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# Reduced-Temperature Transient-Liquid-Phase Bonding of Alumina Using a Ag-Cu-Based Brazing Alloy

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## Abstract

The mechanical properties and microstructural evolution of metal-ceramic bonds produced using a transient liquid phase (TLP) are described. Alumina ( $\text{Al}_2\text{O}_3$ ) was joined at 500°C, 600°C, and 700°C using a multilayer In/Cusil-ABA<sup>®</sup> (commercial copper-silver eutectic brazing alloy)/In interlayer. The introduction of thin In cladding layers allows the system to bond at much lower temperatures than those typically used for brazing with Cusil-ABA<sup>®</sup>, thereby protecting temperature-sensitive components. After chemical homogenization, the interlayers retain an operating temperature range similar to that of the brazed joints. TLP bonds made at 500°C, 600°C, and 700°C with holding times ranging from as low as 1.5 h to 24 h had average fracture strengths above 220 MPa. The effects of bonding temperature and time on fracture strength are described. Preliminary analysis of the interlayers shows that the Ag-In or Cu-In intermetallic phases do not form. Considerations unique to systems with two-phase core layers are discussed. Experiments using single-crystal sapphire indicate rapid formation of a reaction layer at 700°C, suggesting the possibility of making strong bonds using lower temperatures and/or shorter processing times.

## Introduction

Today's complex engineered structures require reliable materials with specific properties. Ceramics are used in selected biotechnology, microelectronic, and aerospace applications where one or more properties such as biocompatibility, high hardness, excellent wear resistance, low electrical conductivity, high dielectric strength, low thermal expansion, high strength-to-weight ratio, or high-temperature capability are specifically exploited. Properties such as high hardness, which may be advantageous in an application can simultaneously cause difficulties when machining monolithic ceramic preforms into complex shapes. As a result, in numerous applications, joining smaller and more easily shaped ceramic parts to one another or to metallic components is necessary to the fabrication of larger structures with complex shape, or ones in which combinations of properties are sought that no one material can provide.

Joining techniques such as soldering, brazing [1-4] and solid-state diffusion bonding [5-8] can produce structurally reliable, hermetic metal-ceramic bonds. However, each of these techniques has inherent processing and joint performance characteristics that may render them unsuitable for certain applications. Soldering results in joints with limited temperature capability. Active metal brazing at intermediate temperatures (*e.g.*, 800-1000°C) *via* Ag-Cu-based alloys typically provides strong metal-ceramic bonds. Reactive-metal additions (most often Ti) can dramatically improve the wettability of liquid metals on ceramics, and promote strong adhesion. However, the joints typically remelt below the original bonding temperatures, and joint softening initiates at even lower temperatures, limiting the use temperatures for structural applications. In contrast, solid-state diffusion bonding can produce joints that retain strength to above the bonding temperature. However, since relatively slow solid-state diffusion forms the ceramic-metal interface, processing times are often long and bonding temperatures must be a high fraction of the melting temperature. Careful surface preparation producing pristine, flat surfaces can be critical to success. Cracklike interfacial gaps due to nonconformal surfaces, while readily filled by a wetting liquid, are difficult to remove in solid-state diffusion bonding, and can serve as preferred sites for failure initiation [5].

Conventional TLP bonding [9] uses a melting point depressant (MPD) in the interlayer, and relies on adequate solid solubility and rapid diffusion of the MPD into the adjoining bulk materials to progressively increase the melting temperature of the joint region, and decrease the amount of liquid. These restrictive requirements have limited the materials used for interlayers and the materials that could be joined. To alleviate or eliminate these constraints on bulk and interlayer material choices and to expand the range of joining and ultimate use conditions, our implementation of the TLP concept relies on multilayer interlayers in which the counter diffusion of the "MPD", present as a thin layer of a low melting point metal, and the higher melting point core material occur within the interlayer itself. Alloy formation occurs at a significantly reduced length scale, widening the range of candidate interlayer constituents. As in traditional TLP joining, the melting temperatures of the joints in these systems exceed the joining temperatures.

Previous studies have shown that In can be used as a MPD in joining Si or GaAs with Ag-, Sn-, Au-, or Cu-interlayers. Fracture strengths of these joints were not reported, but scanning acoustical microscopy (SAM) with a spatial resolution of 20-25  $\mu\text{m}$  was used to evaluate the bond quality. These samples were typically joined between 200°C to 280°C, with remelting temperatures exceeding 400°C to 700°C, depending on which metal core layer was used [10-15]. In another study, In-coated Ag was used to bond metallized  $\text{Al}_2\text{O}_3$  substrates; shear strengths of 1.4 MPa and 0.75 MPa were reported when using 3- $\mu\text{m}$  and 8- $\mu\text{m}$  thick In films, respectively [16].

This paper describes the TLP joining of  $\text{Al}_2\text{O}_3$  using In/Cusil-ABA<sup>®</sup> (Ag-Cu-based active brazing alloy)/In interlayers. The In cladding layer provides the low-melting-point liquid phase at the metal-ceramic interface. According to the Ag-In and Cu-In binary phase diagrams [17], significant dissolution of the solid Ag and Cu in the liquid In should occur, producing a liquid layer at the joining temperatures that is several times thicker than the original In layer. Dissolution and incorporation of Ti from the Cusil-ABA<sup>®</sup> foil is expected to improve wetting and enhance adhesion relative to Ag-Cu eutectic foils devoid of reactive metal additions. Cusil-ABA<sup>®</sup> must be heated above 780°C (solidus temperature) to form a liquid phase, but with the addition of the thin In layer, liquid formation initiates at much lower temperatures, and joining temperatures as low as 500°C can produce strong joints. Strength test results and both interlayer and interfacial microstructures are analyzed.

