
- Biomaterials
- Piezoelectric ceramic

Figure 50

3.0 State of Brazing Technology and Engineering

Dr. Toshi Oyama of WESGO Metals gave an external perspective on the state of brazing technology and engineering (Figs. 51-87). WESGO Metals is a leading supplier and developer of brazing filler metals. The technology overview focused on commercially available and active brazing alloys for ceramics brazing. Brazing process developments, new heating methods, active metal brazing applications, and brazing alloy manufacturing were highlighted.

The moly-manganese process is still the primary method to metallize ceramics for brazing. However, it is being replaced in more applications by active brazing alloy technology (Figs. 54-55). There is a growing need for this alternative joining technology as other technical ceramics that are not easily metallized, such as silicon nitride, aluminum nitride, and silicon carbide, are selected for different engineering applications.

Commercially available active brazing alloys are typically based on the silver, gold, copper or titanium alloy systems (Figs. 58-60). They cover a broad melting temperature range, from 600 to 1100°C, which provides a potentially wide choice of filler metals to match the given application. Typical active element additions include titanium, zirconium or vanadium. The alloys are being used to join vacuum tube, semiconductor, biomedical, automotive, and aerospace components.

A recent development by Materials Resources International (MRi) has further expanded active joining to temperatures well below conventional brazing technology. The process is called S-Bond™ and can be performed in air. The tin-silver-titanium based alloy melts at temperatures in the soldering range of 250-300°C, directly reacts with oxides to form strong bonds without the use of chemical fluxes or special surface treatments, and minimizes thermal expansion mismatch and residual stresses associated when joining dissimilar materials. Work is ongoing to characterize the S-Bond™ joint properties for a variety of applications (microelectronics, feedthroughs, seals, machine tools, sporting goods, aerospace components). An example is shown in Fig. 62.

Joint design is typically determined from published references, experience, and trial and error methods. New and more efficient computational modeling capabilities offer enhanced tools to predict thermal and stress responses to furnace loading and processing conditions. These simulations can then be used to optimize joint designs.

New heating methods are also being developed that only melt the brazing alloy without extensively heating the base material. Microwave and reactive (or energetic) brazing are two such processes. They effectively reduce or eliminate thermal expansion mismatch and residual stress problems that normally occur during conventional heating of dissimilar materials. Research conducted at John Hopkins University by Tim Weihs is especially promising (Figs. 71-76). Reactive multilayer foils are used to generate and propagate the necessary heat to melt preplaced filler metals. The reaction is initiated at relatively low temperatures.

Work also continues in the study of active brazing (Figs. 77-87). The identification of reaction products and understanding wetting mechanisms are important research objectives. The effects of active element type, concentration, and processing conditions are being correlated to joint properties.

State of Technology
Ceramic Brazing

Toshi Oyama
WESGO Metals

Brazing Workshop
Sandia National Laboratories
April 4, 2001

Figure 51

Outline

- Ceramic Brazing Industry
  - Commercially Available
    Active Brazing Filler Metals
  - Applications for ABA technology
- Brazing Process Development
- New Heating Methods
- Science of Active Brazing
- Brazing Alloy Manufacturing

Figure 52

State of Technology

Ceramic Brazing Industry

Figure 53

Alumina Ceramic

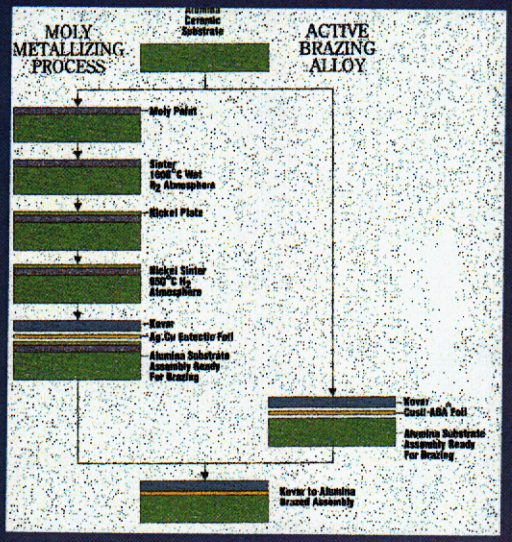


Figure 54

Alumina Ceramic

- Mo-Mn Method is still the main joining method
  - Robust Technology
  - Works in a continuous belt furnace
  - Resistant to change

- ABA technology replaced Mo-Mn process in some applications
- Alumina is being replaced by other ceramic materials

Figure 55

Non-Alumina Ceramic

- New Technical Ceramics
  - Silicon Nitride
  - Aluminum Nitride
  - Silicon Carbide

- Need for joining

  Metallizing v.s. Active Brazing

Figure 56

Commercially Available Active Brazing Filler Metals

Figure 57

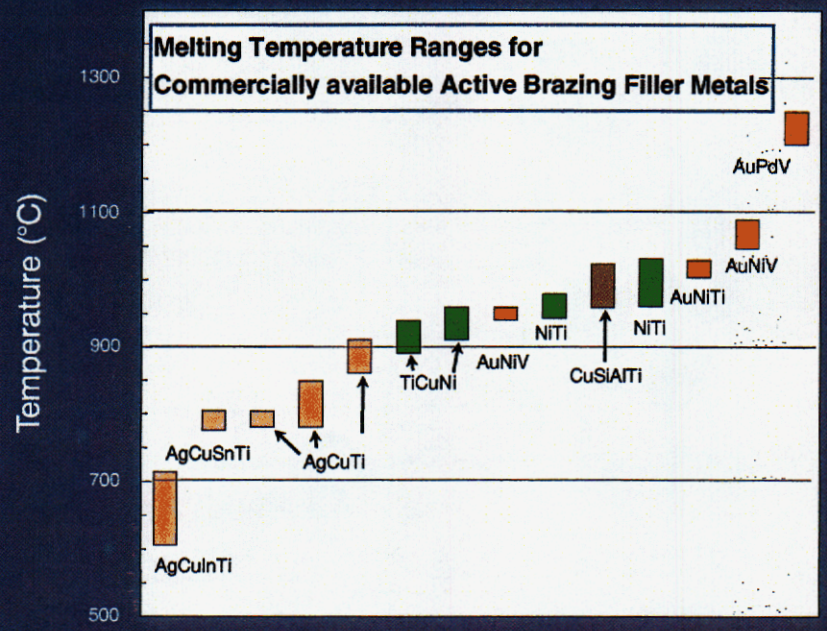


Figure 58

As the wetting properties of the filler metals alter when they are required to flow for any distance, they are always inserted into the joint gap. Accordingly the filler metals are available as preforms or as foil in thicknesses between 0.06 mm and 0.3 mm and widths of up to 70 mm. Other dimensions can be supplied upon special request.

Filler metal designations and technical data:

Filler metals	Composition (% by weight)	Melting range (°C)	Brazing temperature (°C)
CB 1 Ag/Cu/In/Ti	72.5/19.5/5/3	730–760	850– 950 [1]
CB 2 Ag/Ti	96/4	970	1000–1050 [2]
CB 4 Ag/Cu/Ti	70.5/26.5/3	780–805	850– 950 [1]
CB 5 Ag/Cu/Ti	64/34.5/1.5	770–810	850– 950 [1]
CB 1 Sn/Ag/Ti	86/10/4	221–300	850– 950 [1]
CB 2 Pb/In/Ti	92/4/4	320–325	850– 950 [1]

[1] A brazing temperature of 850 °C is possible, but higher temperatures improve wetting properties.
[2] In view of the relatively high vapour pressure of silver, a brazing temperature of 1000 °C should not be exceeded when brazing in a vacuum. A temperature of 1050 °C is possible in argon.

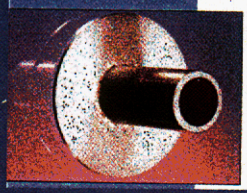
Degussa

Figure 59

BraSiC® filler alloys

Totally new, the range of **BraSiC®** filler alloys is particularly well suited to the brazing of silicon carbide (SiC) base materials (sintered SiC, SiSiC, SiC/SiC composites).

BraSiC® filler alloys can also be used to join other silicon or carbon rich materials like silicon nitride, graphite, diamond and all other carbon base materials.



Remarkable wetting

- Wetting angle lower than 30° on SiC.
- No surface treatment of the substrate is necessary. **BraSiC®** filler alloys dissolves quickly the oxide film which covers SiC.

CEREM cea

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CEA / Grenoble . Département d'Etude des Matériaux / SGM / 17, rue des Martyrs - 38054 Grenoble Cédex 9
Tél. 04 76 88 40 98 - Fax 04 76 88 94 63

Figure 60

Applications for ABA technology

- Vacuum Tubes
- Semiconductor Industries
- Biomedical
- Automotive
- Military
- Others

Figure 61

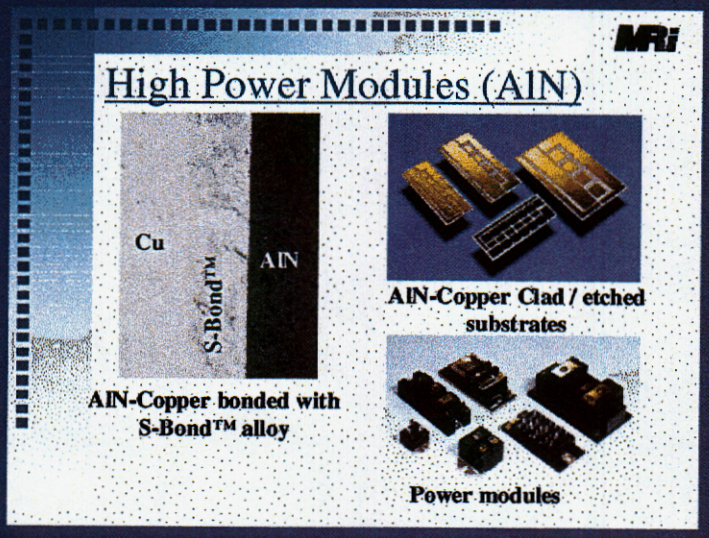


Figure 62

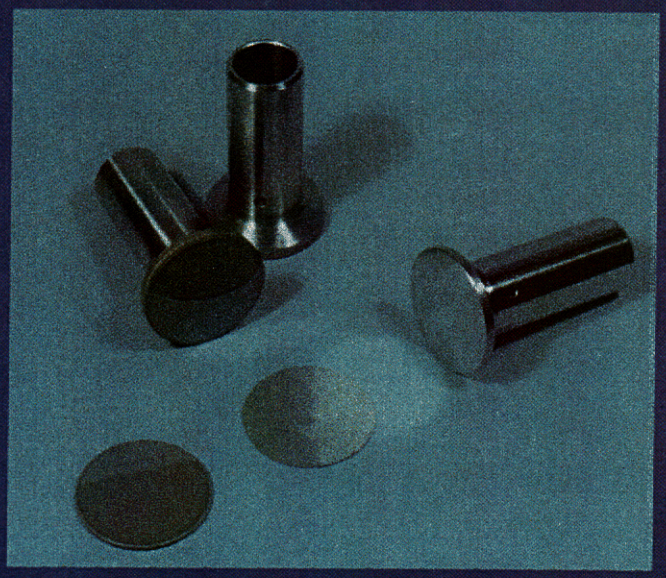


Figure 63

State of Technology

Brazing Process Development

Figure 64

Joint Design

- Joint Design
  - Text Book
  - Experience
  - Trial and Error
- Need Modeling Capability
  - To predict residual stress
  - To predict optimum joint design

Figure 65

Furnace Loading

- Trial and Error
- Experience
- Need Modeling Capability for
  - Maximum Furnace Loading
  - Uniform Temperature throughout the loading

Figure 66

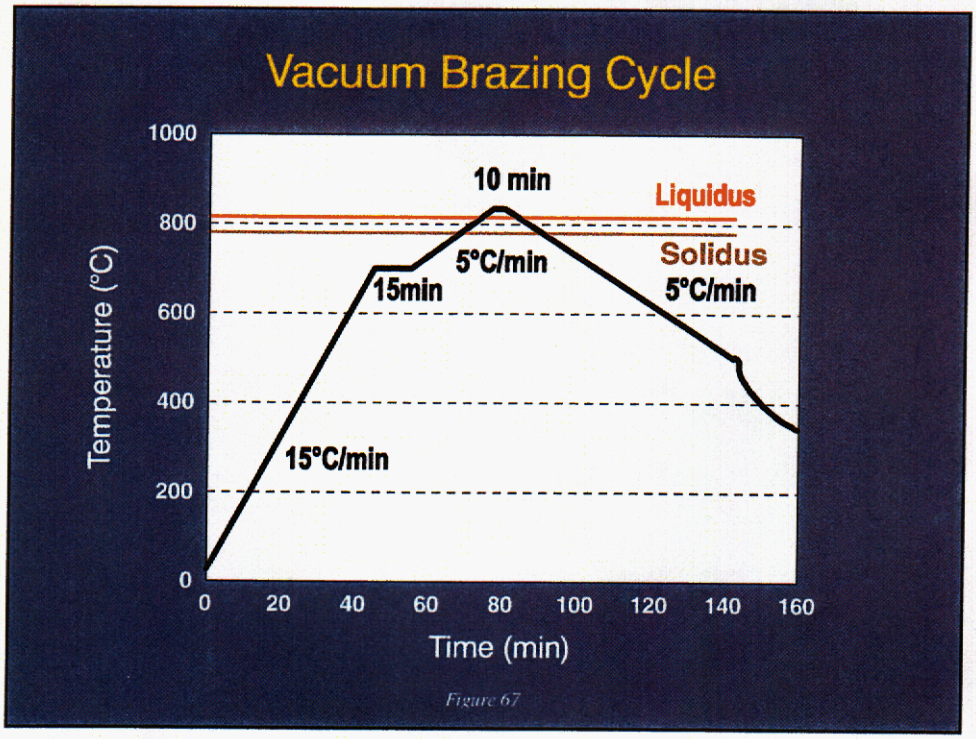


Figure 67

Fixture Design

- Trial and Error
- Experience

- Need Modeling Capability for
  - Prediction of Actual Sample Temperature Distribution
  - Uniform Temperature Distribution

Figure 68

State of Technology

New Heating Methods

Figure 69

New Heating Methods

- Heat and melt only brazing alloys without heating base materials too much.
  - Eliminate thermal expansion mismatch problem
- Microwave Heating
  - Robert Latdke – Technology International
- Reactive Foil
  - Tim Weihs – Johns Hopkins University

Figure 70

Reactive Multilayer Foils: Rapid Heats Sources for Joining, Ignition, and Forming

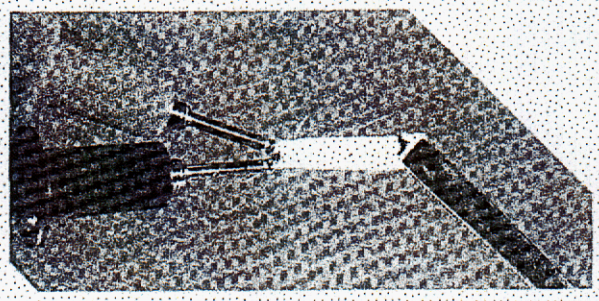
Tim Weihs

Department of Materials Science & Engineering
The Johns Hopkins University
Baltimore, MD 21218

JHU Faculty	Students & Postdocs	Supporting Agencies
Omar Knio	Andy Gavens	NSF - Career
Gang Bao	Swami Jayaraman	NSF - MRSEC
Todd Hufnagel	Kerri Blobaum	Army Research Lab
	Mike Reiss	Applied Physics Lab
LLNL	Dr. Adrian Mann	3M
Troy Barbee, Jr.	Dr. David Van Heerden	NIST

Figure 71

Self-Propagating Reactions in Multilayer Foils



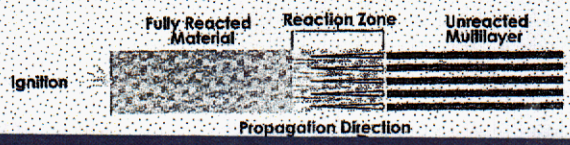
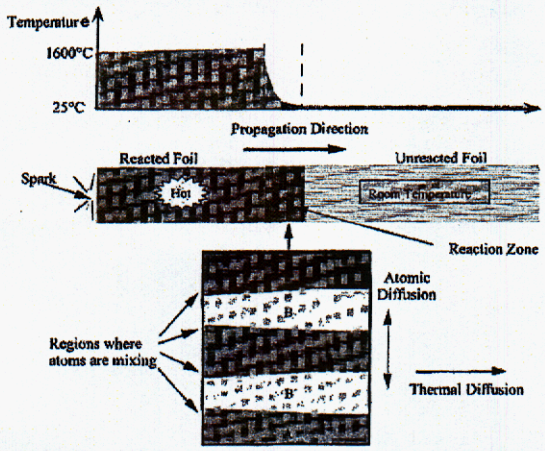


Figure 72

Schematic of Self-Propagating Reaction
(Side View)



Johns Hopkins University

Figure 73

Self-propagating Reactions in Layered Foils: Experimental Observations

- *Ignite with spark, laser, or match at 25°C*
- *Velocities greater than 20 m/s*
- *Temperatures above 1500°C*
- *Heating rates higher than 10^9 °C/sec*

Silicides: *Ni-Si, Zr-Si, Mo-Si, and Rh-Si*

Aluminides: *Ni-Al, Zr-Al, Ti-Al, and Pd-Al*

Johns Hopkins University

Figure 74

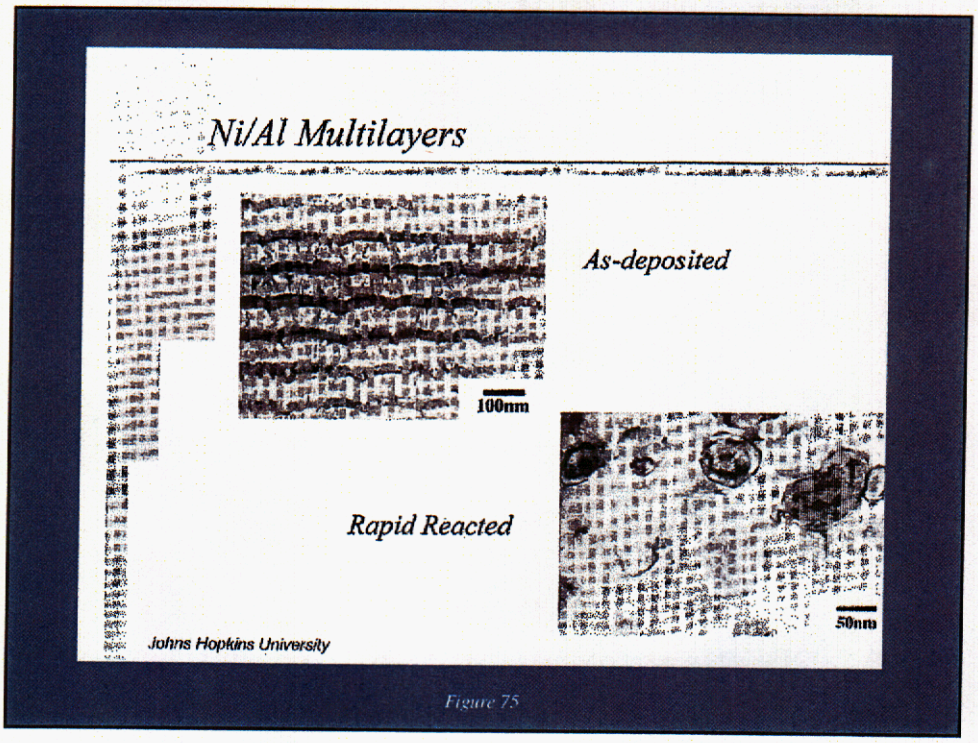


Figure 75

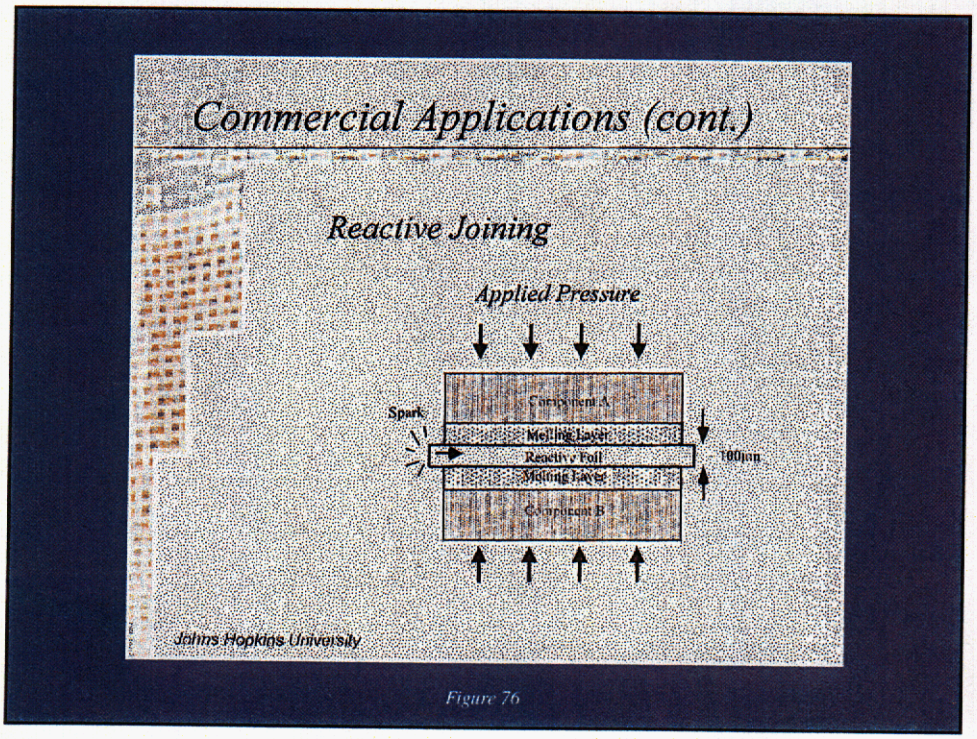
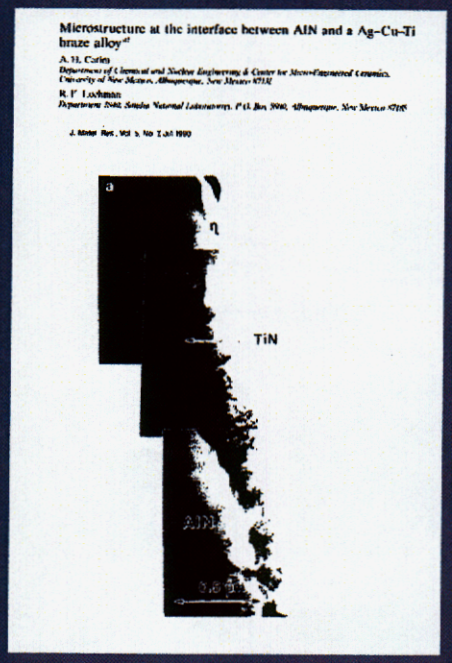