## Experimental Procedures

Polycrystalline  $\text{Al}_2\text{O}_3$  blocks of 99.9% purity (SSA-999W Nikkato Corp., Osaka, Japan) and 2 cm  $\times$  2 cm  $\times$  2 cm in size were used to produce bonded assemblies. The bonding surface of each block was first flattened with a surface grinder, and then polished with diamond slurry of progressively finer grit size (15  $\mu\text{m}$ , 6  $\mu\text{m}$ , 3  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.25  $\mu\text{m}$ ). In some cases, a final chemical-mechanical polish with a colloidal  $\text{SiO}_2$  (0.05  $\mu\text{m}$ ) suspension was employed. Polished blocks were cleaned in distilled water and soap, distilled water, acetone, and isopropyl alcohol for  $\geq 15$  min in each solution in an ultrasonic bath. The clean blocks were then annealed in air (CM Furnaces Inc., Bloomfield, N.J.) for 1 h at 1000°C to remove any residual organics on the surface. High-purity sapphire substrates (Crystal Systems Inc., Salem, MA) were used as optically transparent surrogates for polycrystalline  $\text{Al}_2\text{O}_3$ . The wafers, initially 2.5 cm  $\times$  2.5 cm  $\times$  0.051 cm, were sectioned with a low-speed wafering saw into approximately 0.76 cm  $\times$  0.76 cm  $\times$  0.051 cm pieces. Cleaning and annealing procedures duplicated those used for the polycrystalline  $\text{Al}_2\text{O}_3$ .

In (99.998% pure) and Ag (99.9% pure) wires (Alfa Aesar, Ward Hill, MA) of 0.1 cm diameter were cut into 1.5 cm and 0.5 cm long pieces, respectively, to fit into the two W-wire baskets of a physical vapor deposition system (Mikrons Inc., Portland, OR). Typically, 0.58 g of In and 0.04 g of Ag were loaded into the baskets after being cleaned. The In wires were dipped in *aqua regia* (3 HCl:1  $\text{HNO}_3$ ) acid solution to remove any surface oxides present.  $\text{In}_2\text{O}_3$  is resistant to reduction and does not melt until 850°C, and thus, must be removed to deposit

metallic In, and is undesirable in the coating. It has been shown that a small addition of Ag in the film helps to form a thin intermetallic surface layer that provides effective oxidation protection [12]. One basket was filled with only In and In was deposited onto the polished and cleaned polycrystalline or single crystalline  $\text{Al}_2\text{O}_3$  in the deposition system after a vacuum pressure of approximately  $4 \times 10^{-7}$  torr was achieved. The second basket, containing the remaining In and all the Ag was then heated. In view of the much higher vapor pressure of In, a more rapid deposition of In is expected, and the deposited film is expected to be enriched in Ag as deposition proceeds. The deposited In-rich films were approximately 2.2  $\mu\text{m}$  thick.

Cusil-ABA<sup>®</sup> foils (Wesgo<sup>®</sup> Metals, Hayward, CA), which consist of 63.0 wt.% Ag, 35.25 wt.% Cu, and 1.75 wt.% Ti, were cut into 2 cm  $\times$  2 cm  $\times$  50  $\mu\text{m}$  pieces (for joining polycrystalline blocks) or 0.76 cm  $\times$  0.76 cm  $\times$  50  $\mu\text{m}$  (for joining sapphire) pieces, and cleaned and dried thoroughly. The foil was placed between the two In-coated substrates and the entire assembly was loaded into a vacuum hot press. The overall composition of the interlayer is 61.2 wt.% Ag, 34.2 wt.% Cu, 2.9 wt.% In and 1.7 wt.% Ti. In joining the  $\text{Al}_2\text{O}_3$  blocks, the minimum load exerted by the hydraulic press of the hot press yielded a joining pressure of 4.6 MPa.  $\text{Al}_2\text{O}_3$  blocks were joined at 700°C for 1.5 h, 6 h, and 24 h, and at 600°C and 500°C for 1.5 h and 24 h. For comparative purposes, one  $\text{Al}_2\text{O}_3$ /Cusil-ABA<sup>®</sup>/ $\text{Al}_2\text{O}_3$  bond with no In layer was prepared by diffusion bonding for 1.5 h at 700°C with a 4.6 MPa bonding pressure. In addition, a bond was prepared by brazing at 1000°C using a commercial Incusil-ABA<sup>®</sup> foil which consists of 59 wt.% Ag, 27.25 wt.% Cu, 12.5 wt. % In, and 1.25 wt.% Ti. The smaller load-bearing area of the sapphire wafers resulted in a much higher bonding pressure,  $\approx 16$  MPa. As a result, sapphire/In/Cusil-ABA<sup>®</sup>/In/sapphire bonds were also prepared using a dead weight to provide a more modest pressure of 0.6 MPa during joining. The sapphire assemblies were joined at 700°C for 15 min and subjected to additional post-bonding anneals.

The  $\text{Al}_2\text{O}_3$ /In/Cusil-ABA<sup>®</sup>/In/ $\text{Al}_2\text{O}_3$  assemblies were machined into 4 cm  $\times$  2 cm  $\times$  0.33 cm plates. One of the 4 cm  $\times$  2 cm surfaces of each plate was ground flat using a surface grinder and polished in the same fashion as the  $\text{Al}_2\text{O}_3$  blocks. The polished plates were subsequently machined into sets of 4 cm  $\times$  0.3 cm  $\times$  0.3 cm beams. The polished faces of the beams served as the tensile surfaces in the 4-point mechanical bend test. The adjacent edges of the tensile surface were beveled with a 6- $\mu\text{m}$  diamond wheel to remove large surface defects. The joined blocks produced a maximum of 16 beams (each assembly can be cut into 4 plates, and each plate produces 4 beams), but some beams did not survive machining, complicating comparison of the strengths and strength distributions. The final beams were numbered to distinguish their relative positions within each joined set of blocks (*e.g.*, plate and beam numbers). The beams were cleaned in a manner similar to the substrate-cleaning method described above.