Figure 76

Science of Active Brazing

- Some TEM works on reaction products
- Wetting mechanism not well understood

Figure 77



Microstructure at the interface between AlN and a Ag–Cu–Ti braze alloy[a]

A. H. Carim

R. F. Lochman

a

η

TiN

AlN

Figure 78

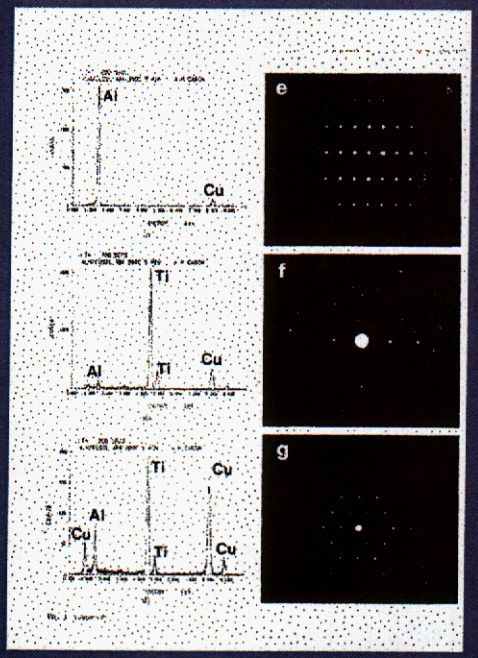


Figure 79

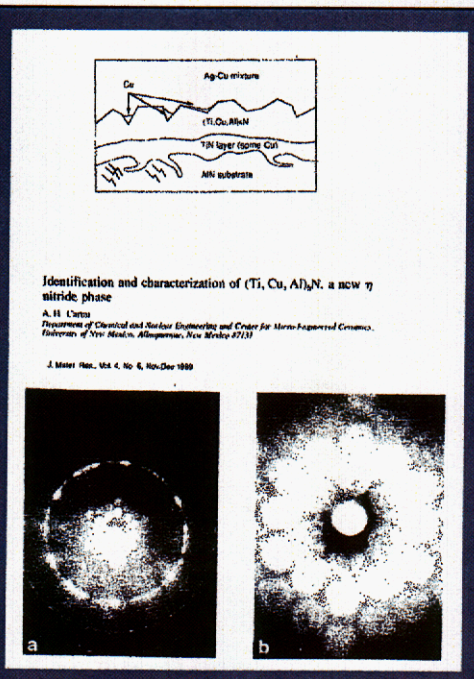
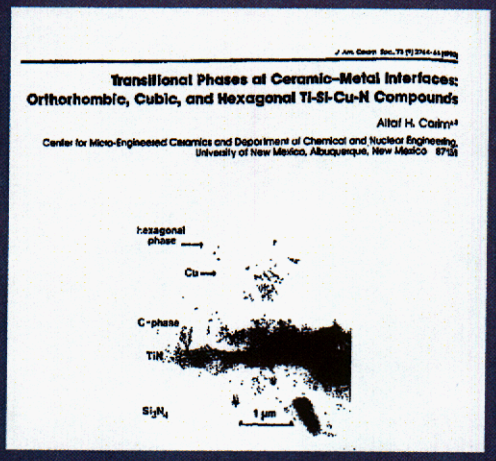


Figure 80



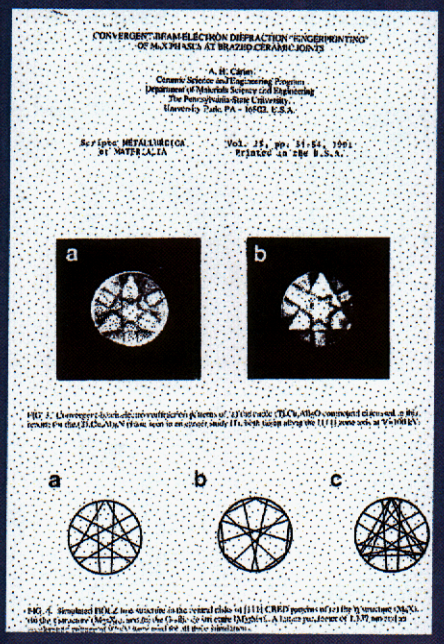
J. Am. Ceram. Soc., 73 [9] 2744–51 (1990)

Transitional Phases at Ceramic–Metal Interfaces: Orthorhombic, Cubic, and Hexagonal Ti-Si-Cu-N Compounds

Allaf H. Cairns*,†

Center for Micro-Engineered Ceramics and Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico 87131

Figure 81



CONVERGENT-BEAM ELECTRON DIFFRACTION "FINGERPRINTING" OF MAX PHASES AT BRAZED CERAMIC JOINTS

A. H. Cairns
Ceramic Science and Engineering Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA - 16802, U.S.A.

Scripta METALLURGICA et MATERIALIA
Vol. 25, pp. 51-54, 1991
Printed in the U.S.A.

Figure 82

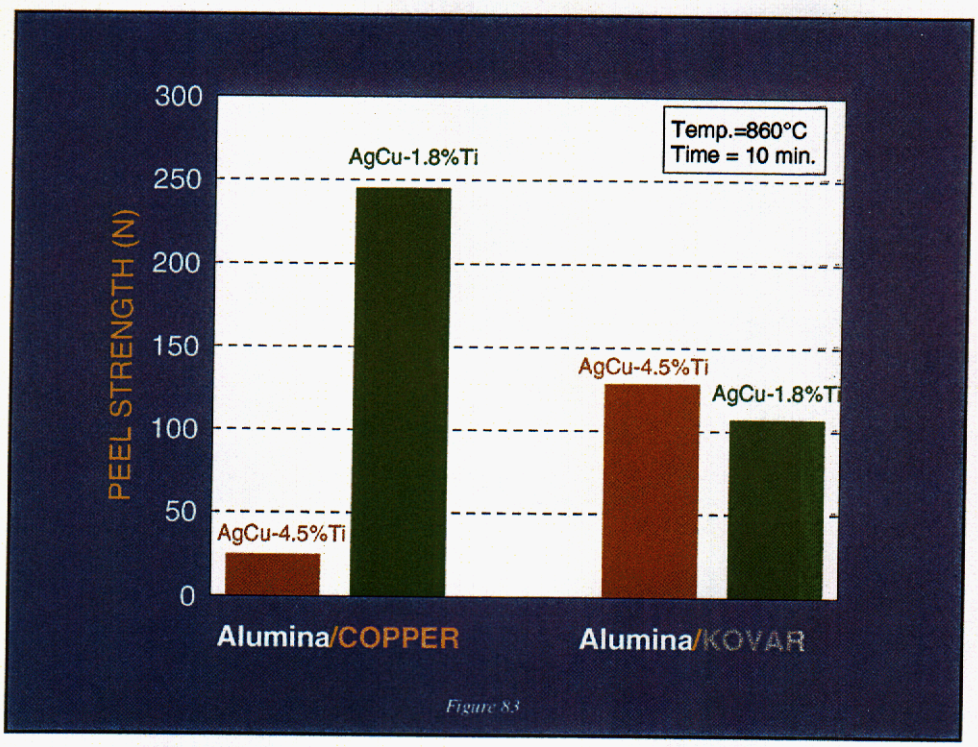


Figure 83

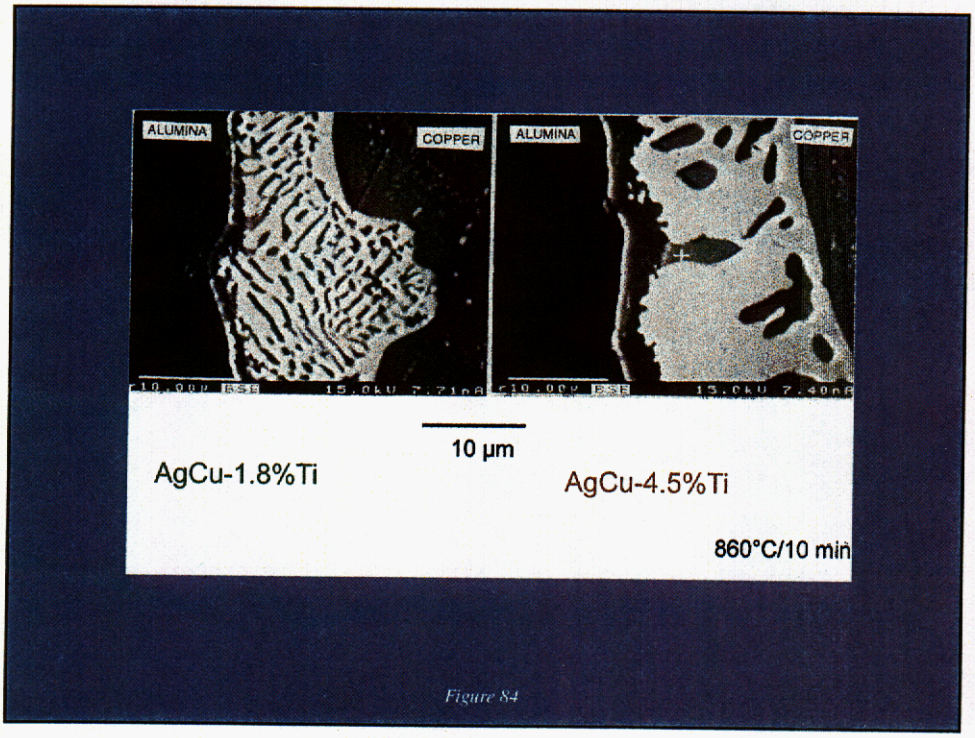


Figure 84

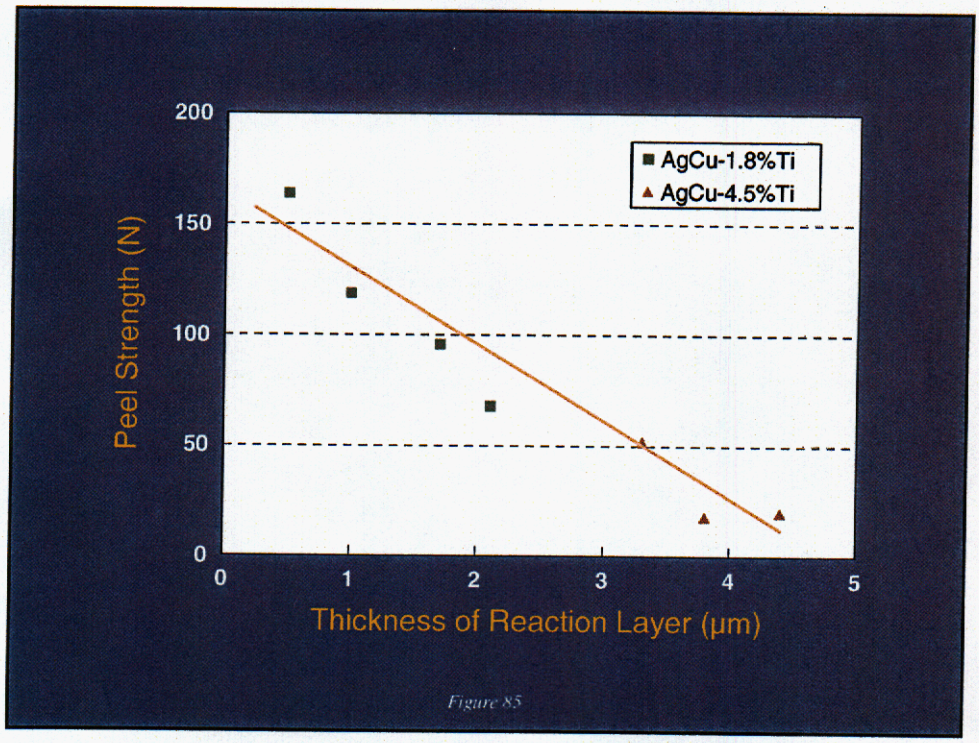
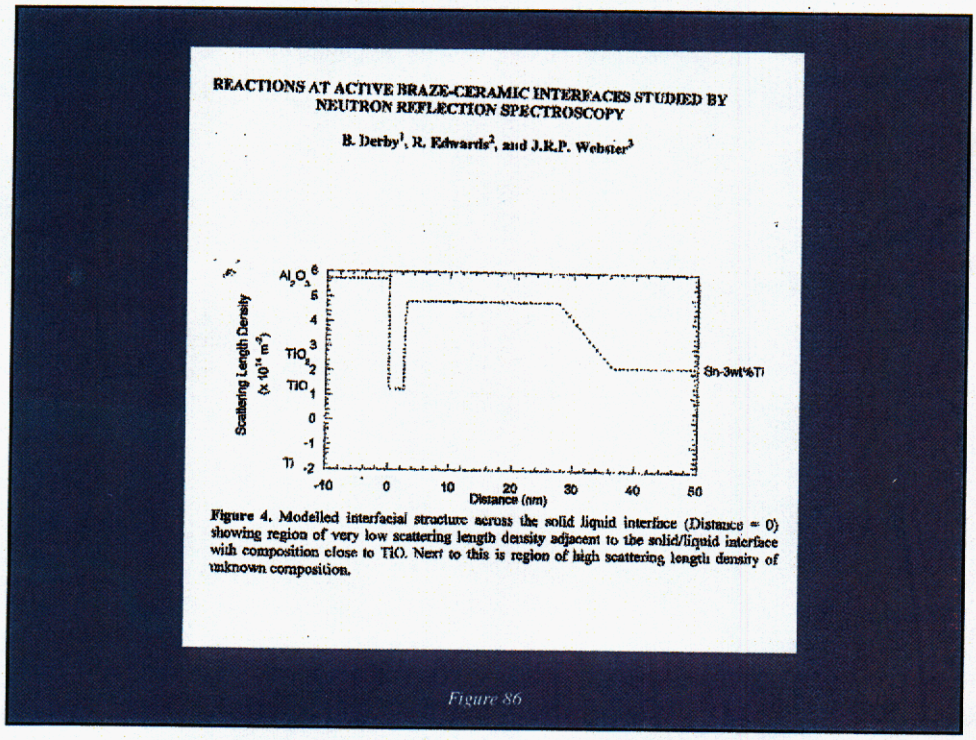


Figure 85



REACTIONS AT ACTIVE BRAZE-CERAMIC INTERFACES STUDIED BY NEUTRON REFLECTION SPECTROSCOPY

B. Derby[1], R. Edwards[2], and J.R.P. Webster[3]

Figure 4. Modelled interfacial structure across the solid liquid interface (Distance = 0) showing region of very low scattering length density adjacent to the solid/liquid interface with composition close to TiO. Next to this is region of high scattering length density of unknown composition.

Figure 86

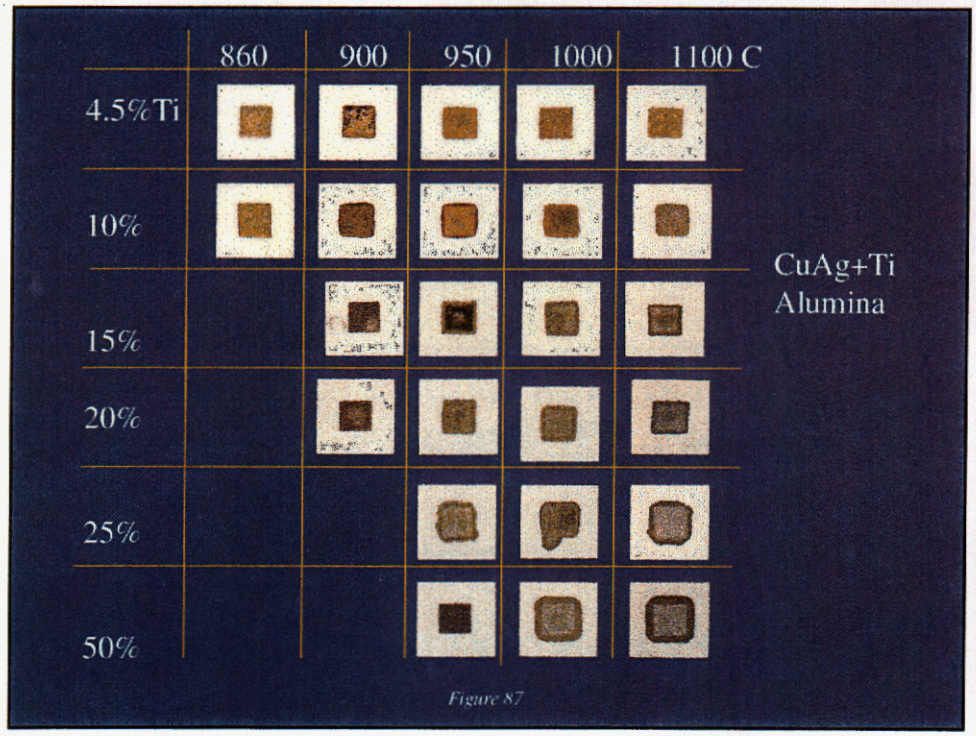


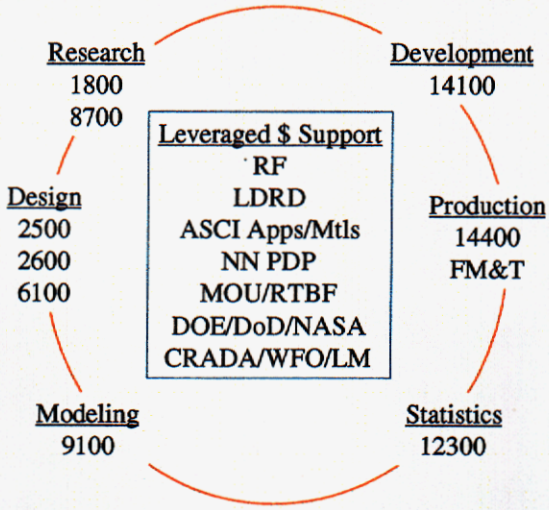
Figure 87

4.0 Sandia Ceramic-Metal Brazing Programs

F. M. Hosking summarized Sandia National Laboratories' ceramics brazing programs (Figs. 88-94). The links between research, design, and production activities were emphasized, including connections to outside organization. These links strengthen Sandia's position in the international brazing community. Figure 91 shows some of the brazing expertise that resides at Sandia.