The interlayers in the cleaned and numbered beams were examined using both optical and scanning electron microscopy. Due to the high contrast in color between the various phases

present in the interlayers, selective etching was not necessary to distinguish the phases. Energy-dispersive spectroscopy (EDS) was used to obtain the chemical compositions of these phases. After extensive observation in the microscope, the beams were subjected to a 4-point-bend test in a mechanical tester (Instron, Canton, MA). The testing jig consisted of a 0.9 cm inner span and 2.5 cm outer span. The tests were performed using a crosshead speed of 0.005 cm/min and a 100 kg load cell was used to measure the loads.

The sapphire/In/Cusil-ABA<sup>®</sup> joints were also examined using an optical microscope. Since sapphire is optically transparent, these samples provide a plan view of the entire metal-ceramic interface. A microhardness indenter was used to introduce fiducial marks on the external faces of the joined assembly, allowing selected areas of the underlying metal-ceramic interface to be identified and easily located. These fiducial marks allowed the microstructure of specific regions of the metal-ceramic interface to be recorded after bonding and after subsequent anneals in an inert gas (argon) furnace at 700°C for 45 min (1 h total at 700°C), and then an additional 2 h (3 h total at 700°C). Comparisons of the microstructures provide insight on the temporal evolution of the interfacial microstructure.

## Results and Discussion

To assess the success of TLP-based methods of joining we first present results for the unbonded Al<sub>2</sub>O<sub>3</sub> used as this provides a strength target for the joined assemblies. Results for joined assemblies prepared by diffusion bonding provide a second standard of comparison, one we hope to exceed. The results for bonded assemblies are discussed with attention to the effect of bonding temperature and duration on the properties. Finally, interfacial microstructure evolution behavior in model assemblies based on sapphire is presented.

### Fracture properties of the reference alumina

Under ideal conditions, all joints would fail at stresses that approach the fracture strengths of unbonded (monolithic) Al<sub>2</sub>O<sub>3</sub> beams, and most failures would occur in the ceramic. This would indicate that the metal-ceramic interface formed is at least as strong as the ceramic, and that the interface does not include numerous strength-limiting flaws. In addition, for ceramic-dominated failure one would expect the strength distribution to be similar to that of the unbonded Al<sub>2</sub>O<sub>3</sub>, resulting in a similar Weibull modulus.

The Nikkato Al<sub>2</sub>O<sub>3</sub> used has a fine grain size, and some grain growth occurs at elevated temperature. Fracture studies of the as-received base material and the same material after annealing at 1150°C and 1400°C for durations comparable to a typical bonding cycle have shown that at some temperature >1150°C the strength improves with annealing. For the present experiments, the bonding temperatures are sufficiently low that the fracture statistics of beams prepared from as-received material and after a 6 h anneal at 1150°C provide plausible values for the optimum properties to be expected in joined assemblies. A combination of the (similar) datasets for these two materials indicates that the average fracture strength is 320 MPa with a standard deviation of 40 MPa, and the Weibull modulus is ≈7.6 (see Table 1).

### Fracture properties of diffusion-bonded assemblies

The average strength of a diffusion-bonded assembly often increases with increasing bonding temperature and bonding pressure. Increasing the temperature allows for more extensive diffusional flow, and increasing the pressure can also allow for larger driving forces for diffusional flow and activate plastic deformation. These factors increase the area fraction of metal-ceramic contact at the metal-ceramic interface. The bonding temperature (973K) in the present study is a high fraction (92%) of the solidus temperature (1053K) and thus solid-state diffusion and plasticity may be sufficiently activated to contribute significantly to joint formation.

Surface roughness and flatness are important parameters affecting the quality of joints developed by diffusion bonding. Surface roughness measurements performed on similarly processed Al<sub>2</sub>O<sub>3</sub> indicate that Ra (the mean of the absolute values of the height deviations from a perfectly flat surface) is <1 μm when measurements are performed over scan lengths of ≈1 cm. This suggests that on average, the peak-to-valley distances are <4 μm, and thus, Al<sub>2</sub>O<sub>3</sub> surface roughness should not serve as an impediment to successful bonding.

Diffusion bonding at 700°C for 1.5 h with an applied pressure of 4.6 MPa can produce strong beams, however, there is a considerable fall-off in the strength statistics relative to the reference Al<sub>2</sub>O<sub>3</sub>. The average fracture strength of beams that survived machining is 225 MPa, however, the standard deviation is ≈100 MPa, and the Weibull modulus has decreased to ≈1.5. Roughly 40% of the tested beams failed along the metal-ceramic interface. In reality, the drop-off in joint properties (relative to the reference Al<sub>2</sub>O<sub>3</sub>) is even more severe, and the tendency for interfacial failure even stronger. As pointed out, in some cases plates and beams failed during preparation. For the diffusion-bonded specimens, nearly 40% of the potential beams failed during machining. In TLP-bonded samples, some beams with fracture strengths in the 20-60 MPa range survived to the testing stage. This suggests a bimodal strength distribution and the presence of regions of weak (possibly incompletely bonded) interfaces in the diffusion-bonded assembly. If an upper limit of 60 MPa is assigned to the beams that failed during machining, the mean strength drops to ≈170 MPa. A Weibull modulus would misrepresent such a bimodal distribution but a lower value is obtained if the data is “force fit” to a Weibull distribution. A reduction in the bonding temperature would be expected to further degrade the properties of the joints.

### Characteristics of joints prepared by TLP bonding

Figures 1a and 1b show the effect of bonding temperature and bonding time on four-point bend strengths of the Al<sub>2</sub>O<sub>3</sub>/In/Cusil-ABA<sup>®</sup>/In/Al<sub>2</sub>O<sub>3</sub> joints, and Table 1 summarizes the relevant statistical data for all beams that survived machining. The results obtained at 700°C will be discussed fully. Since the bonding temperature has multiple effects, discussion of the bonding results obtained at lower temperatures will be deferred to a later part of the paper.

For TLP bonds produced at 700°C, the average fracture strength is in the range of 230 to 270 MPa, with no clear dependence on the bonding time. Relative to diffusion-bonded samples,

significantly fewer samples failed during machining, and thus the reported numbers are a more accurate depiction of the joint properties than those tabulated for the diffusion-bonded assemblies. In addition, a large number of the tested beams failed at stresses ranging between the values obtained in brazed joints based on Incusil-ABA<sup>®</sup> and for the unbonded reference Al<sub>2</sub>O<sub>3</sub>. Fracture strengths in TLP-bonded samples reach values as high as 400 MPa, and are consistently well above those in the study of Lin [16]. However, the standard deviations in the strength are significantly larger than those for the reference material, and comparable to those obtained for the tested set of diffusion-bonded samples. The Weibull modulus ranges from a low of 1.0 to a high of 2.4, significantly lower than those for the reference Al<sub>2</sub>O<sub>3</sub>. As might be expected, increases in the Weibull modulus parallel increases in the percentage of ceramic failures.

The relatively high frequency of interfacial failures points to several potential problems with the process as implemented. If all samples failed along the interface, and fracture strengths were uniformly low, one might assume that the interlayer chemistry is such that adhesion is uniformly weak. Instead, in the present study, some beams undergo ceramic failure and have high fracture strength. This suggests spatial variability in the interface microstructure, or chemistry, or both. In prior studies of TLP bonding in which thin liquid films formed between the ceramic and core layer, examination of the fracture surfaces of beams that failed along the metal-ceramic interface revealed incomplete metal-ceramic contact. Comparisons of fracture surfaces from samples with relatively lower and higher strength showed a trend towards higher strength as the area fractions of contact increased. Incomplete contact can result from poor surface preparation, an inadequate amount of liquid to fill the interfacial gaps, or a liquid with poor wetting characteristics. In prior work it was found that elements that decrease the contact angle of the liquid on the ceramic could be introduced during melting and associated dissolution of the core layer. This contact angle reduction provides a higher driving force for liquid redistribution and void-filling by the liquid. The use of Cusil-ABA<sup>®</sup> as a core layer was intended to supply Ti to the liquid, and thereby improve the wetting characteristics.

	Avg. $\sigma_F$	Standard Deviation	Weibull modulus	% Interfacial failure
TLP bond 700°C 1.5h	276	102	1.64	40.0
TLP bond 700°C 6h	231	106	1.03	81.8
TLP bond 700°C 24h	272	88	2.38	28.6
Diffusion bond 700°C 1.5h	225	104	1.52	38.5
TLP bond 600°C 1.5h	256	64.2	3.94	12.5
TLP bond 600°C 24h	227	128	1.18	66.7
TLP bond 500°C 24h	267	77.2	2.76	20.0
Incusil ABA brazed bond 1000°C 10h	261	34.5	7.87	0
Reference alumina	320	39.7	7.65	n/a