Sandia's R&D initiatives include science-based modeling and materials and process characterization (Fig. 92). An important element of these activities is the ability to correlate the materials and processing conditions to joint properties and performance. Modeling is playing a larger role in this effort. A suite of simulation tools is being developed and validated to predict thermal, flow, geometric, and mechanical responses to the brazing environment (Fig. 93). Coupling the experimental and computational capabilities, more efficient process characterization is possible. This was demonstrated by the large tensile button study that was recently conducted for the MC4277 component (Fig. 94). The effect of key brazing variables (ceramic metallization thickness, braze volume, brazing time and temperature) on interfacial reactions, hermeticity, and joint strength were determined, which provided a realistic space solution to the brazing conditions.

Integrated Sandia Ceramic Brazing Programs



Brazing Science & Technology

Figure 88

External Sandia Ceramic/Metal Brazing Links

Other External Interactions

DOE Laboratories:
(LANL, LBL, LLL, ORNL)

Professional Societies:
(AWS, ACerS, ASM International TMS, MRS, ASME, ASTM, ...)

Universities:
(CSM, Illinois, MIT, RPI, UNM, Lehigh, UTEP, ...)

Industrial:
(AlliedSignal, Honeywell, Raytheon, Pratt & Whitney, McDermott Technologies, WESGO, Alberox, Ceradyne, ...)

Brazing Science & Technology

Figure 89

Research and Engineering Programs Are Leveraged to Support Ceramic / Metal Brazing

Fundamental Research:
- Wetting & Spreading Dynamics of Solder & Braze Alloys (LDRD)
- Atomistic Computations for Modeling Microstructural Evolution (LDRD)
- Fundamental Reaction Mechanisms for Ceramics/Metal Brazing (RF)

Design & Production:
- MC4300 Active Brazing Alloy Characterization (Cusil ABA, Nicoro + 2% Ti)
- MC4277 Joining Subteam (LTBS, BMCT, Two-Step Au-Cu Braze, Fixturing)
- W76-1/80-2,3 Stronglinks (Electrical Contact & LAC Headers)
- Ceramics Metallization & Failure Analysis
- µFiringSet (Thin Film Contact & Closure Joints)
- Special Nuclear Material (SNM) Storage Containers (Rebrazeable Joints)
- Industrial Interactions (ABA & High Temperature Ceramics Brazing)

Brazing Science & Technology *Figure 90*

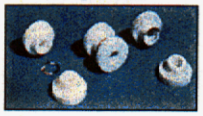
SNL Brazing Technology Expertise Resides in Various Line Organizations

Science & Technology Expertise	Staff Contacts	Org(s)
Materials & Process Science (Basic and Applied R&D)	Hosking, Stephens, Loehman, Glass, Monroe, Cadden, Walker	1833, 1843, 8724, 14171
Materials Characterization	Kotula, Michael, Hlava, Yang	1822, 8723
Design Engineer (Tubes, Stronglinks, FiringSets, SNM)	Brainard, Busick, Boettcher, Nicolaysen, Smith, Pierce	2564, 2612, 2613, 2616, 6141
Process/Production Engineer	Malizia, Meredith, Fitzgerald	14405, FM&T
FEA Stress Analysis	Burchett, Wellman	9132, 9123
FEA Thermal & Flow Modeling	Dempsey, Hogan, Givler	9117, 9114
Atomistic/Molecular Modeling	Webb, Hoyt	1834
Statistical Design & Analysis	Crowder	12323

Brazing Science & Technology *Figure 91*

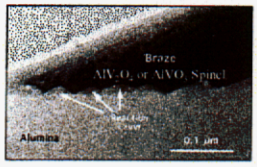
Ceramic / Metal Brazing R&D Initiatives

Properties

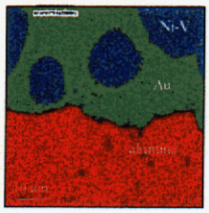


Processing

Interfacial Reactions



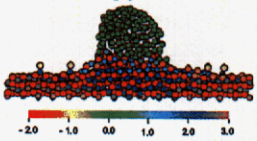
Characterization



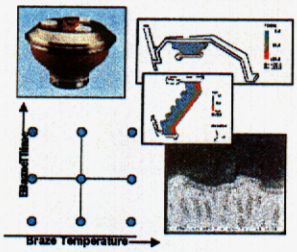
2500 Å Si on 99.8% alumina

Fundamental Modeling

Al on Al_2O_3 Simulation



Process Characterization



Brazing Science & Technology

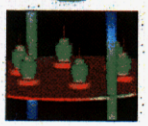
Figure 92

Sandia National Laboratories

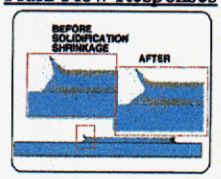
Ceramic / Metal Braze Modeling Initiatives

Thermal Responses

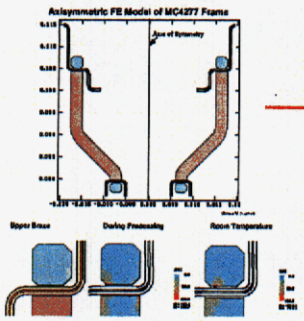
Fixtured Assembly



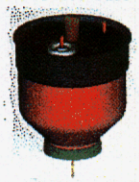
Fluid Flow Responses



Mechanical Responses



MC4277 Tube



Design & Production Principles

Brazing Science & Technology

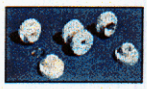
Figure 93

Sandia National Laboratories

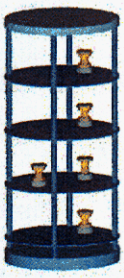
Braze Modeling Core Team (BMCT) Is Utilizing All Tools to Characterize Braze Process

MC4277 Large Tensile Button Study (LTBS):

- Time above liquidus temperature (970°C)
- Programmed peak brazing temperature
- Nickel plate thickness
- 50Au-50Cu braze washer thickness
- Metallize thickness
  - Ceramic type: 94% alumina
  - Kovar washer interlayer
  - Eleven furnace runs; five samples per test condition
  - Evaluate button alignment, hermeticity, tensile strength, Ni dissolution, joint structure/compositions, braze flow/geometry



Space vs. Point Solution



Frame Assembly Furnace Process Sensitivity Analysis:

Variables: heating & cooling ramp rates, temperature holds, hold times, peak temperature, number of work shelves and fixtured parts

Response: predict part & braze interface temperature profiles; couple results with braze flow and stress modeling activities

Brazing Science & Technology *Figure 94*

Sandia National Laboratories

5.0 Computational Design Tools and Application

The presentation by J. E. Johannes described the different modeling activities that are supporting brazing at Sandia (Figs. 95-114). The work is being led by Engineering Sciences Center 9100 and utilizes several ASCI code architecture tools to simulate the braze process (Fig. 97). Each step requires a detailed physics model that is rigorously validated. There are four key elements to the braze modeling effort: thermal, flow, stress, and failure analyses (Fig. 98).

Examples were given on how the models are being applied to support neutron tube design and production. The thermal model is predicting furnace responses that define the optimum process operating space, loading conditions, and heating profile (Figs. 99-100). The more difficult modeling problem is to simulate brazing kinetics and fillet geometry (Figs. 101-103). The existing codes also need to incorporate chemical reactions and compositional changes at the braze interface that affect wetting and flow conditions.

Stress modeling has been applied at Sandia to a variety of brazed assemblies over the course of many years. It is routinely used to predict conditions that cause or reduce high residual stresses and premature failures (Figs. 104-107). The technique is probably the most mature simulation tool available, although the most difficult to validate. Stress analyses are being coupled with newer failure models (Figs. 108-113) to predict ceramic failures and life. Failure probabilities are not exceptionally high, but the simulation tool does provide important insight into potential failure mechanisms for specific design and materials conditions.

As the fidelity and robustness of the four models are improved, individual thermal, fluid flow, stress, and failure responses will be computationally integrated to capture and simulate the life cycle of the braze joint. The goal is to fully simulate the braze process at different scale levels.

Computational Design Tools for Brazing

Ceramic / Metal Brazing Workshop

April 4, 2001

Justine Johannes
Multiphase Transport Department 9114

Contributors: Frank Dempsey, Roy Hogan, (Steve Gianoulakis) - Thermal
Rick Givler, Randy Schunk - Flow
Steve Burchett, Mike Neilson - Stress
Jerry Wellman - Failure

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.

Figure 95

Sandia National Laboratories

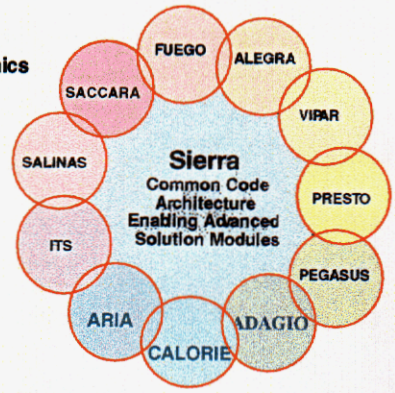
- Objective - Communicate 9100 status on simulating braze processes - capabilities and maturity of the models.
- Outline
  - SNL code development requirements & strategy (details of this were presented earlier).
  - Examples of work that has been done in past for braze modeling with 14000 and ASCI.
  - Future work

Figure 96

Sandia National Laboratories

SNL 9100 ASCI Code Architecture
Tools for Simulating the Braze Process

VIPAR	Parachute performance code, vortex method coupled with transient dynamics
PRONTO	Transient dynamics Lagrangian solid mechanics
JAS	Quasi-static solid mechanics
COYOTE	Thermal mechanics with chemistry
GOMA	Incompressible fluid mechanics with free surfaces
PEGASUS	Neutron Tube Physics
FUEGO	Fire simulation
SALINAS	Linear structural dynamics
SACCARA	Compressible fluid mechanics
ITS	Radiation transport



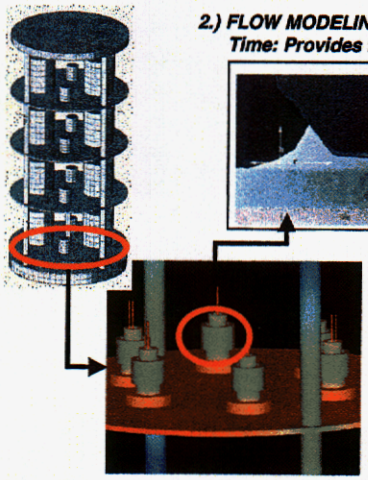
Characterizing production to product reliability requires coupled multiphysics simulations.

Figure 97

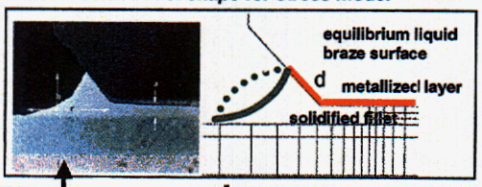
Sandia National Laboratories

Goal is to Model the Integrated Process
Linking Manufacturing Process to Reliability

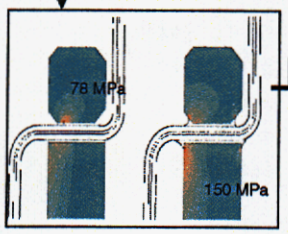
Each Step Requires Detailed Physics Model & Validation



2.) FLOW MODELING:Model Solidification Process with Temp vs. Time: Provides fillet shape for stress model



3.) Stresses computed based on temp. history and fillet shape



4.) Compute failure probability of joint

1.) Thermal Modeling of Braze Furnace Temp vs. time response

Figure 98

Sandia National Laboratories

Thermal Modeling

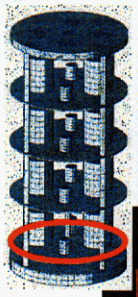
Point of Contacts Roy Hogan & Frank Dempsey

- Has been applied in past to address manufacturing issues
- ASCI currently funding more detailed meshing effort
- Testing new thermal code on furnace mesh

Figure 99

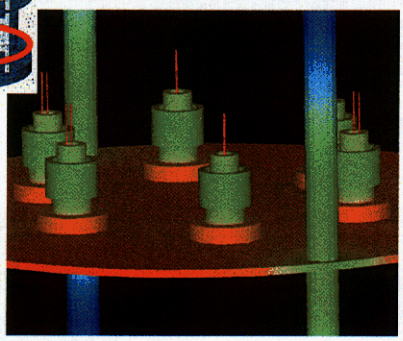
Sandia National Laboratories

Modeling manufacturing processes of brazes failing on bottom shelf of furnace



Preliminary simulations showed:

- on bottom shelf, $T_{joint} < T_{melt}$ (no braze)
- on upper shelves , $T_{joint} = T_{melt}$ (not robust)



- Conducted numerical "experiments" using new process parameters
- New process selected, implemented, and verified
- Results:
  - **30% increase in yield**
  - **more robust process**
  - **"right" the first time**

Figure 100

Sandia National Laboratories

Braze Flow Modeling

Point of Contact Rick Givler

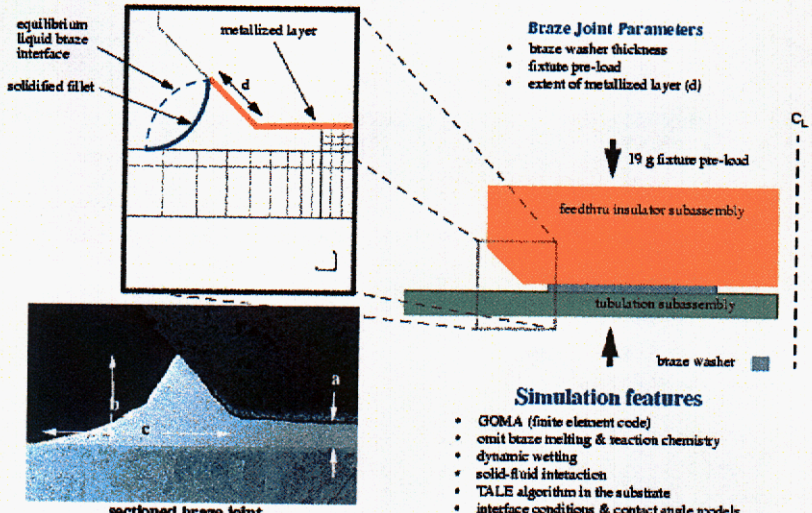
- Modeling of flow/wetting is less mature and not as well understood as the other aspects of braze modeling.
- 14000 and ASCI are currently funding work to advance braze flow modeling.

Figure 101

Sandia National Laboratories

BRAZE-FLOW MODELING

R. C. Givler & P. R. Schunk, 9111



Simulation features

- GOMA (finite element code)
- omit braze melting & reaction chemistry
- dynamic wetting
- solid-fluid interaction
- TALE algorithm in the substrate
- interface conditions & contact angle models
- volumetric shrinkage model for fillet shape

rcgivle/brazing/neutron_tube/braze_flow_modelling.fra

Figure 102

Sandia National Laboratories

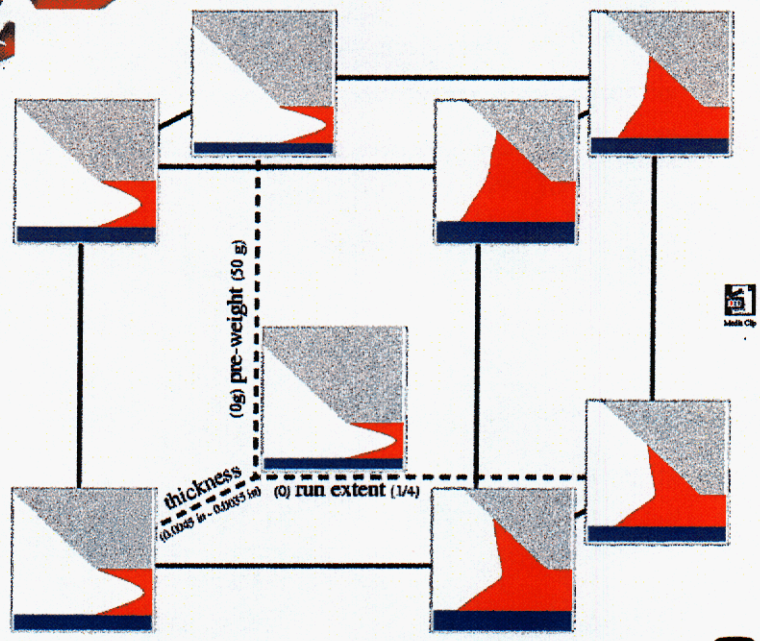


Figure 103

Sandia National Laboratories

Braze Stress Modeling

Point of Contact Steve Burchett

- **Modeling of stresses has been applied to brazing process to recommend improved process.**
- **Models mature and currently funded by 14000 MOU.**

Figure 104

Sandia National Laboratories

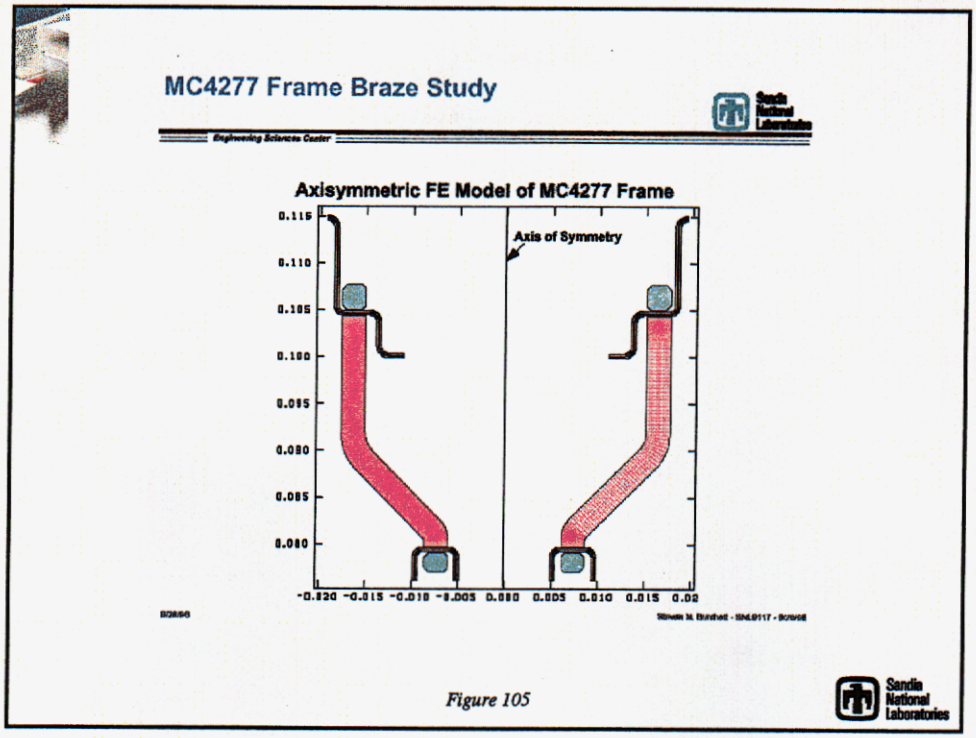


Figure 105

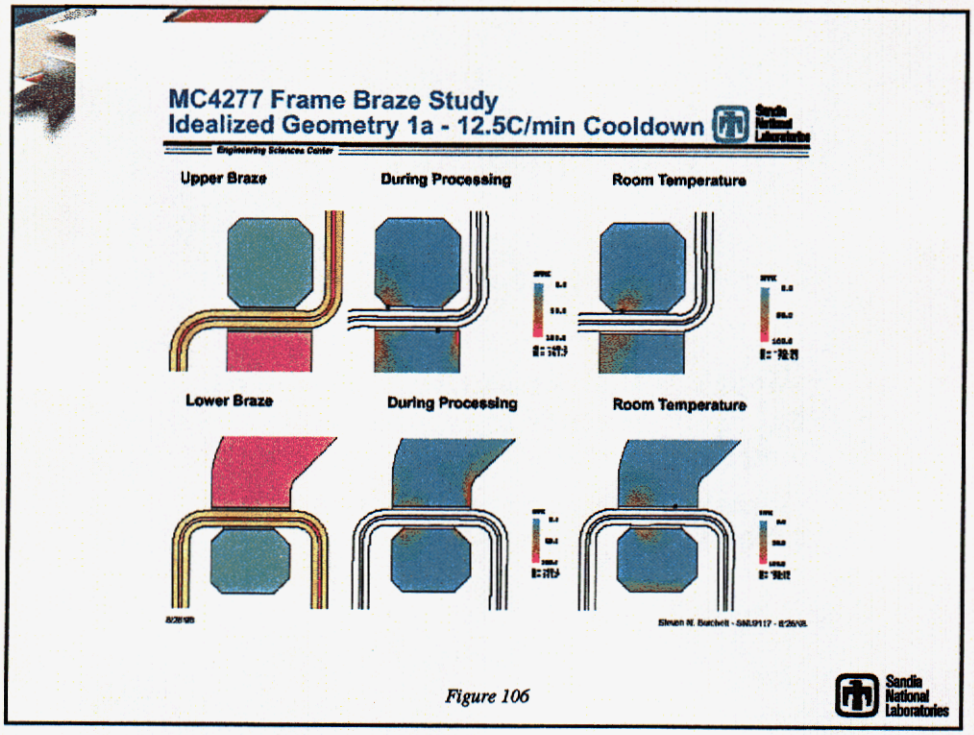


Figure 106

MC4277 Frame Braze Study
SUMMARY

Engineering Sciences Center

Table 1: Maximum Stresses - Constant Rate (12.5C/min) Cooldown

Geometry	Alumina During Processing	Alumina Room Temperature	Cermet During Processing	Cermet Room Temperature
1a	138.9	31.1	141.7	45.5
1b	119.1	42.1	120.8	91.7
1c	167.1	164.4	121.3	95.5
2	121.6	137.2	119.3	91.4
3	118.0	120.9	118.1	89.2
4	109.6	109.7	109.2	73.0
5	88.9	73.8	96.3	34.5
5a	75.0	40.6	89.8	25.8

8/28/98

Steven N. Burchett - SNL911V - 8/28/98

Figure 107

Sandia National Laboratories

Failure Modeling

Jerry Wellman

Figure 108

Sandia National Laboratories

Failure Modeling

Point of Contact Jerry Wellman

- **Failure model at SNL is fairly recent.**
- **Model is just starting to be applied to manufacturing processes.**
- **Funded by 14000, and ASCI**

Figure 109

Sandia National Laboratories

Ceramic Failure Predictions

Motivation: Improve traditional process of "rule-of-thumb" for acceptable stresses.