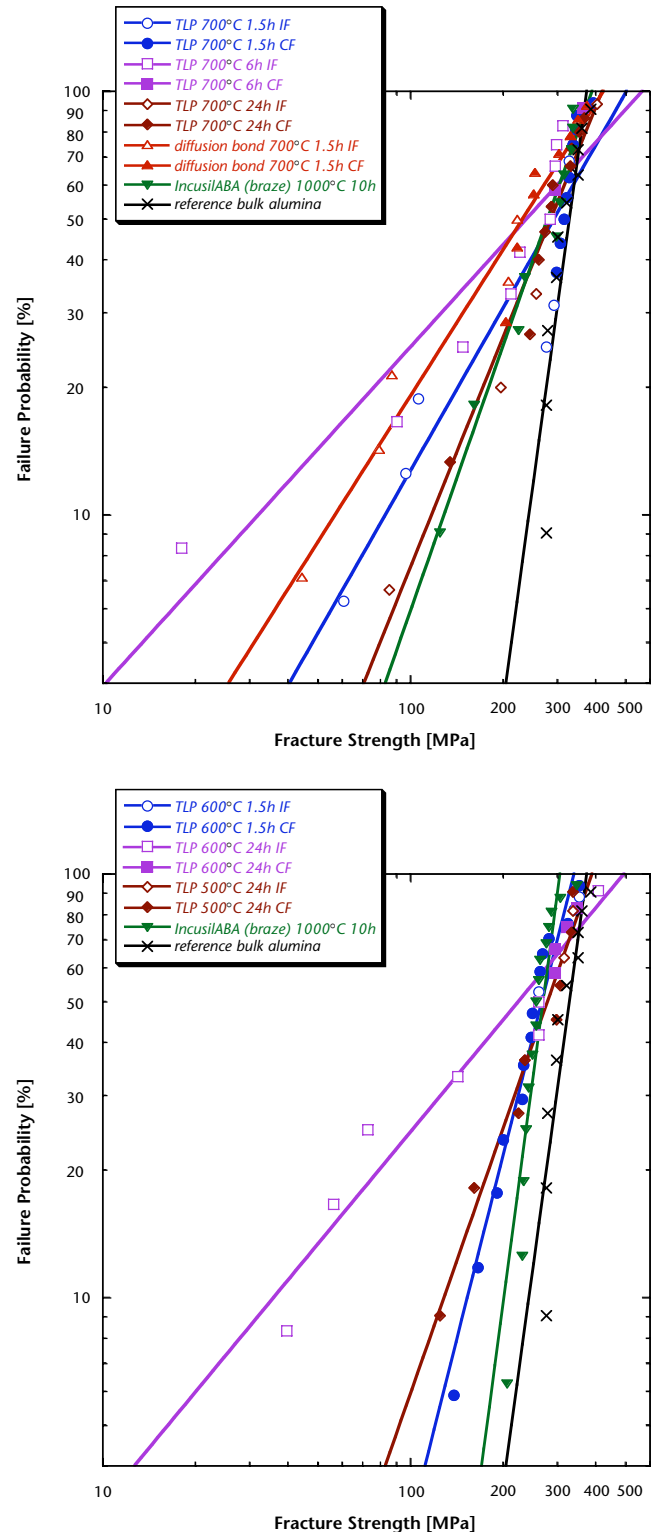


Figure 1 Log failure probability versus log fracture stress for all tested samples. Data for the reference alumina and a brazed joint made with Incusil-ABA<sup>®</sup> are included. Filled symbols represent ceramic failures, while open symbols indicate interfacial failures. Fitted lines are based on all data for a given processing condition. a) bonds formed at 700°C, with hold times of 1.5, 6, and 24 h; b) bonds formed at 600°C and 500°C with hold times of up to 24 h. Strengths approaching those of the reference Al<sub>2</sub>O<sub>3</sub> can be achieved.

Available ternary phase diagrams [18] were used to estimate the amount of liquid formed during bonding at 700°C. Phase relations in the In-Cu-Ag ternary system have been studied, but only over a limited temperature range and at a limited number of temperatures (500°C, 505°C, 676°C). At 676°C, an equilibrium between a liquid containing ≈19 at.% In, and Cu-rich and Ag-rich phases can arise. The isothermal sections suggest that the In content of the liquid increases with decreasing temperature. If we assume that dilute additions of Ti do not dramatically alter the phase diagram, then at 700°C one expects a liquid layer that is roughly five times the thickness of the original In film.

Rougher surfaces would require an increased amount of liquid to fill interfacial gaps, and would also impose more stringent demands on the necessary wetting characteristics. The Al<sub>2</sub>O<sub>3</sub> surfaces are flat and smooth (Ra < 1 μm), and dissolution of Al<sub>2</sub>O<sub>3</sub> into the liquid is negligible at the bonding temperatures. Hence the Al<sub>2</sub>O<sub>3</sub> surfaces should remain smooth. When single-phase core layers are used, a relatively uniform dissolution is expected in regions of core layer-liquid contact. For a liquid film between flat and parallel ceramic and metal surfaces, liquid redistribution and filling of interfacial voids requires that the sum of the contact angles of the liquid on the ceramic ( $\theta_1$ ) and on the core layer metal ( $\theta_2$ ) be less than 180°. When two-phase core layers such as Cusil-ABA<sup>®</sup> are used, the situation becomes more complex. The Cu-rich phase in Cusil-ABA<sup>®</sup> that dissolves to saturate the liquid with Cu is the minority phase in the alloy. Taking the molar volumes of Cu and Ag into account, the area fraction of this phase at the interface should be less than 0.5. However, the equilibrium liquid (at 676°C) contains significantly more Cu than Ag. Therefore a preferential dissolution of Cu must occur to saturate the liquid, and Cu-rich surface grains would be preferentially removed, potentially creating significant depressions in the original foil surface. This can localize the liquid, inhibit liquid redistribution, and result in spatial nonuniformity in the times required for liquid disappearance. The likelihood of interfacial porosity and incomplete metal-ceramic contact increases.

The multiphase character of the core layer can also introduce additional barriers to achieving a liquid with the desired wetting characteristics. One expects that the liquid phase will form acute contact angles on the two dominant solid phases in the core layer. In general, nonreactive liquid metals and alloys form obtuse contact angles on Al<sub>2</sub>O<sub>3</sub>. The incorporation of Ti into the liquid is expected to reduce the contact angle on the ceramic, and thus to help satisfy the condition that  $\theta_1 + \theta_2 < 180^\circ$ . In brazing, the entire interlayer melts, and as a result, the initial physical distribution of the Ti in the foil is not critical. In TLP bonding, Ti can be incorporated into the liquid during dissolution, and also by much slower solid-state diffusion of Ti through the residual Cusil-ABA<sup>®</sup>. As a result, for TLP bonding the physical distribution of Ti may well be a critical issue. The as-received Cusil-ABA<sup>®</sup> foil consists of Cu-rich and Cu-Ti intermetallic particles within a Ag-rich matrix. The majority of the Ti is incorporated in the Cu-Ti intermetallic particles, and it is likely that only those Cu-Ti intermetallic particles that are in contact with the liquid dissolve and provide Ti that could improve the wetting behavior. The optimum foil microstructure and chemistry for TLP bonding and brazing could differ substantially.

Optical and scanning electron microscopy were used to examine a wide range of samples. Figure 2 shows a cross-sectional SEM micrograph of a beam, and the results of EDS analysis across the interlayer along the path indicated. As expected, the foil microstructure contains Cu-rich and Ag-rich phases, and also residual Cu-Ti rich particles. Unfortunately, neither EDS nor WDS were able to distinguish the In signal from that of Ag. The diffusion profile of In as a function of processing temperature and time would give a better idea of the role of the transient liquid layer in the system. The lack of any In signal in the Cu-rich and Cu-Ti particles (where detection of In would be more likely) may indicate that most or all of the In diffuses through the Ag-phase. Other characterization methods to measure the In content will be explored in the future.

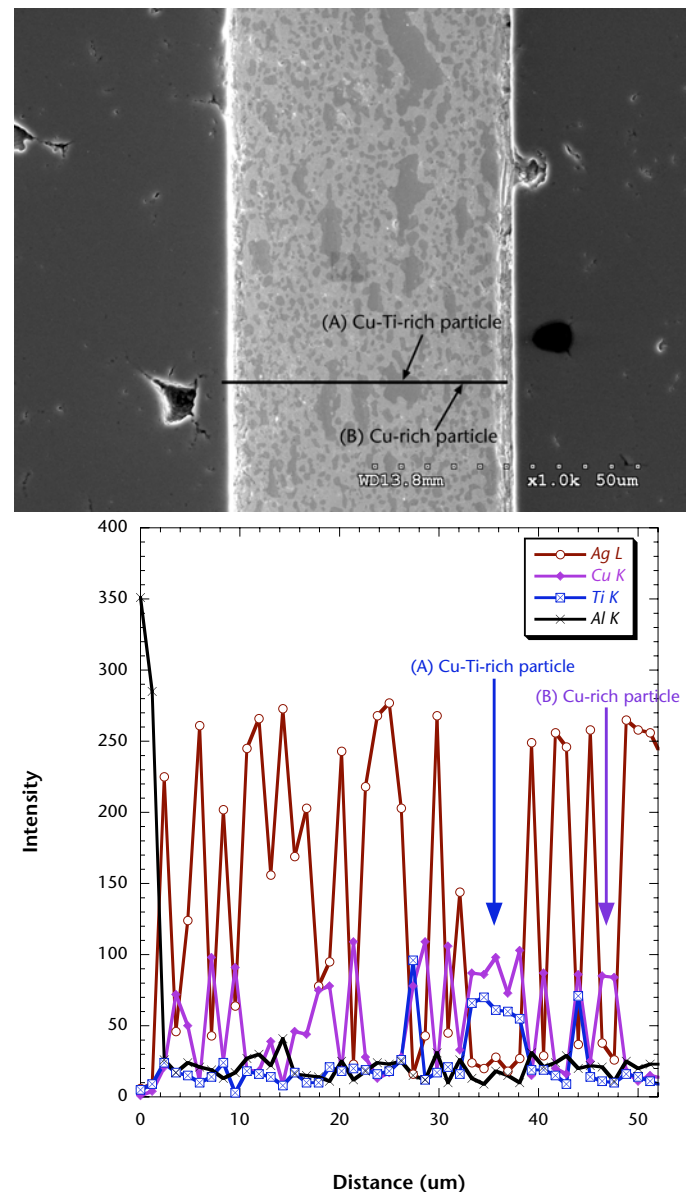


Figure 2 SEM image and EDS scan of a sample bonded at 700°C for 1.5 h. Regions marked A in the scan coincide with a Cu-Ti rich particle. The Cu-rich phase is labeled B. The majority of the scan involves Ag-rich phases. The beam failed in the ceramic when tested.

In brazed joints, an enhancement of the Ti content near the metal-ceramic interface is generally seen in EDS scans, and is associated with formation of a reaction layer. In the sample bonded for 1.5 h at 700°C (Fig. 2), and in all other samples tested, no enhancement of Ti in the near-interfacial region was detected. This strongly suggests that one step towards improving joint quality and strength uniformity will be to explore interlayer designs that promote more extensive Ti dissolution. Use of reactive metal brazes with higher Ti contents may be helpful. In the interfacial region shown in Fig. 2, no large or obvious flaws are seen along the metal-ceramic interface. This sample failed in the ceramic when tested, indicating that strong joints are possible even when reaction layers are too thin to be detected.

Extending the hold time at 700°C was expected to promote either more complete removal of the liquid phase, or more complete homogenization of the interlayer following liquid disappearance, and coarsening of the foil microstructure. Figure 3 provides an example of two regions in the interlayer of a sample processed for 24 h at 700°C. Clearly, the microstructures are very different. The finer scale structure is not unlike that in Fig. 2 after 1.5 h at 700°C, and is similar to that seen in other samples. The coarser microstructure, which was evident at multiple locations within the interlayer of the sample processed for 24 h (and in no other sample in this study) suggests substantial localized coarsening occurred. (We cannot preclude the possibility that this microstructural nonuniformity was present in this particular section of the as-received foil.) In these regions with coarser microstructure, no Cu-Ti rich particles are evident. Since the beams and plates prepared from the assembly are numbered, it was possible to determine which beams ultimately contained this coarser interlayer microstructure. The affected beams failed in the ceramic and exhibited high fracture strengths. Thus, the difference in foil microstructure does not appear to have a detrimental effect on joint strength.

An additional effect of extending the hold time is that it allows for more extensive diffusion of Ti to the metal-ceramic interface. The results summarized in Table 1 indicate that the samples bonded for 24 h had the lowest incidence of interfacial failure and the highest Weibull modulus among samples prepared at 700°C, but even in those annealed for 24 h, no Ti-containing reaction layer was detected. This does not necessarily indicate that no layer is formed, but merely that it is too thin to be detected in a cross-section by EDS. Preliminary results from higher resolution TEM experiments examining bonds made at 700°C with 1.5 h and 24 h bonding times do show a thin reaction layer of as-yet undetermined composition along the metal-ceramic interface.