- **Post-processing model uses EXODUSII FE data base (data base used for Engineering Sciences codes) to predict failure probability.**
- **Uses NASA/CARES software basis (Weibull Statistics)**
  - ✓**Valid for brittle materials (ceramics, glasses, etc.) where failure is weakest link control**
  - ✓**Requires Weibull shape parameter (characteristic strength) and Weibull modulus (scatter) for analysis.**
  - ✓**Uses ASTM standard testing (4-pt bend bar) to gather Weibull parameters.**
  - ✓**Multiaxile stress state treatment (PIA and Weibull statistics)**
  - ✓**Integrates stress over a volume**
  - ✓**Minimizes mesh sensitivity**

Figure 110

Sandia National Laboratories

Does it Work?

- **Tension Test**
  - Uniform, uniaxial stress field
  - At applied stress equal to characteristic strength, failure probability equal 63.2% (exact from weibull statistics)
- **4-pt Bend Bar**
  - ASTM Standard - Dimensions identical to test specimens
  - Mesh sensitivity - Converges to "right" answer
  - Accuracy - At applied load corresponding to average strength, probability of failure converges to ~50%
- **Braze Button (CUSIL on Alumina)**
  - Failure probability = 0. (Need to adjust material properties to achieve non-trivial result)
  - Singular stress field - no convergence with mesh refinement (Mesh independence will require introduction of length scale)
  - Mesh sensitivityis mild enough that results are still useful
- **Applications**

Sandia National Laboratories

Figure 111

Sandia National Laboratories

4-Pt Bend Specimen

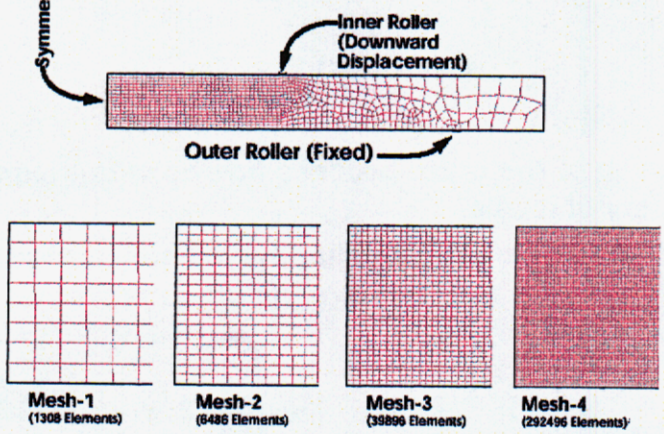


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Figure 112

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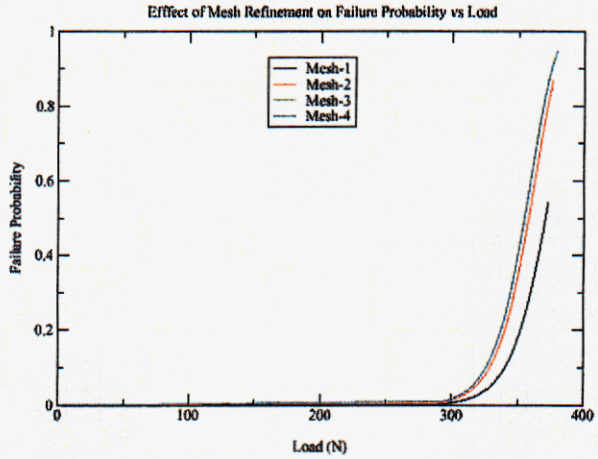
4-Pt Bend Results



Sandia National Laboratories

Figure 113

Sandia National Laboratories

Conclusions

- Modeling of the braze process has been done on a variety of levels.
- Thermal and Stress modeling have been applied to characterize and improve the braze process.

Figure 114

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6.0 Defense Programs (DP) Production Perspective

N. A. Lapetina provided a production perspective on ceramic-metal brazing. One of the principal benefactors of Sandia's brazing research is neutron generator production. This Defense Programs enterprise has invested heavily in advancing brazing technology. Neutron tube components are being fabricated with both conventional and active metal brazing processes (Figs. 115-124). Critical attributes include braze flow, hermeticity, joint strength, and dimensional integrity. Braze processing technologies affect four important component phases: conceptual design, development engineering, production, and service (Figs. 119-122). Each phase has different issues to address, but similar requirements that demand a high level of confidence and reliability in the brazing materials and process used.

Fiscal Year 2001 (FY01) production investments in brazing are summarized in Fig. 123. They emphasize process characterization through statistically-designed experiments and modeling. Most of these efforts are highlighted throughout this document. As part of the process, the Manufacturing Systems Science & Technology Program Office has developed a Technology Roadmap that lists prioritized brazing-related needs through FY05 (Fig. 124). The roadmap captures key technology requirements, such as active metal brazing, integrated modeling (thermal, flow, tolerance, stress, and failure analyses), process characterization (space versus point analysis), lower melting braze processes, other heating methods (RF/induction), process-based quality (reduce or eliminate inspection), and a braze design advisor. Sandia design and production organizations are committed to improving the fundamental understanding of their brazing processes.

DP Production Perspective

Neil Lapetina
Neutron Generator Production

4 April 2001

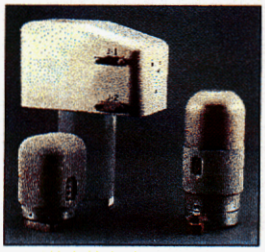
Figure 115

Sandia National Laboratories

Sandia's Neutron Generator Production Mission Assignment

Requirements

- Compact
- Long Life
- Reliable
- High Voltage
- Severe Environments



Processes

- Cleaning
- Thin-Film Deposition
- Metallizing & Plating
- Brazing & Welding
- Encapsulation
- Coating
- Product Testing
- etc

Realities

- Complex Materials
- High-Vacuum Technology
- Dimensional Precision
- Low-Volume Production

Figure 116

Sandia National Laboratories

Production Schedule

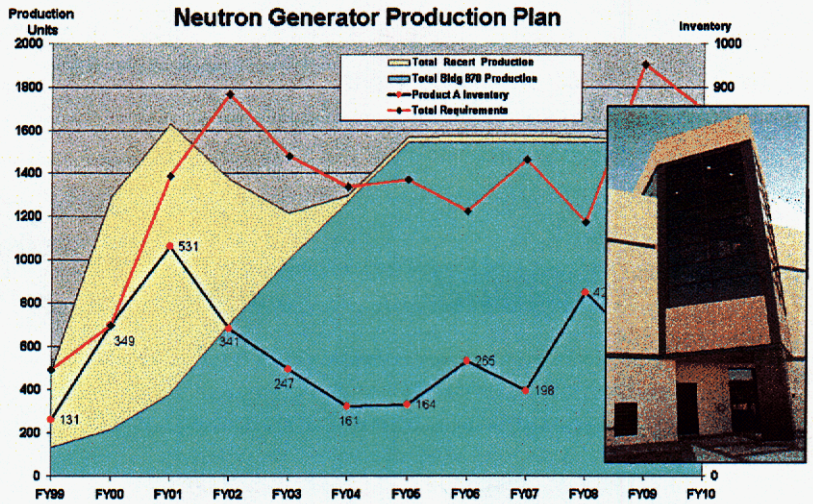


Figure 117

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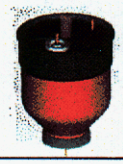
Brazing Required to Support NG Production

MC4277 Neutron Tube



- *In Production*
- *Conventional H_2 Brazing*
  - *Cu,Cu-Au*
- *Backup Rings*

Controlatrons

- *In Production & Development*
- *Conventional H_2 Brazing*
  - *Cu,Cu-Au*

MC4300 Neutron Tube

- *In Development*
- *Conventional H_2 Brazing*
  - *Cusil*
- *No Backup Rings*
- *Considering Active Brazing*
  - *Cusil ABA, Nicoro+2%Ti (Vacuum)*

Critical Attributes:

- Strength (Coupon)
- Residual Stresses
- Hermeticity
- Dimensional Integrity
- Braze Flow
- Rad Hardness
- etc

Figure 118

Sandia National Laboratories

Critical Braze Issues: Conceptual Design Phase

- In the absence of braze design advisors, must rely extensively on experienced engineers and past design successes
- Still striving to get the right information to the right person at the right time (i.e., concurrent engineering)
- If active brazing proved easy to implement, we'd baseline it!

Figure 119

Braze Issues: Development Engineering Phase

- Still doing the old cut-n-try approach...predictive capability still limited
  - Research community not interested in this approach
  - Design/Production communities frustrated with the interruptions this approach at times causes
- Tend to quickly converge on point designs as opposed to characterizing process space
  - That is, until recently...
- Existing modeling & simulation good for relative comparisons and not for failure predictions
  - Exception: residual stress modeling & failure prediction

Figure 120

Critical Braze Issues: Production Phase

- Yields (or lack of)...big cost factor
  - Scraps used to represent ~25% of total product costs
  - Primary defects: dimensional integrity, lack of fill, leaks
- Cycle times
  - Brazing (primarily the preparatory steps) represent ~20% of total cycle times
  - Driven by number of braze-related processing steps
  - Not driven by braze run times
- Still rely on inspection

Figure 121

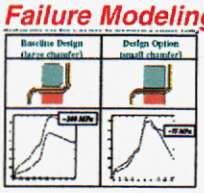
Critical Braze Issues: Service Phase

- Effects of Post-Processing Steps & Field (STS) Environments on Braze Joints
- Aging

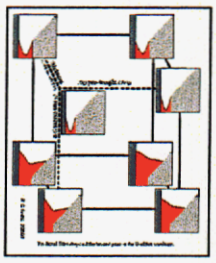
Figure 122

FY01 Investments to Improve Fundamental Understanding of Braze Processes

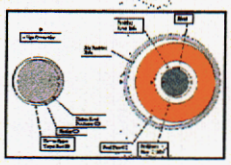
Residual Stress & Failure Modeling



Braze Flow Modeling



Tolerance Analysis



Furnace Modeling

Tensile Button Testing

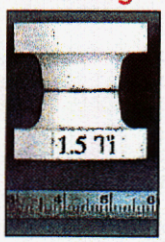


Figure 123

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4 Apr 01 Ceramic/Metal Brazing Workshop

MSST Technology Roadmap: Brazing-Related Needs

TR ID	Technology Need	Priority	1998	1999	2000	2001	2002	2003	2004	2005
25	Integrate braze flow, furnace and braze failure models to establish comprehensive NG braze stress modeling capability. Validate this integrated model and conduct parametric sensitivity analyses to define "operational boxes" of brazing processes.	B	1998	--	--	--	2002			
33	Implement braze video viewing capability on production floor	B	1998	--	--	--	--	--	--	2005
18	Conduct tolerance analysis for NT braze joints and fixtures; apply to braze joint designs to simplify braze joints/fixtures and improve quality.	B		1999	--	--	2002			
20	Establish/utilize capability to predict and optimize thermal profiles for all NT braze assemblies and apply to model-based process characterization. Integrate analysis with braze flow and stress analyses.	B		1999	--	--	2002			
21	Apply 2D/3D flow of molten braze material model to MC4277 flange, frame & header brazes; conduct sensitivity analysis.	B		1999	--	--	2002			
28	Develop active braze process for MC4300 to reduce cycle time and labor hours by 20%.	B		1999	--	--	2002			
82	Develop processes that are unique to the universal MC4300 NT	A		1999	--	--	--	2003		
24	Model stresses in MC4300 flange, header & lead attachment braze joints; make recommendations to reduce stresses and improve robustness.	B			2000	--	2002			
27	Analyze ROI for outsourcing metallizing and Ni plating to reduce production costs; implement if warranted.	B			2000	--	2002			
34	Apply braze process characterization work to improve braze operations beginning with MC4277 Header Arm (FY00-01) and MC4277 Frame Arm (FY02-03)	B			2000	--	--	2003		
35	Develop Braze Design Advisor	C			2000	--	--	2003		
68	Develop revolutionary joining/fabrication techniques for NG/NT applications	C			2000	--	--	--	--	2005
26	Establish ability to 10x or Xray inspect partially blind braze region in MC4300 Header Assembly, establish PBO and/or eliminate the 10x braze inspection requirement	B				2001	--	--	2004	
29	Establish capability to predict brazing chemical reactions and their effects on wetting, braze flow and mechanical properties; enhance validity of braze flow model to a broader spectrum of brazing designs/processes.	B				2001	--	--	--	2005
203	Develop & qualify capability to deposit Moly thin-films on Kovar to support active braze concept.	B				2001	2002			
30	Automate pre-braze assemblies to minimize risk of assembly related defects	C						2003	--	2005
31	Evaluate brazing techniques with lower processing temperatures (500-750C) and/or residual stresses; e.g., transient liquid phase brazing, solid state joining (i.e., diffusion bonding).	C						2003	--	2005
37	Metal-to-metal brazing that requires only localized heating, eg. RF	C						2003	--	2005

Some funding applied

Unfunded

Figure 124

Sandia National Laboratories

7.0 Fundamental Wetting and Interfacial Reactions

An important element of Sandia's brazing research initiative is the work being done to characterize the fundamental wetting and interfacial reactions that occur between different active metal brazing alloys and alumina ceramics. R. E. Loehman summarized recent research from Sandia's Research Foundations program (Figs. 125-147). The objective of this work is to understand how active elements promote ceramic bonding and also provide insight into general reaction mechanisms.

Filler metals containing titanium are the most common type of active brazing alloy. For example, a very well defined reaction layer is developed between alumina and the Ag-Cu-Ti ternary system (Fig 128). Other transition elements should also be as effective. The Gibbs free energies of formation for the titanium, zirconium, vanadium, and hafnium transition metal oxides imply relative oxide stability (Fig. 130).

High temperature experiments in a controlled-atmosphere furnace are being conducted to characterize the active metal wetting behavior on a range of alumina materials (Figs. 131-135). The vanadium containing alloys do not wet alumina as well as those containing titanium or zirconium. The vanadium reaction product is generally more difficult to resolve and appears to be thin and intermittent. Additional work has shown that alumina specimens brazed with this alloy have lower tensile strengths and fail along the ceramic interface. Adhesion does improve with increasing glassy phase in the ceramic. Research suggests that silica in this phase is the primary constituent that promotes a vanadium reaction. Wetting samples show that vanadium forms a more complex reaction product with silica than other active elements such as titanium (Fig. 140). As the concentration of silica in alumina is increased, the presence of silica on the ceramic surface also increases and improves the reaction activity with vanadium (Fig. 141). Thermodynamic calculations appear to agree with these observations (Fig. 144-145). Experiments on sapphire and high purity alumina also suggest that a discrete spinel reaction can occur between the vanadium and alumina, which further complicates the underlying reaction mechanism for vanadium. Simple reduction-oxidation reactions do not explain the observed results. Further research is required and ongoing to better understand these phenomena.

Sandia National Laboratories

Workshop on Ceramic / Metal Brazing:
From Fundamentals to Applications

WETTING AND REACTION MECHANISMS IN ACTIVE METAL BRAZE ALLOYS

R.E. Loehman, S.J. Glass, and F.M. Hosking,

Sandia National Laboratories
Albuquerque, NM

C.H. Cadden

Sandia National Laboratories
Livermore, CA.