In an effort to study the microstructural changes that occur at the metal-ceramic interface with increasing time at temperature, multiple sapphire/In/Cusil-ABA®/In/sapphire bonds were made. As mentioned previously, due to the limitations of the hot press and the smaller cross-sectional areas of the sapphire, the 4.6 MPa load used to make the Al<sub>2</sub>O<sub>3</sub> joints could not be reproduced. In an initial attempt at sample preparation, a bonding pressure of ≈16 MPa was imposed. The resulting sample closely resembled a sapphire/Cusil ABA®/sapphire

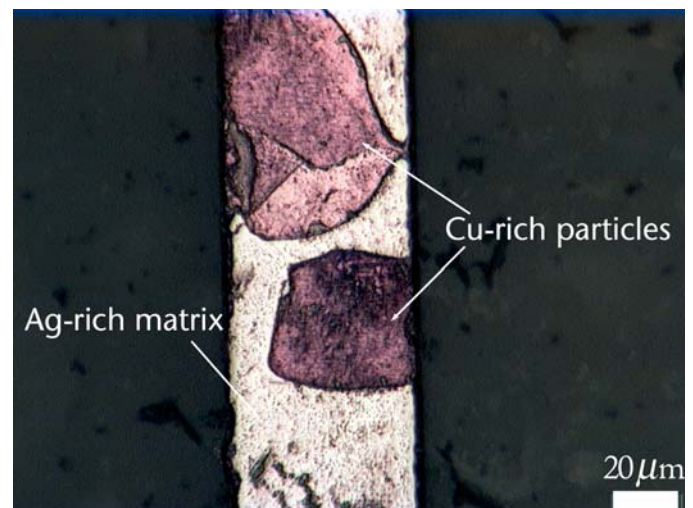
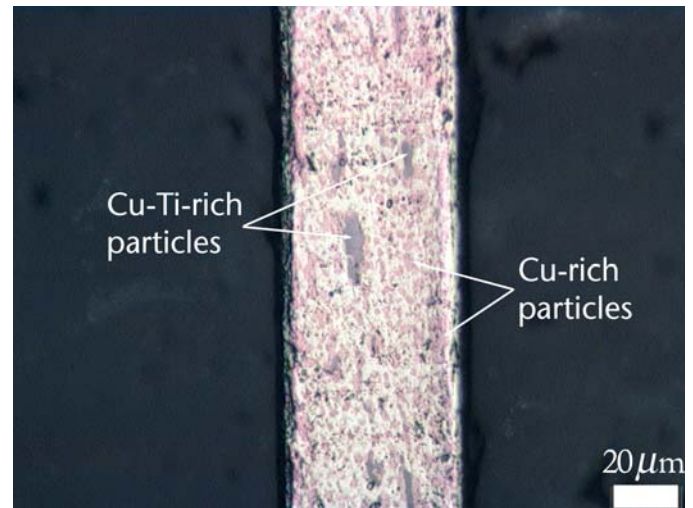


Figure 3 Cross-sectional optical micrographs of the Al<sub>2</sub>O<sub>3</sub>/In/Cusil-ABA®/In/Al<sub>2</sub>O<sub>3</sub> bond regions showing examples of the microstructural extremes.

diffusion-bonded interface, with the exception of a few regions where a reaction layer formed. We speculate that this reaction layer is due to Ti, and its formation is the result of core layer dissolution and reaction of Ti with the sapphire. Furthermore, after the initial bonding period of 1.5 h at 700°C, this reaction layer and many of the other distinctive features of the interfacial microstructure remained stable during an additional 4.5 h anneal at 700°C.

To eliminate/lessen the possibility of excessive pressure squeezing out the liquid phase, stainless steel weights were placed on top of the joining assembly to decrease the applied load to 0.6 MPa. Figures 4a-c show a well-bonded region of the sapphire/In/Cusil-ABA®/In/sapphire joint made at 700°C and held for 15 min, 1 h, and 3 h, respectively. While there are some features that suggest heterogeneity of the interfacial chemistry (*via* color and reflectivity differences), a well-bonded region such as the one shown consists of a relatively stable reaction layer. The lack of any major microstructural differences in these reaction layers resulting from further annealing of the sample suggests that the liquid layer contains an adequate amount of Ti to promote wetting during the initial bonding period. However, because of the reaction layer, it is difficult to observe the In

redistribution or assess the extent of In dissolution into the core layer. It is possible that either all or most of the In was already dissolved into the core layer after only 15 min. Alternatively, an In-containing liquid layer may form below the surface of the Ti reaction layer. The presence of the reaction layer may indicate that at 700°C shorter processing times, on the order of 15 min, may be sufficient to produce high interfacial strengths. The microstructural observations, when coupled with the previously discussed TEM results suggest that the reaction layers may form in less than 15 min at 700°C.

Reductions in bonding temperature are expected to influence the process in multiple ways. As noted previously, the available isothermal sections in the In-Cu-Ag ternary system suggest that the stability range of the liquid shifts toward the In corner with decreasing temperature. As a result, as the joining temperature decreases, a thinner liquid film will be present, and less dissolution of Cu- and Ag-rich phases in the core layer will be necessary. At the lowest temperatures explored, the equilibrium phase diagrams suggest that a liquid phase and the Cu-rich and Ag-rich phases in Cusil-ABA® do not coexist at equilibrium. The liquid may thus be consumed by the formation of a transient ternary intermetallic phase. In either case, less liquid will be available to fill interfacial gaps. Reducing the temperature can also further reduce the (already small) amount of Ti in the liquid. A reduction in the bonding temperature will also decrease the rate of In diffusion into the core layer, and increase the likelihood that residual liquid freezes during cooling rather than disappearing at temperature. Successful joining also relies on a suitable combination of contact angles and wetting characteristics for the liquid on the two adjoining solids, the ceramic and the Cusil-ABA®. Clearly, temperature can affect the liquid composition, the contact angles, and thus influence the driving force for liquid redistribution.