Supported by DOE Contract DE-AC04-94AL85000 at Sandia National Laboratories

Figure 125

Outline

- Background on active metal reactions and bonding
- Reaction experiments on a matrix of compositions

  V and Ti as active elements in Au-Ni alloy

  substrates with varying ratios of Al_2O_3 and SiO_2
- Microstructural and compositional analyses of interfaces to infer reaction mechanisms
- Summary and Conclusions

Figure 126

The Need for Improved Joining Techniques Motivates Study of Active Metal Reaction Mechanisms

- Central question is how do active elements promote ceramic bonding
- Ti-Ag-Cu alloys are standard but are limited to 400°C
- In most cases Ti segregates to ceramic interface and reacts
- Is this the mechanism for other active elements, such as Zr and V?
- Study of other systems may give us insight into general mechanisms

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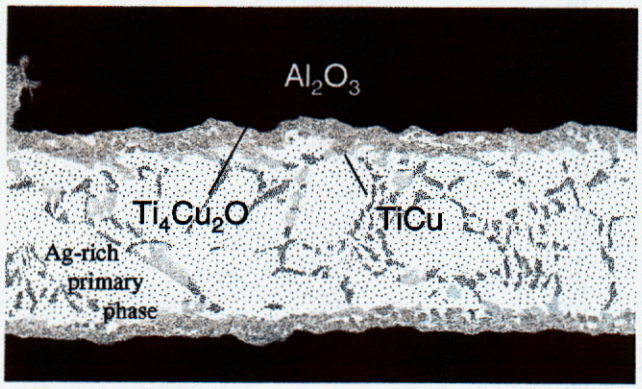
Figure 127

When Ag-Cu-Ti is Heated on Alumina the Ti Segregates to the Interface and Reacts With It



B.N. Turman, et al., SAND97-2785, NTIS, Nov., 1997

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Figure 128

Ti is a Well-Known Promoter of Interfacial Reactions in Active Metal Braze Alloys

- used as small additions (1-4 wt%) to non-wetting alloys or coated directly to ceramic
- Ti promotes wetting of ceramic and then typically reacts by a redox mechanism
- reaction zones are usually thin and refractory

V appears to behave similarly as an active alloying addition

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Figure 129

Gibbs Energies of Formation Show Relative Stabilities of Transition Metal Oxides

ΔG^0_f at 1300K for $M + O_2 = MO_2$

Oxide	ΔG^0_f, kJ/mol O_2
VO_2	- 483.5
TiO_2	- 707.7
ZrO_2	- 854.5
HfO_2	- 909.1

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Figure 130

We Compared Reactions of V and Ti-Containing Alloys on Four Ceramics with Differing Al_2O_3/SiO_2 Ratios

- Ceramics
  - Sapphire
  - Coors 96% alumina (balance Ca, Mg silicate glass)
  - Mullite ($Al_6Si_2O_{13}$, sintered, high purity) 40 mol% SiO_2
  - Fused Silica
- Alloys
  - Nioro-V (82.0w% Au, 15.5% Ni, 0.75% Mo, 1.75% V) 4.1at%V
  - Nioro-Ti (81.3w% Au, 18.0% Ni, 0.75% Ti) 2.7at%

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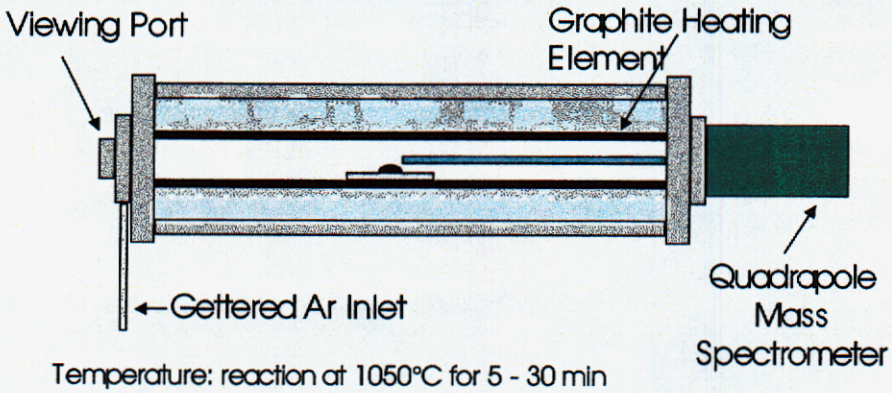
Figure 131

High Temperature Reactions Were Studied in a Controlled-Atmosphere Furnace



Temperature: reaction at 1050°C for 5 - 30 min

Atmosphere: gettered Ar

Controls: W/Re thermocouples

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Figure 132

NioroABA Wets Sapphire When Heated at 1000°C in UHP Argon

82w%Au-16Ni-0.7Mo-1.75V on sapphire

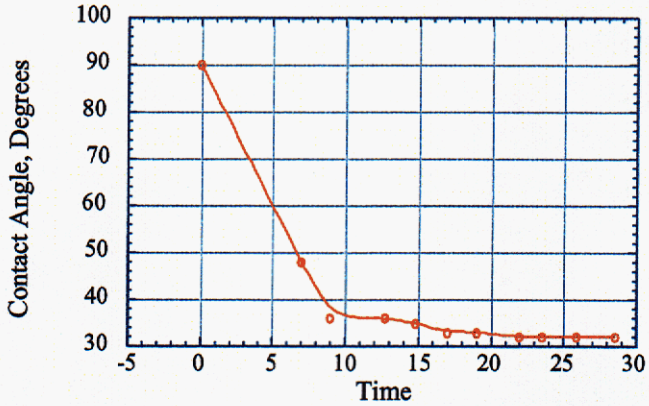

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Figure 133

Compositional Maps Show Segregation in the Alloy

No Evidence of V-Containing Reaction Layer

NioroABA (1.75w% V) on sapphire for 5 min at 1000°C

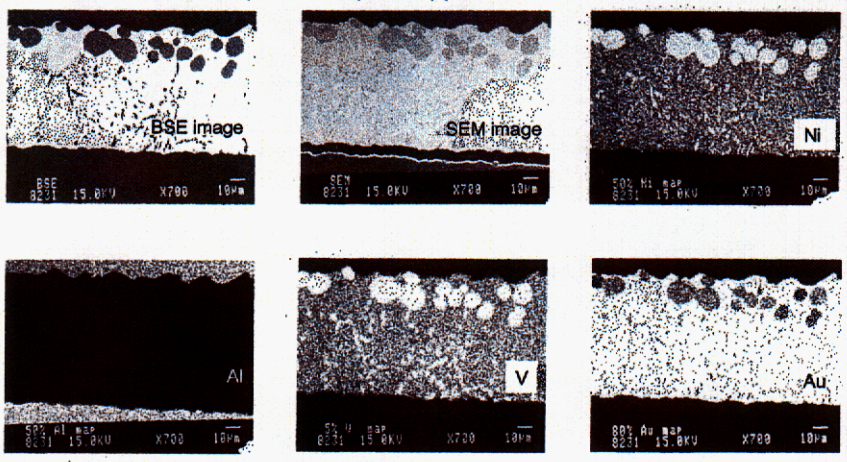

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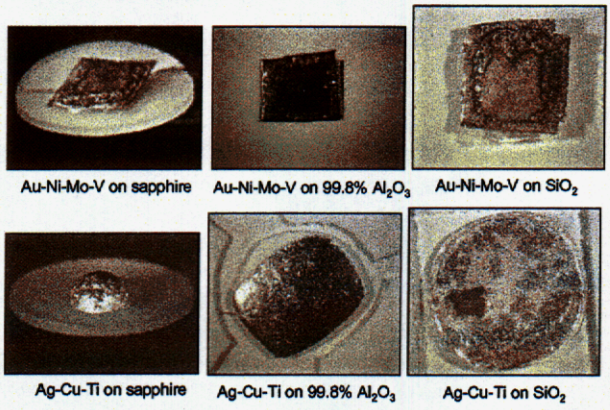
Figure 134

V-Containing Braze Alloys Do Not Wet Alumina Ceramics as Well as Those That Contain Ti

- Au-Ni-Mo-V melts & bonds to the ceramic, but does not change its original footprint
- Ag-Cu-Ti melts, retracts to form a bead and then spreads to its equilibrium contact angle



Alloy foil heated on sapphire, 99.8% Al_2O_3, and SiO_2 for 30 minutes at 1000°C in a gettered vacuum atmosphere

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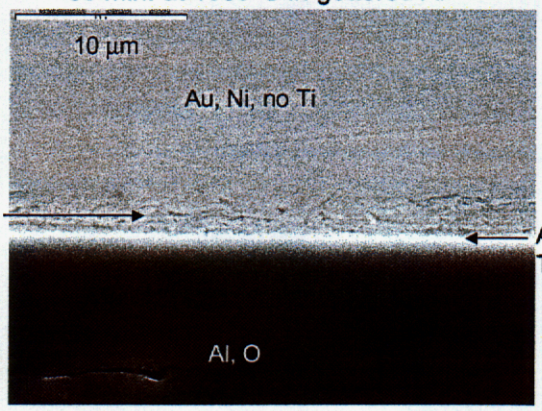
Figure 135

Nioro- 0.75%Ti Wets Sapphire at 1050°C and Bonds to it After Cooling

30 min. at 1050°C in gettered Ar



Ti segregates to the interface, which is rough, but no evidence of new phases

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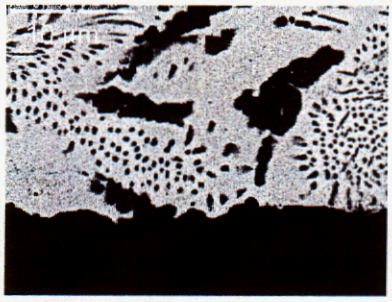
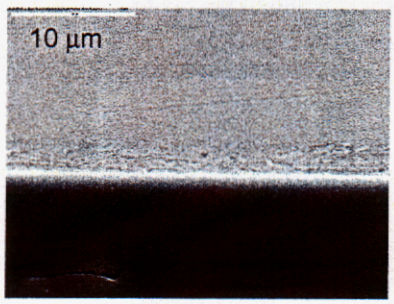
Figure 136

Rough Interface Shows More Interaction Between Sapphire and the Nioro-V Alloy Than With the Nioro-Ti

Nioro-1.75%V on sapphire



Nioro-0.75%Ti on sapphire



Reacted for 30 min at 1050°C

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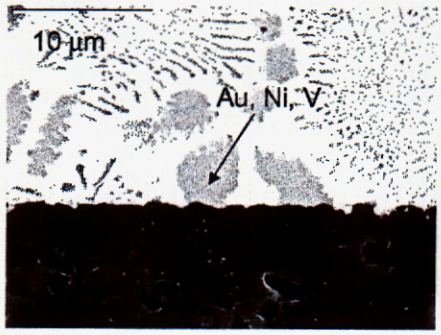
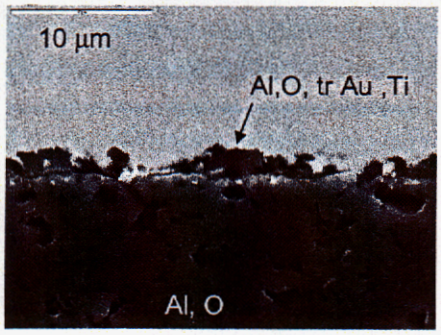
Figure 137

Both V and Ti-Containing Alloys Wet 96% Alumina and Bond to It

Nioro- 1.75%V



Nioro- 0.75%Ti



Alloys heated on Coors 96% alumina for 30 min at 1050°C in gettered Ar

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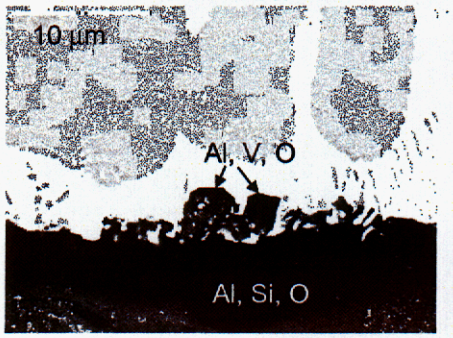
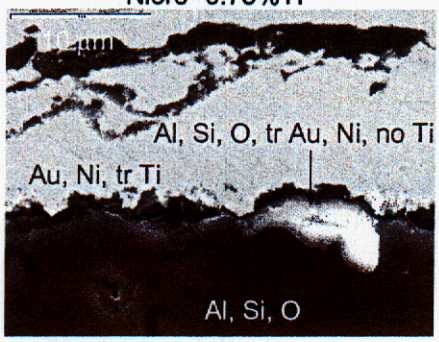
Figure 138

Both Alloys Show Evidence of Reaction With Mullite

Nioro- 1.75%V



Nioro- 0.75%TI



Alloys heated on sintered, 98% dense mullite for 30 min at 1050°C in gettered Ar

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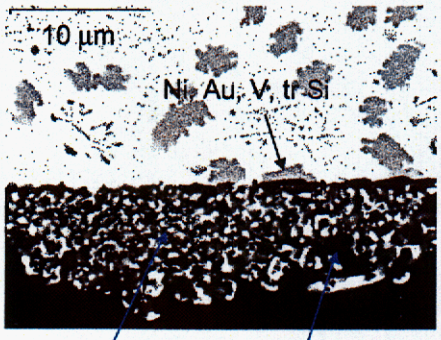
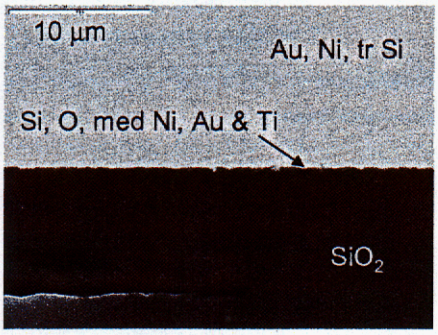
Figure 139

Nioro- V Shows a More Complex Reaction Zone at the Fused Silica Surface Than Does Nioro- Ti

Nioro- 1.75%V



Nioro- 0.75%Ti



Dark phase: st V & Si, Au, Ni, O

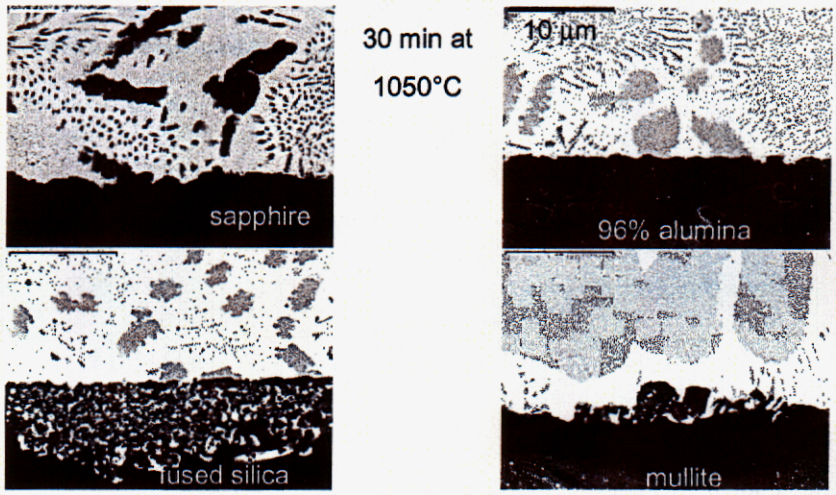
Bright phase: Au, tr Ni, V, Si

Both were reacted for 30 min at 1050°C in gettered Ar

Sandia National Labs - Advanced Materials Laboratory

Figure 140

Nioro- 1.75%V Reacts more Extensively, the Higher the SiO_2 Concentration in the Ceramic



Sandia National Labs - Advanced Materials Laboratory

Figure 141

EDS Analysis Shows Compositional Segregation at Ceramic Interface

Nioro-V heated on sapphire for 5 min at 1000°C

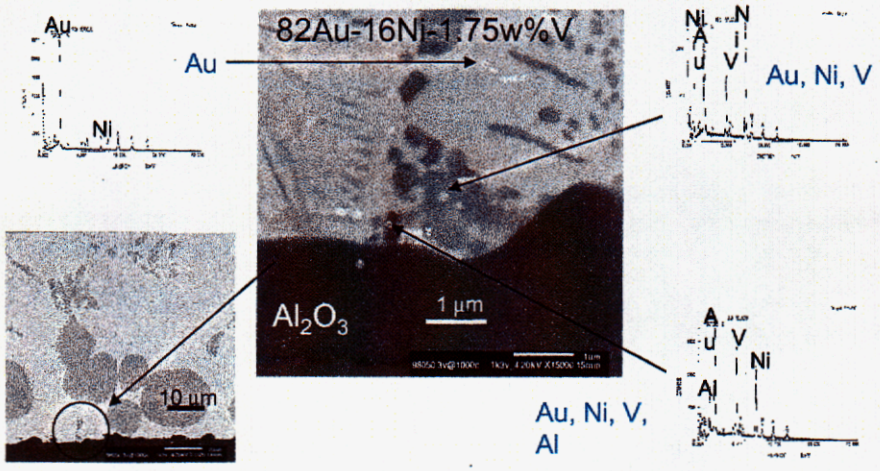


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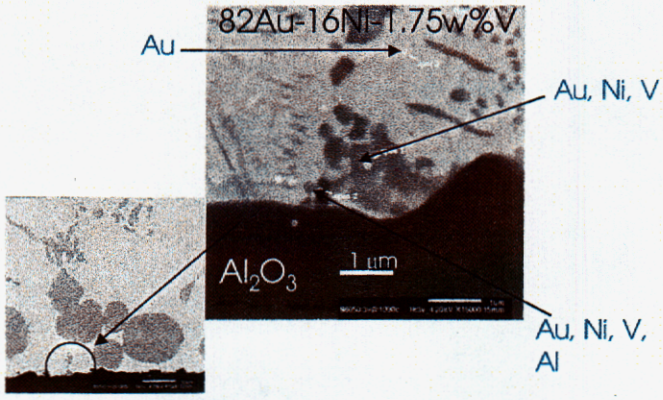
Figure 142

EDS Analysis Suggests Possibility of Reaction Between V in the Nioro Braze Alloy and Sapphire



V (Nioro) + Al_2O_3 (sapphire) = VO_x + Al (alloy), 5 min at 1000°C

Sandia National Labs - Advanced Materials Laboratory *Figure 143*

Simple Redox Reaction Between V and Al_2O_3 Does Not Provide Sufficient Thermodynamic Driving Force

$$3V + Al_2O_3 \rightarrow 3VO + 2Al$$

$$\Delta G^\circ_f(1300K) = +302.0 \text{ KJ}$$

Might obtain further driving force from reaction of Al (AlV_2O_4?) or from its solution in the alloy

Sandia National Labs - Advanced Materials Laboratory *Figure 144*

Simple Thermodynamic Calculations Show Reaction of V is More Favorable With SiO_2 Than With Al_2O_3

$$3V + Al_2O_3 \rightarrow 3VO + 2Al$$

$$\Delta G^\circ_f(1300K) = +302.0 \text{ KJ}$$

$$2V + SiO_2 \rightarrow 2VO + Si$$

$$\Delta G^\circ_f(1300K) = +36.3 \text{ KJ}$$

However, additional reaction still must be invoked to give a negative Gibbs energy

Sandia National Labs - Advanced Materials Laboratory *Figure 145*

Summary and Conclusions

- Both Au-Ni-V and Au-Ni-Ti alloys wet the ceramics at 1050°C and bond to them
- The Au-Ni-V alloy reacts more extensively with all the substrates than the Au-Ni-Ti alloy
- Some evidence that both V and Ti segregate to the interface
- Reaction of the Au-Ni-V alloy increases with increasing SiO_2 content in the ceramic
- Some of these differences may be due to the higher active element concentration in the Au-Ni-V alloy (4.1at%V vs. 2.7%Ti)

Sandia National Labs - Advanced Materials Laboratory *Figure 146*

Summary and Conclusions (Continued)

- Simple redox reactions do not provide sufficient driving force for the observed reactions
- Further analysis should focus on complex reaction products or metal solution in the alloy
- One practical result is demonstrating that bonding of Nioro-V depends on silicate grain boundary phase in the 94% alumina

Sandia National Labs - Advanced Materials Laboratory

Figure 147

8.0 Atomistic and Molecular Braze Interface Modeling

Another fundamental element of Sandia's brazing research initiative is to develop and validate atomistic and molecular-scale models that can predict metal-ceramic interfacial reactions and structure (Figs. 148-161). E. B. Webb and T. P. Swiler discussed the motivations for this effort. Product miniaturization and the need for more accurate aging and reliability models are prime justifications.

Atomistic modeling will provide finer detail at the braze interface, including dynamic and structural conditions. Modeling accuracy requires interatomic potentials, which are not always readily available. Metal systems are usually simpler to study, since most potentials are either known or can be calculated. Molecular Dynamics (MD) simulations of reactive wetting and spreading for silver and copper are in good agreement with the Ag-Cu binary phase diagram (Figs. 152-153). Similar analyses are being conducted to determine interfacial structures and reaction dynamics for the Ag-Cu system (Fig. 154).

Wetting and spreading simulations for ceramic-metal systems are more difficult to do, since metallic, ionic, and sub-oxide range potentials must be obtained to successfully compute the interfacial reactions. Reduction/oxidation are inherent at most of these interfaces.

Electrostatic Plus (ES^+) potentials for aluminum and alumina are being used to demonstrate the atomistic modeling technique (Figs. 155-159). As the complexity of the reaction products increase, computations become more difficult, time consuming, and computational expensive.

A list of atomistic modeling needs and opportunities was presented (Figs. 160-161). Computational and experimental collaborations and potentials code development will be necessary to understand and describe the interfacial behavior of active brazing elements on ceramic surfaces. Once these are accomplished, specific characteristics, such as reaction thickness and composition, residual stress distribution, atmosphere effects, grain boundary and surface feature reactions, and constitutive relationships, can be captured in the simulations.

Atomistic Braze Interface Modeling

Edmund B. Webb III (Org. 1834)
Thomas P. Swiler (Org. 15312)

LDRD – Wetting and Spreading Dynamics of Solder and Braze Alloys

ASCI – Fundamental Mechanisms for Ceramic-Metal Brazing Rxns.

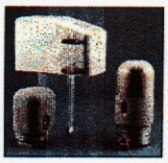
(G. Kellogg, M. Hosking, G. Grest, R. Hwang, D. Jennison, P. Kotula, R. Loehman, R. Plass, N. Shinn, M. Smith, J. Stephens, F. Yost)

Figure 148

Sandia National Laboratories

Motivation – Why Atoms?

- the cost of atomistic detail are size/time constraints
- Miniaturization
  > traditional joining knowledge challenged by the new driving forces at high surface to volume ratios



- Need more accurate aging/reliability models for complex systems
  > impetus for evolution is great in join regions
  > increased atomistic understanding will produce better constitutive relationships

Figure 149

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Atomistic Modeling Provides Great Detail

- Molecular dynamics (MD) … trajectory of every atom; Monte Carlo … equilibrium properties

→ *interfacial structure (composition, coordination)*

→ *dynamics (diffusion coefficients, spreading rates)*

→ *residual stress distributions*

→ *T/atmosphere dependence*

→ *precise control over surface structure (grain boundaries)*

Figure 150

Sandia National Laboratories

Classical Modeling Requires Accurate Interatomic Potentials

- *ab initio* methods are highly accurate but most subject to size/time constraints

- microstructure and continuum models lack detail to refine constitutive relations

- classical atomistic modeling fills the size/time gap

→ *Accurate mapping to materials systems*

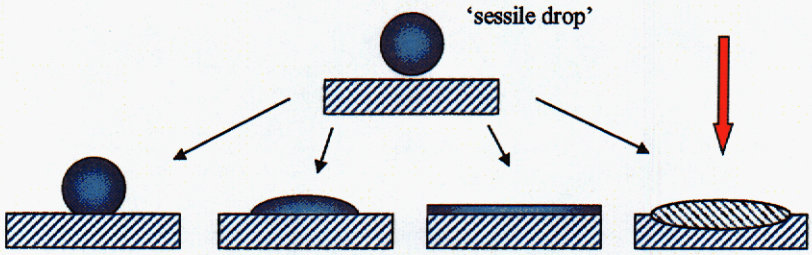
Metals … many-body potentials
Oxides … long-range charge interactions, covalent effects
Reactions … alloying, oxidation/reduction

Figure 151

Sandia National Laboratories

MD Simulations of Reactive Wetting and Spreading

- Fundamental to joining process



- Metal systems (embedded atom method potentials)

Figure 152

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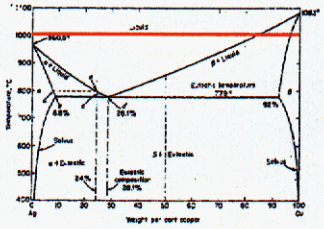
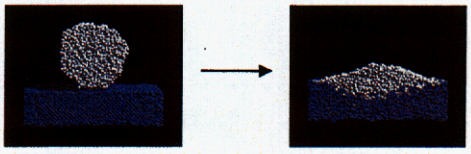
Wetting and Spreading Simulations in Metal Systems





Blue - Cu
White - Ag
T=1300K

- Ag(l) on Cu(100)
- Potentials predict alloying in agreement with phase diagram

Figure 153

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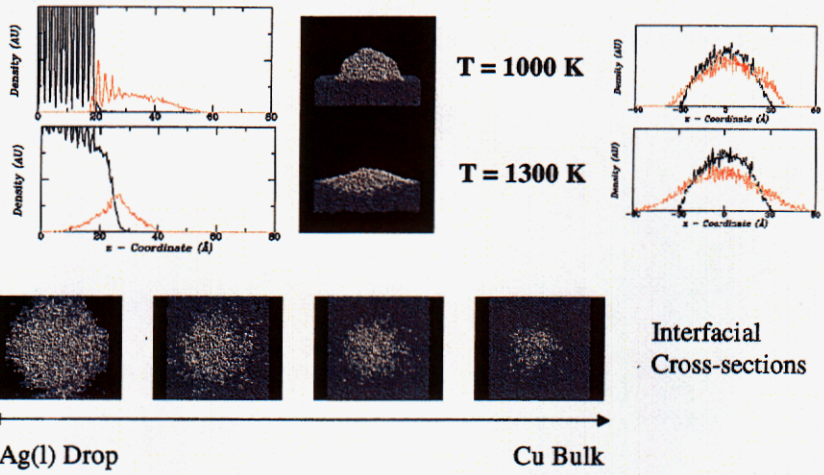
Currently Analyzing Interfacial Structure and Dynamics for Large Systems



Sandia National Laboratories

Figure 154

Wetting and Spreading Simulations in Metal/Ceramic Systems

- more challenging interfaces to model using classical atomistics
- need a potential which embodies pure metallic interactions, pure ionic interactions, and the interim sub-oxide range
- oxidation/reduction reactions inherent to these interfaces
- charge must be able to change as a reasonable function of environment

→ ES-EAM (ES+, Qeq, etc.)

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Figure 155

ES+ Potential for Al/O System

- Streitz & Mintmire; *PRB* **50**(16)11996; 1994
  - > fit to properties of Al and α - Al_2O_3
  - > alumina surface energies/relaxations, elastic response, fracture
- LSU - oxidation of aluminum nanoclusters, sintering alumina, atmospheric effects on crack growth (million atom simulations)
- favorable comparison of bulk κ - Al_2O_3 with *ab initio* results; now doing interfacial tests

Figure 156

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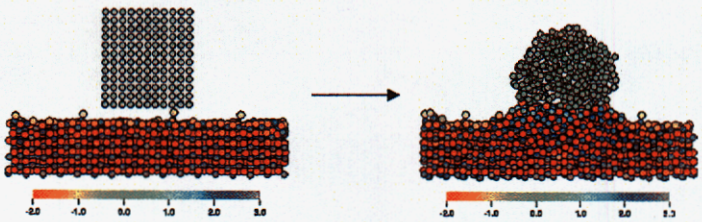
Wetting and Spreading Simulations in Metal/Ceramic Systems

T = 1600K
α - Al_2O_3 (0001) surface

green – metallic Al (q~0)
red – bulk alumina O (q~-2)
purple – bulk alumina Al (q~+3)



Viewing oxidation/reduction at the atomistic scale

Figure 157

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Analyzing the Metal/Ceramic Interface

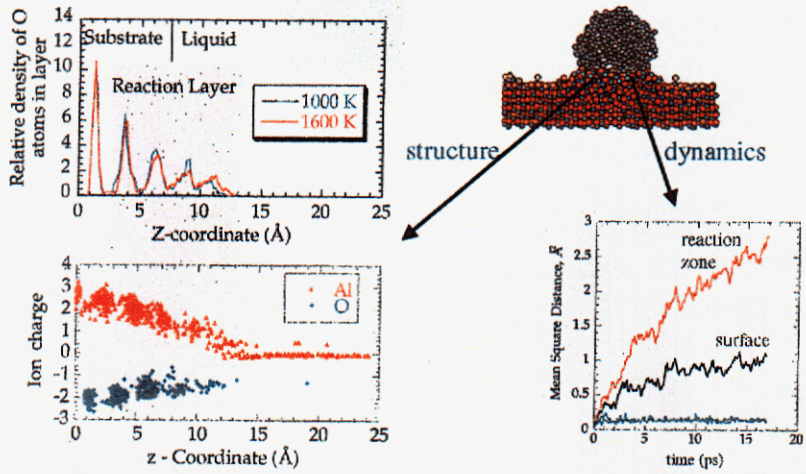

Figure 158

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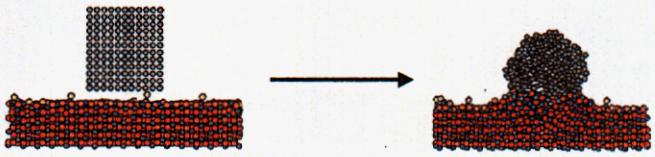
Complex Potential is Computationally Intensive



- 3338 atoms total; t = 10 ps
- need larger system sizes and longer durations but …
- this calculation took ~3 weeks on a DEC alpha 600 MHz processor

Figure 159

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Needs & Opportunities

- collaborations absolutely essential
  - > nano and micro scale modeling, experiment, characterization
  - > *ab initio* calculations; experiment
- must use a scalable, parallel code for ES+ type potentials
  - > connection with LSU group (code/expertise)
- understanding interfacial behavior of active elements is key to adequately describing braze systems (Ti, V, etc.)

Figure 160

Sandia National Laboratories

Needs & Opportunities

- accurate description of interfacial thickness and composition as f(T,composition,etc)
- residual stress distribution
- effect of atmosphere
- reactions at grain boundaries, steps, and other surface features
- better constitutive relations, more accurate models, increased accuracy of reliability/lifetime predictions

Figure 161

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9.0 New Analytical Characterization Tools

The third element of Sandia's brazing research initiative is the materials characterization of brazing reaction products, microstructures, phases, and compositions (Figs. 162-167). Automated x-ray spectral image analysis (AXSIA) is the latest analytical tool that is being applied to studying ceramic-metal interfacial reactions. The technique provides phase spectra and images that are normally difficult to obtain using conventional point or area solutions. P. G. Kotula described the capabilities of this new analytical tool. It allows quantitative identification and comparison of complex reaction products and phases in braze and solder joints (Figs. 168-171). It also can be used to investigate active metal-ceramic reactions that directly contribute to hermetic braze joints (Fig. 169).

Spectral imaging is particularly useful on samples that have random or discrete interfacial reactions (Figs. 172-175). Rather than guessing or being lucky in finding the right sample location for analysis, AXSIA reveals important phase information without foreknowledge of any point analysis or elemental mapping. The resulting spectral image shows each phase and its distribution in the microstructure. This is usually done first at a micro-scale level with scanning electron microscopy (SEM). More detailed, nano-scale analyses can be performed by selecting specific areas of interest from the SEM spectral image. For example, the interfacial reaction between Ag-Cu-Hf active filler metal and alumina is not continuous or thick. Spectral imaging has been used to find areas along the braze-ceramic interface where the reaction product occurs (Fig. 172). Scanning transmission electron microscopy (STEM) samples can then be prepared in-situ by a focus ion beam (FIB) milling process. Reaction thickness and phase identification analyses quickly follow.

This powerful imaging software tool is being applied to other materials characterization techniques. The result will enable the materials research community to track more subtle changes in microstructures and chemistry with greater analytical sensitivity and faster solution times.

Advanced Characterization of Brazes: Automated Analysis of X-ray Spectrum Images

Paul Kotula and Mike Keenan

Sandia National Laboratories, Albuquerque, NM 87185

Acknowledgements
Joe Michael, Dave Haaland, Fred Koehler at SNL

Figure 162

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.

Sandia National Laboratories

AXSIA: Automated X-ray Spectral Image Analysis
The Big Picture

- Developed under RF (DP-10, Aging and Reliability) to provide greater sensitivity to small, aging-related chemical changes…but it's application is much broader than this

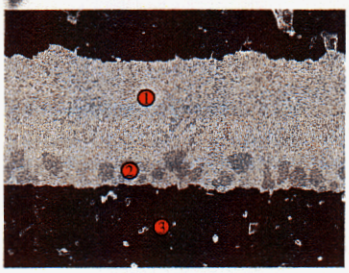
- Leveraged against Brazing RF, BES Corrosion program, and a number of our bigger customers who all benefit from AXSIA

- Provides detailed chemical information about braze microstructures for process feedback, fundamental research, and modeling. All spanning from hundreds of microns to tens of nanometers

Figure 163

Sandia National Laboratories

AXSIA: Automated X-ray Spectral-Image Analysis



SEM image of a Nioro-Vanadium braze to alumina

- How do you comprehensively survey the chemistry of a large area of a microstructure?
- Point analyses can be subjective–where to take them from and how many.
- 2D distributions of chemical phases are needed but simple mapping alone is not the answer. Mapping has potential artifacts and requires fore-knowledge.

'Phase images' are needed–a spectrum from each phase and an image describing where in the microstructure it's found

Ultimate goal–Detection of subtle changes due to aging, earlier or with less severe accelerated aging

Figure 164

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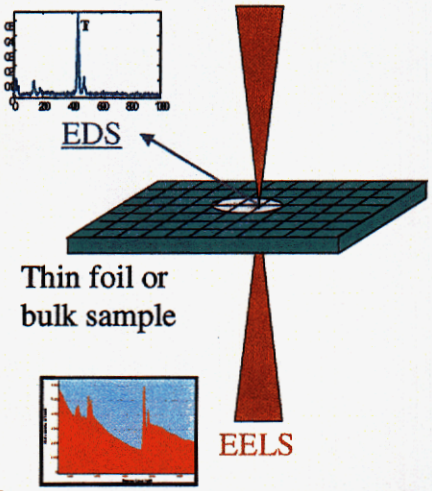
Spectral Imaging/Spectral Series

Electron probe (STEM, SEM)



Spectral Series (dynamic exp.)

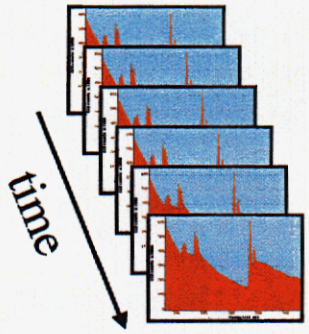


Figure 165

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AXSIA: Automated X-ray Spectral-Image Analysis

Approach

- Start off with a spectral image–a complete x-ray spectrum from each pixel in a 2D array, sampling the microstructural region of interest (hundreds of microns on a side (SEM) to nanometers on a side (TEM))
- Perform a complete statistical analysis (information extraction) on every spectrum in the spectrum image using the AXSIA software. **Analysis time** on a spectrum image with over 16,000 spectra is only **about a minute.**
- The result is a spectrum from each phase in the microstructure and an image describing that phase's location in the microstructure: 16000 spectra are reduced to a handful with no loss of chemical information

Figure 166

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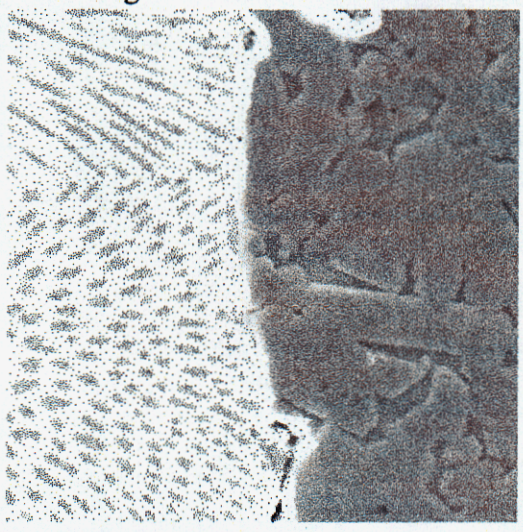
AXSIA: Automated X-ray Spectral-Image Analysis

SEM image of a braze interface-no discernable interfacial phase



We could do point analyses but are likely to miss something

With spectrum imaging in the SEM , we can comprehensively survey 30x30μm or more at a time (10x10nm in the STEM)

Figure 167

50 μm field of view

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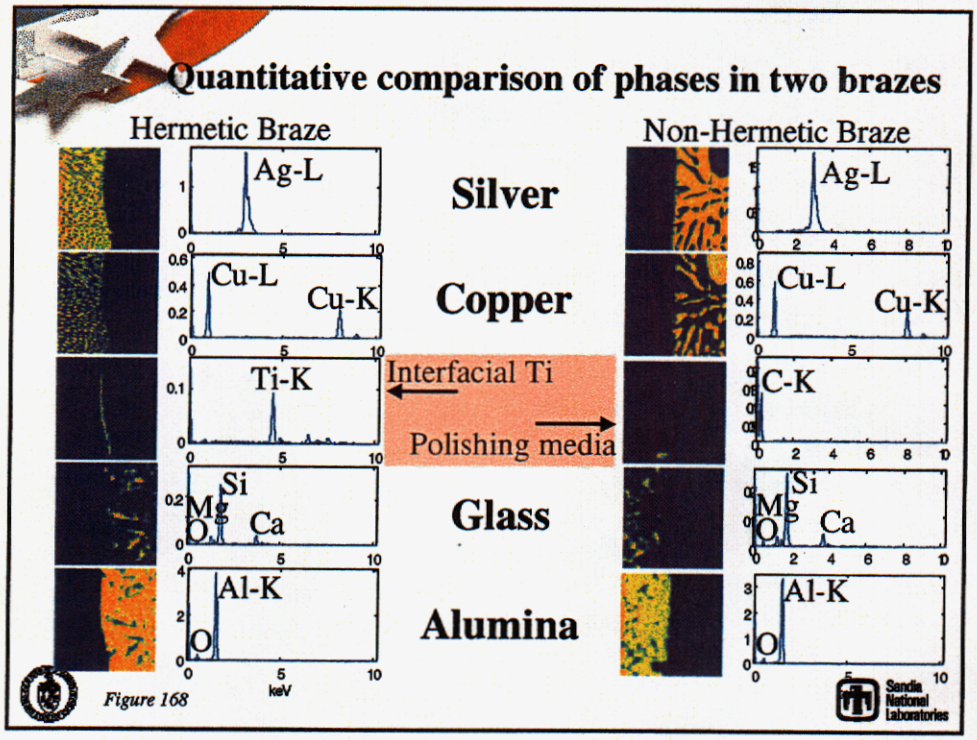
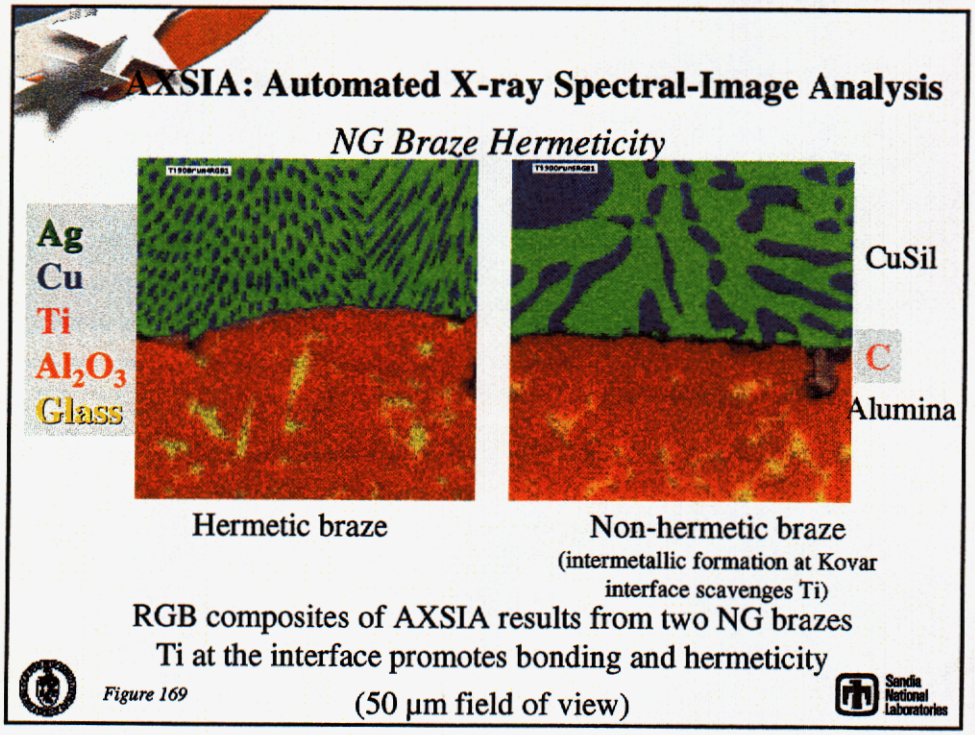

Quantitative comparison of phases in two brazes
Hermetic Braze
Non-Hermetic Braze
Ag-L
Silver
Cu-L
Cu-K
Copper
Ti-K
Interfacial Ti
Polishing media
C-K
Si
Mg
O
Ca
Glass
Al-K
Alumina
keV
Figure 168
Sandia National Laboratories


AXSIA: Automated X-ray Spectral-Image Analysis
NG Braze Hermeticity
Ag
Cu
Ti
Al_2O_3
Glass
CuSil
C
Alumina
Hermetic braze
Non-hermetic braze
(intermetallic formation at Kovar interface scavenges Ti)
RGB composites of AXSIA results from two NG brazes
Ti at the interface promotes bonding and hermeticity
(50 μm field of view)
Figure 169
Sandia National Laboratories

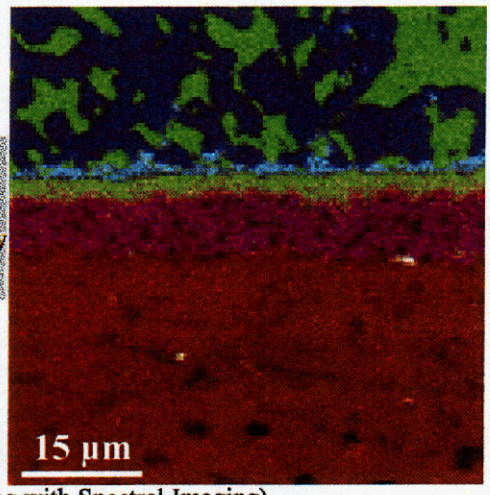
Analysis of a solder interface: 8 phases