The results shown in Figure 1b indicate that despite all of these potential complications, the interlayer system is able to produce joints with useful levels of strength at both 600°C and even at 500°C. In fact, joints processed in 1.5 h at 600°C had the lowest incidence of interfacial failure among the TLP-based joints, and the highest Weibull modulus,  $\approx 4$ . The assembly produced in 1.5 h at 500°C failed during machining into plates and beams. However, high average strengths, comparable to those obtained when brazing with Incusil-ABA® were obtained in TLP-based joints processed at 500°C for 24 h. Thus, the use of cladding layers provides a potential route to reducing the joining temperature range of commercial reactive-metal brazes.

## Conclusions

Studies of TLP-based joining methods using commercial Cusil-ABA® core layers in conjunction with In-based, low melting point cladding layers have shown that strong joints can be produced using joining temperatures between 500-700°C, well below those normally used for brazing. TLP-based bonds exhibit a mixture of ceramic and interfacial fracture paths, with the fraction of interfacial failures varying with processing conditions. A major challenge will be to decrease the frequency of low-stress interfacial failures, which contribute to significant

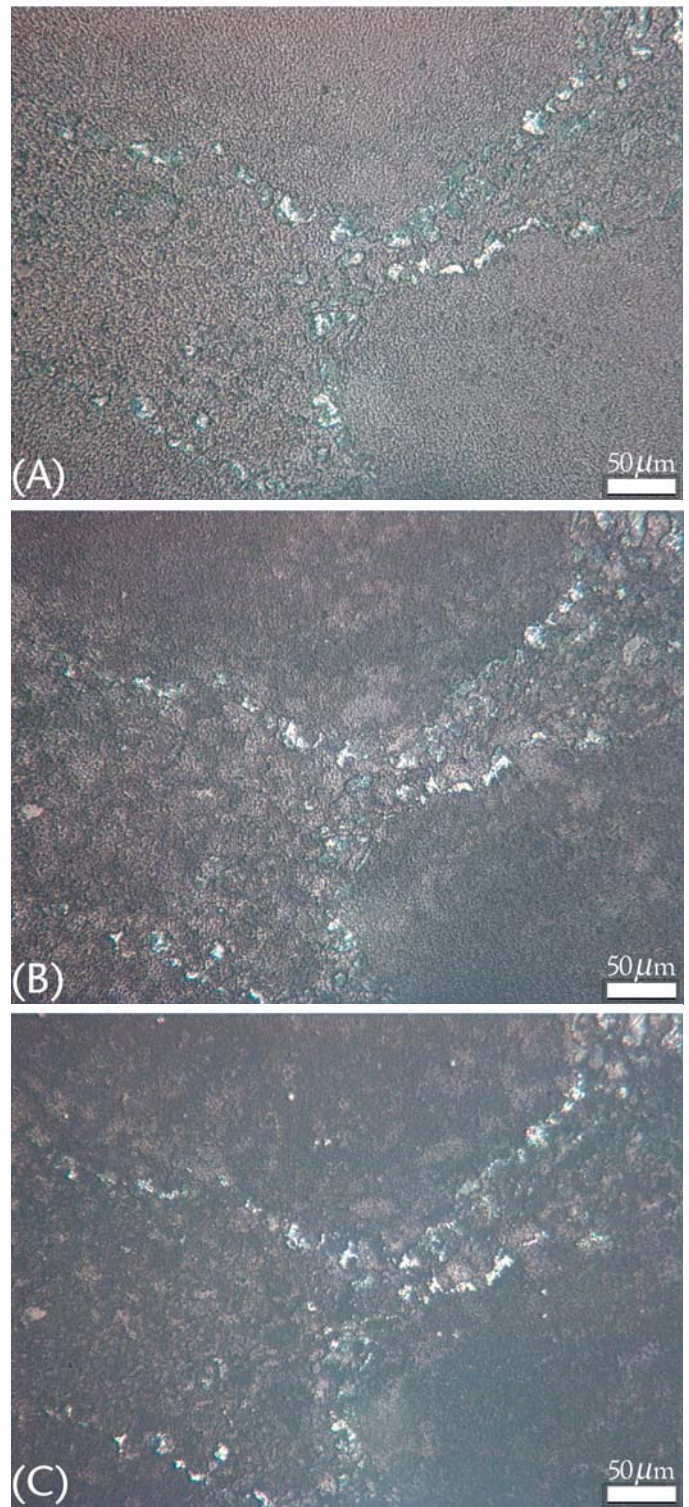


Figure 4 Interfacial microstructure of sapphire/In/Cusil-ABA®/In/sapphire joint after a) 15 min, b) 1 h, and c) 3 h at 700°C.

scatter in the strength and reduce the Weibull modulus. Avenues to be pursued include variations in the interlayer composition and microstructure, and also in the amount of liquid formed. Due to the multiple effects of temperature on the amount and composition of the liquid formed, the topography of the two-phase core layer, and potentially on the wetting characteristics of the liquid, further studies will be needed to



isolate and quantify the effects of In coating thickness and temperature on the resulting joint properties. The observations that strong interfaces can be produced under a wide range of conditions encourage further effort.

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