RGB representation of the phases

Alumina = Red	Pb = Green
Sn = Blue	Cu-Sn = Cyan
W = Magenta	Ni-Co = Yellow
Glass = Black	TiO_2 = White

14 minute acquisition
1 minute calculation

50 msec total dwell/pixel



NORAN Vantage DSI (Digital Imaging with Spectral Imaging)
JEOL 5900-LV, W filament, 20kV, 10mm² detector (138eV),
128x128 pixels, 1024 channels, 500 Frames@ 0.1 msec/pixel, 30% Dead time

Figure 170

Sandia National Laboratories

Analysis of a solder interface: 8 phases

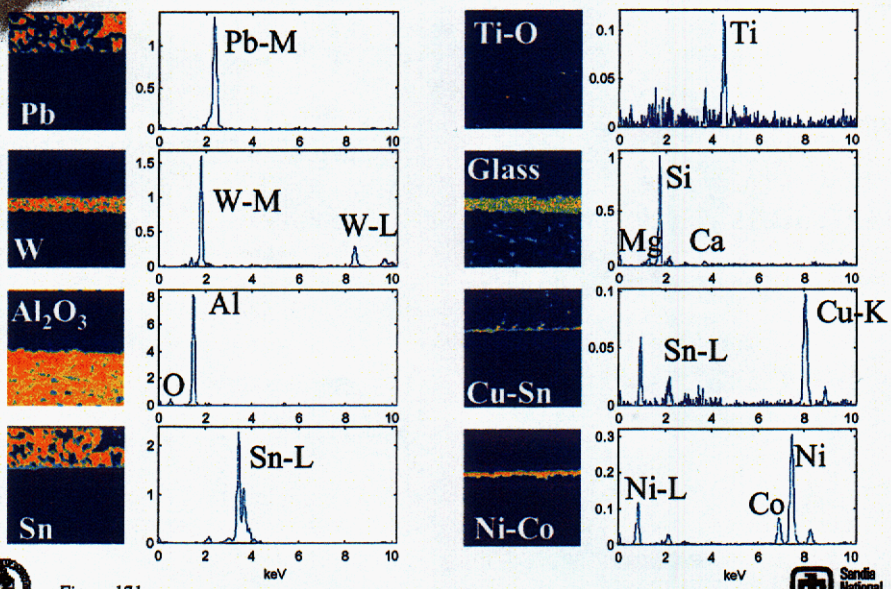


Figure 171

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AXSIA: Finding the needle in the haystack

Red=Al_2O_3
Green = Ag
Blue = Cu
Yellow = Hf

(150 nm/pixel-resolution limited by x-ray generation volume)

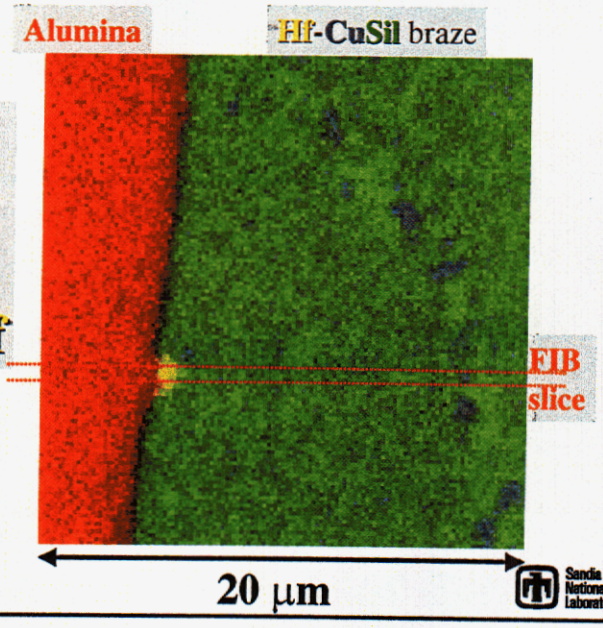

Figure 172

Sandia National Laboratories

AXSIA of Hf-CuSil/Alumina Interface

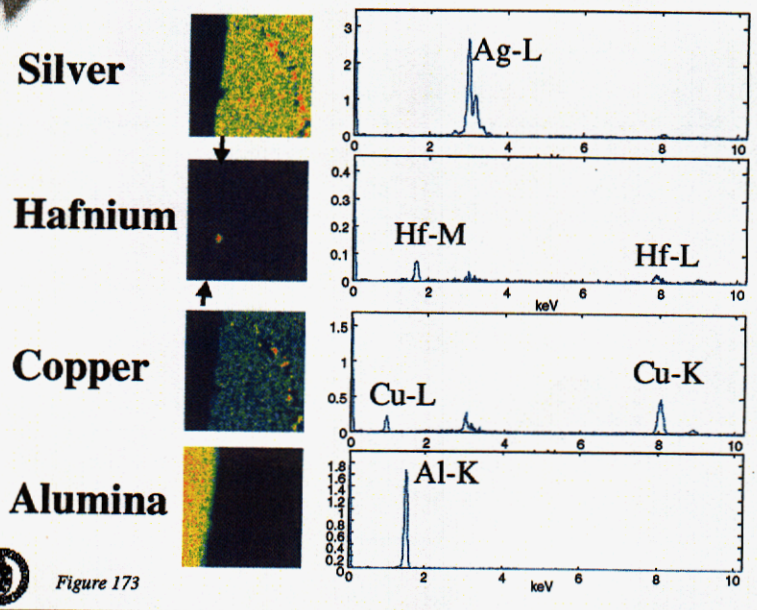

Figure 173

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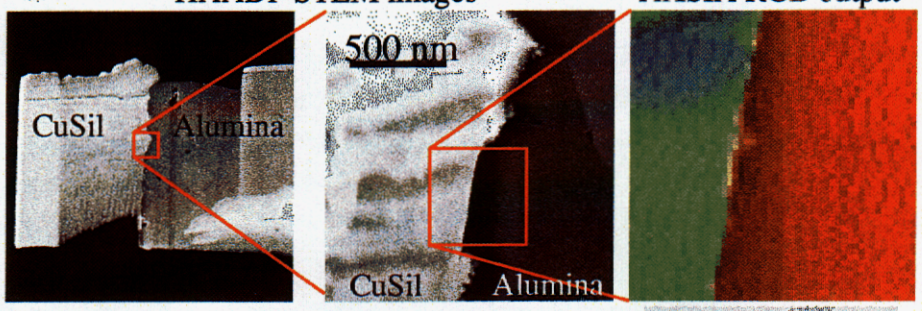
From micro- to nano-scale analysis

HAADF STEM images

AXSIA RGB output



FIB specimen cut from braze

Cu	Alumina
Ag	Hf-O

AXSIA output of STEM x-ray spectrum image
less than 10nm Hf-O layer at interface
(this represents moderate resolution STEM…~1nm is best)

Figure 174

Sandia National Laboratories

AXSIA Output, STEM x-ray SI of Hf-CuSil /Alumina

Silver

Copper

Hafnia

Alumina

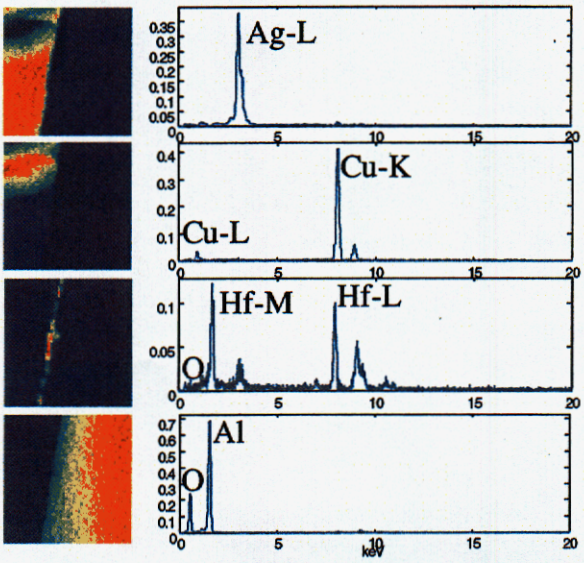


Figure 175

Sandia National Laboratories

AXSIA: Automated X-ray Spectral-Image Analysis

Impact

- We have developed the next generation of microanalysis tools at Sandia…AXSIA, with future development impacting other spectrum imaging characterization techniques (XRF, Auger, SIMS, EELS, etc.) Now have the capability to track subtle changes in a microstructure with greater sensitivity than before…Process changes, FA, etc.
- Will impact understanding of interfaces at the nanometer scale and try to answer the question: **How do active metals promote brazing?**
- Already utilize AXSIA for almost all internal customers problems Neutron Generators, Microelectronics (failure analysis and process feedback), MEMS, Corrosion, LIGA, Solders, etc.
- Licensed AXSIA to Thermo NORAN, Inc.

Figure 176

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10.0 Development and Production Brazing Support

A critical link to Sandia's brazing research initiatives is the application of the resulting brazing knowledge and expertise to DP design and production needs. Integration of these R&D activities is important if the right technological information is to be delivered and implemented within the required program times and costs. J. J. Stephens highlighted current DP brazing engineering support (Figs. 177-198). The work utilizes materials, processing, and modeling capabilities

There are three areas that have received particular engineering attention; active metal braze alloys, braze process characterization, and braze alloy mechanical properties. Ceramic-ceramic and metal-ceramic braze joints in DP components are the drivers for these activities. The principal focus in new component designs is the development of alternative and viable active metal brazing processes.

Process surveys have shown that active metal brazing can significantly reduce the number of processing steps necessary to braze ceramic assemblies. In some cases, this reduction can be as high as 20-25 percent by the elimination of ceramic metallization, firing, plating, and cleaning steps. The technology challenge for active metal brazing is to demonstrate process repeatability, compatibility, and reliability. This requires the scientific and engineering knowledge of how the process works, is controlled, and can be optimized.

A key issue in active metal brazing is the characterization of the braze/ceramic interface. The reaction product and resulting joint structure can significantly vary, depending on the type of active constituent (Fig.181). This can be complicated by competing reactions with other base materials that comprise the braze joint. To further complicate the problem, these reactions can be enhanced or stopped, depending on the type of filler metal system, active element, or barrier coating used. Alumina-AgCuTi-Kovar™ braze joints are good examples where reaction by the filler metal with the Fe-Ni-Co alloy causes scavenging of titanium and poor bonding to the alumina piece (Fig. 182). Nonhermetic, lower strength joints are the result. The same reaction does not occur between two alumina parts. The problem can be corrected by using a different active element, such as zirconium, which is not as sensitive to the scavenging reaction, or a

barrier coating, such as Mo (Fig. 183), which can inhibit Kovar™ dissolution. There is also evidence to suggest that the AgCuTi braze process may be more reliable at higher brazing temperatures (Fig. 184). As processes are better characterized and new active metal brazes are developed, such as those containing active intermetallic compounds, thermodynamic, phase equilibrium, and solubility data need to be considered when making decisions.

An important part of process characterization is understanding how critical process variables affect process outputs, such as braze joint hermeticity, strength, and microstructure. The outcome of such a study is a statistically designed space solution to the brazing materials and processing conditions, rather than a limited point response. This approach is valid for both conventional and active metal brazing systems. An example is the large tensile button study (LTBS) that is quantifying the effects of alumina ceramic type, Mo-Mn metallization thickness, Ni-overplate thickness, braze thickness (i.e., volume), brazing temperature, and brazing time on properties with ASTM F19 tensile specimens (Fig. 189-193). The study will define the optimum production conditions for making reliable 50Au-50Cu metal-ceramic braze joints. Kovar™ interlayer and alumina alignment conditions appear critical to the success of the process.

Another important applications area is the development of a properties database for brazing alloys (Figs. 194-197). For example, lower strength filler metals can better accommodate strain mismatches across metal-ceramic joints. In general, elevated temperature tensile and creep properties are needed when designing reliable braze joints. Order-disorder reactions are a particular problem for some alloy systems, such as the 81.5Au-16.5Cu-2Ni filler metal, which can generate high residual stresses that cause cracks and failures in the ceramic or at the metal-ceramic interface. Conversely, creep properties for 50Au-50Cu indicate that ordering is very sluggish and does not create the same ordering problem.

In summary, active metal braze alloys show promise for hermetic applications, process characterization is identifying optimal braze processing conditions, and a wide range of braze alloy properties is available to meet the specific joint requirement.

April 4, 2001 Ceramic/Metal Braze Workshop

Development and Production Brazing

John J. Stephens
Joining and Coating Dept. (1833)
Sandia National Laboratories
Albuquerque, NM 87185-0889

Figure 177

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Sandia Has Developed Extensive Expertise in Brazing Technology

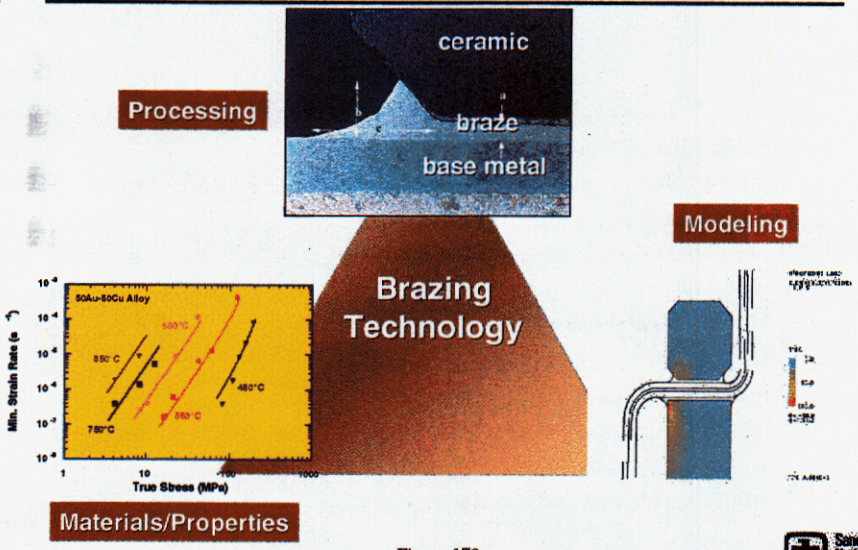

Figure 178

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Brazing Technology:
Development and Production Brazing

- Active Metal Braze Alloys
  - Compatibility Issues: *Cu-Ag-Ti in Kovar/Alumina joints.*
  - Alternative approaches: *Zr active element addition.*
    Direct braze using conventional braze alloy w/reactive metal member.
- Process Characterization Activities
  - Braze Processes: *use of ASTM F19 tensile buttons w/Kovar interlayer to capture actual joint materials.*
- Mechanical Properties Considerations - Braze Alloys

  General strength considerations - different from metal/metal brazing.

  Avoid use of braze alloys that order during component processing or service.

Figure 179

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Active Metal Brazing Finds Applications in Ceramic-Ceramic and Metal-Ceramic Joining

- ***Potential:***

  Active metal brazing can reduce the number of process steps in component production (as many as 20%).

- ***Engineering Challenges:***
  - **"Mo-Mn" process has a long history.**
  - **Compatibility issues in Kovar/ Cu-Ag-Ti/Alumina braze joints.**

- ***Scientific Opportunities:***

  There is a critical need to understand the nature of the braze/ceramic interface.

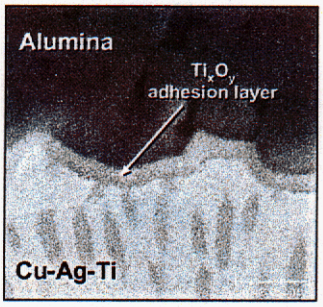

Figure 180

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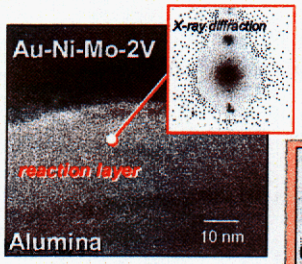
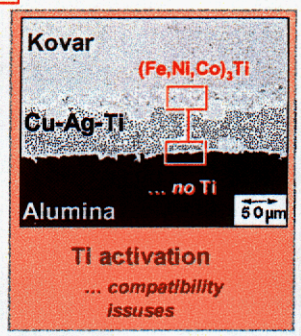
Scientific Issues are Focused on the Structural Details of the Braze/Ceramic Interface



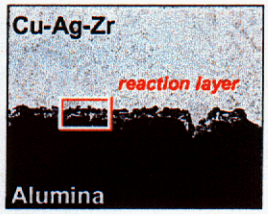
V activation

Successful use of ABA technology requires a thorough understanding of interface reactions.



Ti activation

... compatibility issuses



Zr activation

Figure 181

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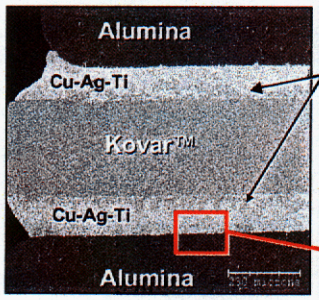
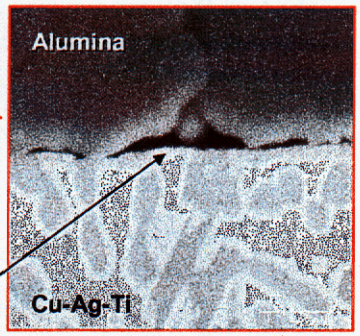
Ti Scavenging is a Problem for Kovar/Alumina Braze Joints w/Ag-Cu-Ti (Cusil ABA)



Ti is diverted from the Cu-Ag-Ti/alumina interface by the formation of Fe_3Ti compound forms.

The braze joints are NON-HERMETIC



A Ti_xO_y adhesion layer DID NOT form at the Cu-Ag-Ti/alumina interface.

Figure 182

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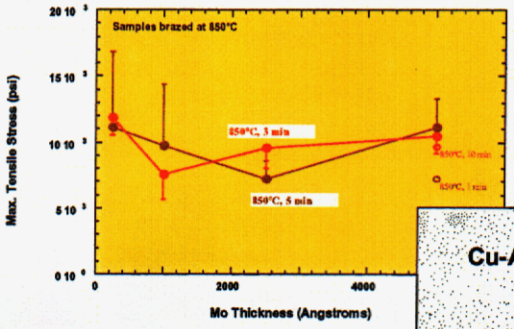
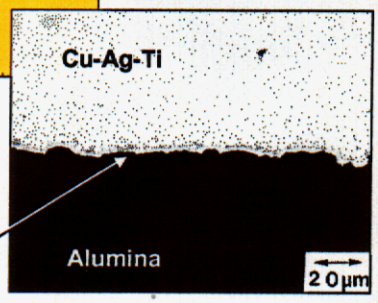
Mo-coated Kovar™ Prevents Fe_3Ti Growth, Allowing Formation of the Ti_xO_y Adhesion Layer



Mo thicknesses as low as 250 Angstroms produced hermetic joints with acceptable strength.



Continuous TixOy adhesion layer forms at the Cu-Ag-Ti/alumina interface (5000 Angstrom Mo).

Figure 183

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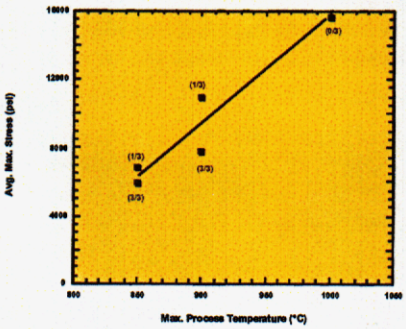
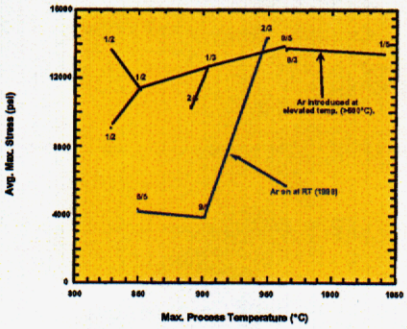
Recent Results w/Bare Kovar Using CusilABA Suggest That Reliable Yields May Be Obtained at T>960°C





- Results suggest that above 960°C, perhaps the scavenge phases dissolve into the brazement.
- The higher temperatures may present problems for specific joint geometries.

Figure 184

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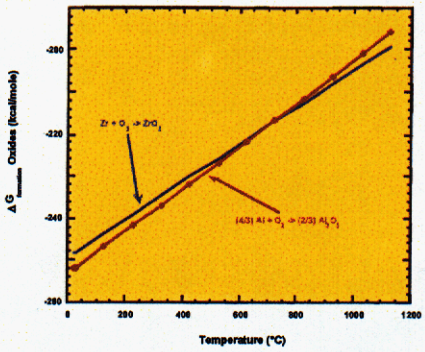
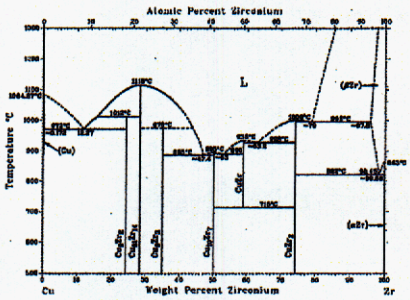
Thermodynamic and Phase Diagram Considerations - Zr Active Element Addition





- **Above a temperature of 730°C, ZrO_2 is more stable than Al_2O_3.**
- **Low melting point eutectics near $Cu_{10}Zr_7$ (885°C) and $Ni_{21}Zr_8$ + $Ni_{10}Zr_7$ (1070°C) show promise for active metal brazing.**

Figure 185

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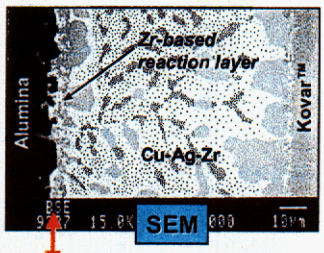
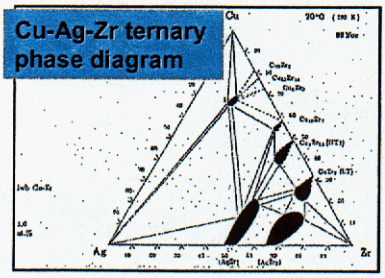
Cu-Ag-Zr Active Alloy Avoids Active Element Scavenging in Kovar™/Alumina Braze Joints

- **29Cu-69Ag-2Zr (wt.%)**

  Zr source: $Cu_4Ag_1Zr_1$.
- **ZrO_2 forms at the interface between Cu-Ag-Zr and alumina**
- **This alloy requires very low partial pressure O_2 environments.**





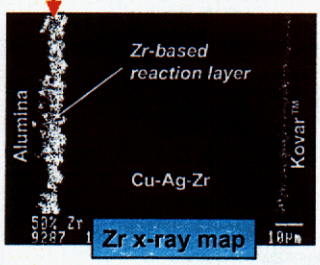


Figure 186

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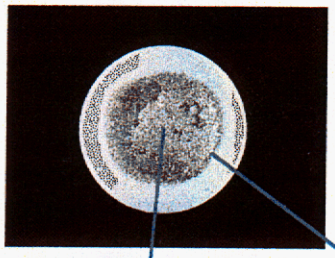
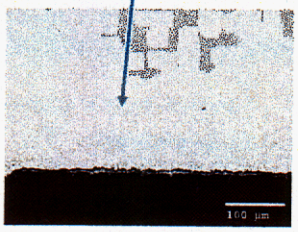
Powder Mixture Results: 98wt.%Cusil and 2%$Cu_{10}Zr_7$



Sample run for 925°C, 15 min., in vacuum. Substrate: AL-500 ceramic.



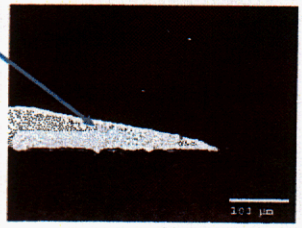


Figure 187

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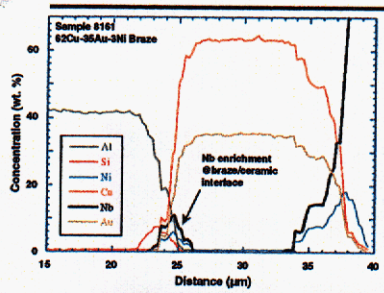
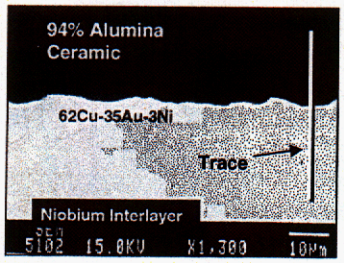
"Direct Braze" Process Uses Conventional Braze Alloys and Active Metal Interlayer





Nb provides "active" element

94% Al_2O_3, sapphire ceramics

Requires:

Solubility of interlayer (Nb) in the liquid braze alloy

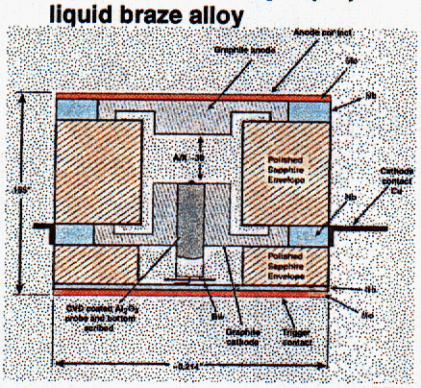


Figure 188

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Process Variables - Large Tensile Button Study (LTBS) Using 50Au-50Cu Braze

- **PeakTemperature (control)**
  (998, 1012, 1026°C)
- **Ramp Rate Above 2nd Soak**
  (2, 4, 6°C/min.)
- **Braze preform thickness**
  (0.002, 0.003, 0.004 in.)
- **Ni plate thickness**
  (0.0001, 0.0002, 0.0004 in.)
- **Metallize thickness**
  (0.0002, 0.0006, 0.0012 in.)
- **Ceramic type (94% alumina)**
  Diamonite vs. SANDI-94

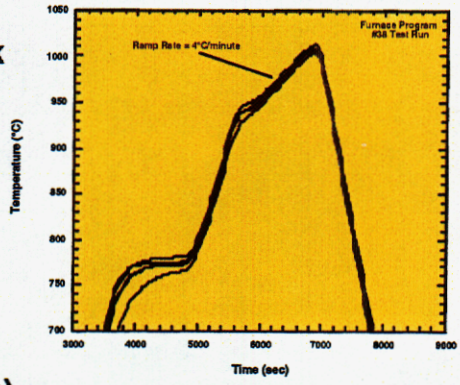

Figure 189

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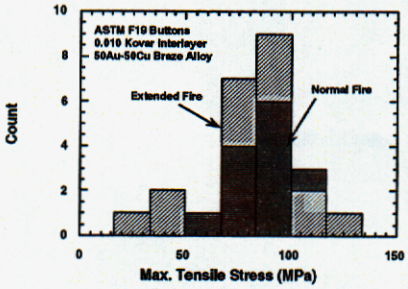
"Short" Tensile Button Study: Kovar Interlayer and Button/Button Alignment Are Key Items

- Avg. strength obtained w/ Normal Metallize Firing is comparable to Extended Firing.
- Modify braze fixture and Kovar interlayer dimensions to improve Kovar interlayer alignment.



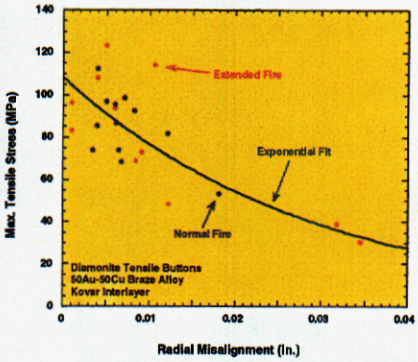


Figure 190

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ASTM F19 Tensile Button: Functional Testing of Braze Joints

- Braze sample, leak check, followed by tensile pull to fracture.
  - We prefer to use brazing fixtures which are not graphite to ensure furnace compatibility.
  - Center-aligning braze fixture used.
- We use a 0.010 inch thick Kovar washer interlayer + double braze joint (single washer on both sides of interlayer) for all brazed button samples - representative of actual braze joint configuration.

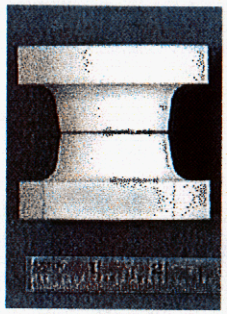

Figure 191

Full Sample Matrix - Large Tensile Button Study

- 11 furnace runs - constant # of fixtures (20).
- 5 samples per condition, 4 to pull, 1 to EMPA.
- Metallize thickness: 0.0002, 0.0006, 0.0012 in.
- Ni plate thickness: 0.0001, 0.0002, 0.0004 in.
- Braze washer thickness: 0.002, 0.003, 0.004 in.

Run Number	Braze Time	Braze Temp	Nickel Plate Thick.	Braze Washer Thick	Metallize Thick.	Ceramic Type	Furnace Run
1	1	1	1	1	1	S	1
2	3	1	1	1	3	S	2
3	1	3	1	1	3	D	3
4	3	3	1	1	1	D	4
5	1	1	3	1	3	D	1
6	3	1	3	1	1	D	2
7	1	3	3	1	1	S	3
8	3	3	3	1	3	S	4
9	1	1	1	3	1	D	1
10	3	1	1	3	3	D	2
11	1	3	1	3	3	S	3
12	3	3	1	3	1	S	4
13	1	1	3	3	3	S	1
14	3	1	3	3	1	S	2
15	1	3	3	3	1	D	3
16	3	3	3	3	3	D	4
17	1	2	2	2	2	D	5
18	3	2	2	2	2	S	6
19	2	1	2	2	2	S	7
20	2	3	2	2	2	D	8
21	2	2	1	2	2	D	9
22	2	2	3	2	2	S	9
23	2	2	2	1	2	S	10
24	2	2	2	3	2	D	10
25	2	2	2	2	1	D	11
26	2	2	2	2	3	S	11
27	2	2	2	2	2	S	9
28	2	2	2	2	2	S	10
29	2	2	2	2	2	D	11
30	2	2	2	2	2	D	11

Figure 192

Status - Large Tensile Button Study

- Complete sample matrix brazed - 11 furnace runs done.
- Samples have been inspected for interlayer misalignment and top/bottom misalignment.
  - awaiting leak check of samples.
  - combine inspection data and leak check to determine samples for cross section (eliminate worst misalignment from pull testing.
  - tensile pull testing of samples.
  - electron microprobe traces of mounted samples to determine alloying levels.

Figure 193

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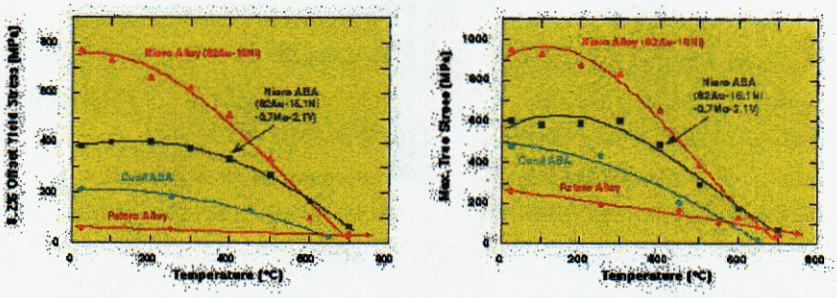
A Wide Range of Strengths Are Available w/ Various Braze Alloys



- For metal/ceramic brazing, lower-strength alloys that can accommodate strain mismatch across the braze joint are more useful.

Note: Data for Nioro, Nioro ABA and Paloro were measured in tension; data for Cusil ABA were generated in compression.

Figure 194

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Elevated Temperature Properties Data for Braze Alloys - Required for Braze Joint Design

Elemental brazes (data from the literature): Cu, Ag and Au.

Conventional braze alloys (braze to metallized ceramic):

50Au-50Cu	47Au-50Cu-3Ni	62Cu-35Au-3Ni
92Au-8 Pd	82Au-18Ni	82Au-18In
72Ag-28Cu	61.5Ag-24Cu-14.5In	88Au-12Ge

Active Metal Braze Alloys (braze to bare ceramic):

- Paloro + 2%V [90Au-8Pd-2V]
- Nioro ABA [82Au-15.5Ni-0.75Mo-1.75V]
- Cusil ABA [63Ag-35.25Cu-1.75Ti]
- Incusil ABA [59Ag-27.25Cu-12.5In-1.25Ti]

Figure 195

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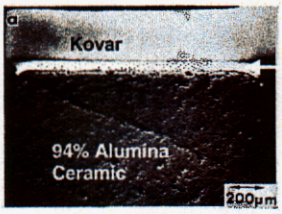
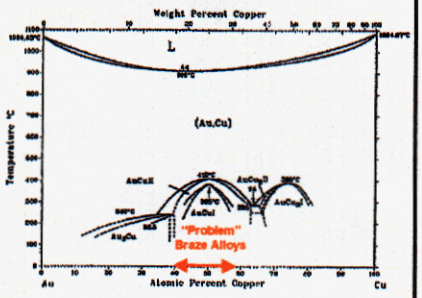
Order-Disorder Reactions in Braze Alloys Can Cause Damaging Residual Stresses

- Metal/81.5Au-16.5Cu-2Ni/ceramic braze joint was cracked and non-hermetic after 2 hr. bakeout at 300°C.
- Work by J. Wittenauer, Lockheed, confirmed that 81.5Au-16.5Cu-2Ni alloy does order @ 300°C.
- Ordering caused an increase in strength and loss of ductility



Cracked unit brazed w/ 81.5Au-16.5Cu-2Ni alloy



Condition	S_y (ksi)	UTS(ksi)	Elong.(%)	VHN
As-received	58.6	109	46	192
Ann: 300°C/2hr	149	172	12	304

Figure 196

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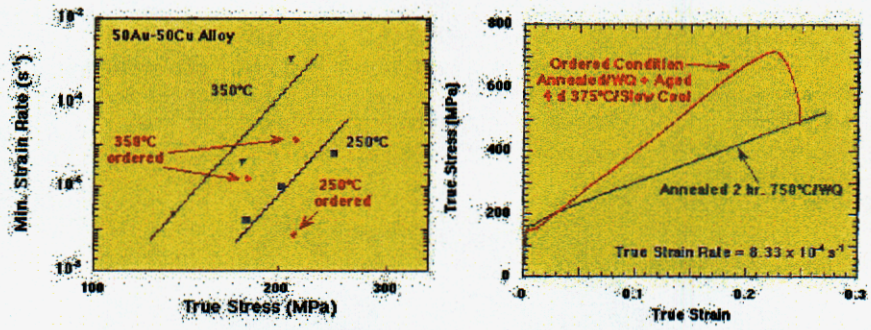
Creep Properties of 50Au-50Cu Alloy Indicated that Ordering Is Very Sluggish and Not a Problem



- Relative to the 2 hr. 750°C/WQ baseline, the 350°C/250°C ordered data represents an avg. ~20% increase in creep strength.
- Room temperature stress-strain properties: yield stress unchanged, ordered condition has higher work-hardening slope.

Figure 197

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Summary and Conclusions

- *Active braze alloys show promise for hermetic applications.*
  - Braze alloy compatibility w/specific joint materials must be considered.
- ***Process characterization with tensile buttons permits the identification of optimal braze process conditions.***
  - **Interlayer and button alignment are critical quantities.**
  - **A large sample matrix is hard to complete in a production facility.**
- ***Braze alloys include a wide range of available strengths.***
  - **For metal/ceramic brazing, use alloys with relatively low creep/tensile strength to accommodate mismatch strains.**
  - **Avoid alloys that order if that results in a significant increase in strength or a volume change.**

Figure 198

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Sandia National Laboratories

11.0 Brazing Needs, Opportunities, Potential Barriers, and Actions

Following the brazing presentations, a facilitated discussion was held to identify critical needs, opportunities, and barriers to brazing science and technology at Sandia, including activities that require less emphasis. The most important issues that were identified are summarized here. The items are not ranked and are listed as they were posted. The exercise also identified necessary actions to sustain the workshop exchange of ideas and further strengthen Sandia's brazing science and technology programs.

Brazing Research Needs

- Determine evaporated/sputtered film adhesion on ceramics
- How are others using Cusil ABA (Ag-Cu-Ti) on Kovar™?
- What are fundamentals of wetting at high temperatures?
- How does the active layer really work (fundamental understanding)?
- Fundamental process characterization
- High temperature mechanical properties of braze joints
- Lack of corrosion studies for braze joints
- Modeling codes do not capture all relevant materials physics
- Need more first principles calculations
- Need to characterize effects of joint alloying on standard braze alloys
- Characterize properties of interface at atomic scale
- How do kinetics play into brazing cycle?
- Integrate understanding of physical and chemical processes at interface
- What's "clean" for brazing?
- How to better control filler metal flow?
- Confirm whether post-processing and aging are not a concern for braze joints
- Physical processing of ceramic surface to increase reactivity with braze alloy
- Failure modeling input (will it work on real parts?)
- How do we represent reaction/metallize layers in stress models?
- Need more coordinated, overall effort to support brazing

- Develop technique to measure residual stresses in ceramic-metal joints
- Compile a list of published and unpublished Sandia ceramic-metal joining related work

Brazing Research Opportunities

- Use current programs to address broader national needs
- Couple atomistic and continuum modeling
- Solve diffusion equations for brazing reactions
- Develop active braze alloys in paste form to broaden joint geometry choices
- Export braze feedthrough technology and costs to other relevant users (DoD, NASA, CRADA's, WFO's, etc.)
- Expand PDP, LDRD, and ASCI/MAVEN program support
- More use of Nicoro+2%Ti
- Teaming/leveraging internal and external brazing efforts
- Better definition of braze joint reliability
- Validation experiments of braze models/codes
- Fundamental process characterization
- Correlation of braze reactions/structure to properties

Brazing Research Barriers

- Convince management and funding sources that brazing still needs more Fundamental R&D
- Need analytical techniques to study braze joints at high temperatures
- Lack of techniques for selective heating of buried interfaces
- Time and resource constraints by production
- Lack of sustained, coordinated support
- Flow of information to/from outside organizations and companies
- Lack of Ownership/sponsor for ceramic joining

Brazing Activities That Require Less Emphasis

- Too much trial and error or point solution work at Sandia
- Too much disconnected work

- Schedules should not be the prime or only research driver
- Evaporating molybdenum or other barrier coatings on Kovar™ to make Cusil ABA work
- Focus on issues that "are not working" versus those that do

What Are the Recommended Actions for the Brazing Group/Initiative?

- Annual meetings
- Group of stakeholder representatives
- Strategy for higher, more stable funding (priority)
- Website to interactively share and discuss brazing issues
- Sandia brazing resource/database site (internal and external)

12.0 Summary and Conclusions

The workshop provided a unique forum for assessing Sandia's brazing science and technology research activities. The presentations and discussions highlighted core facilities and people resources. The integration of these different research, development, and production programs into a cohesive brazing initiative will be critical toward the sustained growth and success of Sandia's brazing capability.

An important outcome of the workshop was to determine the external relevance of Sandia's work by other experts in the brazing community. The two invited speakers, Drs. A. Tomsia and T. Oyama, who assessed the current state of brazing science and technology, gave overviews. It was concluded that Sandia plays an important and, in many cases, leading role in the understanding and advancement of ceramic-metal brazing. In particular, the fundamental work being done on active metal brazing, braze modeling, brazing metallurgy, interfacial reactions, and braze properties greatly complements other industry and university-directed activities.

Sandia is developing a powerful suite of theoretical, experimental, computational, and analytical tools to solve difficult materials and processing problems that are usually applications-driven. Examples were highlighted. Most research has focused on the development and qualification of active metal brazing for manufacturing neutron tube assemblies. A production perspective of how these activities support critical production needs (schedule, costs, reliability) was given, including an overview of progress in the areas of active metal braze alloys, process characterization, and braze alloy mechanical properties.

An important outcome of the workshop was to identify brazing research needs, opportunities, barriers and recommendations. The identified needs and opportunities align very well with Sandia's brazing research capabilities. The greatest barriers to formalizing a successful brazing initiative are the lack of sustained funding, long-range customer commitment, principal program champion(s), and an information-sharing network. An annual workshop or focus group meeting would serve to stimulate these programmatic discussions and develop core strategies. An interactive brazing website could also provide the necessary resource for sharing critical

information among the research, design, and production communities at Sandia, throughout the DOE complex, and with other external customers.

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