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New Approaches to Joining Ceramics for High-Temperature Applications

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Abstract: Micro-designed multilayer interlayers have been used to join both oxide and non-oxide ceramics. The approach allows the formation of ceramic–ceramic joints with high melting point metals at temperatures that are typically several hundred degrees lower than those required for more conventional joining methods. The new joining approach employs a thin transient liquid phase (TLP) layer to allow joining by a brazing-like process. Several distinct interlayers have been used to join alumina ceramics successfully; work using Ni-based interlayers has demonstrated the potentially beneficial impact of "reactive" metal additions to the TLP. The method has also been applied to the joining of silicon-based ceramics, and has led to the fabrication of joints with reproducibly high strengths. © 1997 Published by Elsevier Science Limited

1 INTRODUCTION

Utilizing ceramics effectively in structures that consist either entirely or partly of ceramic components requires an ability to join ceramics to themselves or other materials. A variety of reactive metal brazes permit mass production oriented joining for relatively low temperature ($T < 500\,°C$) applications. The commonly used Cu–Ag eutectic-based brazes produce joints with limited oxidation resistance whose strength degrades when $T \geq 500\,°C$.[1] The development of brazing alloys and processes compatible with higher use temperatures is difficult due to incompatibilities in the requirements for processing and ultimate performance. Conventional joining methods either necessarily (brazing), or typically (diffusion bonding) require joining temperatures that exceed the ultimate use temperature of the joined assembly. If the intended use temperatures are high, the required joining temperatures are thus even higher. At these elevated joining temperatures, many metals will react with ceramics to form reaction layers that are often brittle; this is a particular problem for Si_3N_4 and SiC ceramics. When these reaction layers become excessively thick (or defective), performance is degraded. To avoid component degradation and excessive and deleterious interfacial reaction between components, a low processing temperature is desired.

When the components to be joined are chemically dissimilar, the difficulty of developing a suitable joining method is even greater. In such cases, the most temperature sensitive or reactive component in the assembly will define the relevant processing constraints. Physical property (thermal expansion coefficient and elastic moduli) mismatches may be sufficiently intense to require the use of graded interlayers. Although such functionally graded inserts will smooth the variation in materials properties, they may also replace the need to make one joint between dissimilar materials, e.g. a ceramic–metal joint, with the need to make two joints between similar materials, e.g. a ceramic–ceramic and a metal–metal joint. Reactivity and degradation considerations will, however, again be important if the quality of the ceramic–metal interface within the graded interlayer is compromised by exposure to excessive temperature.

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Our efforts[2–7] and those of our collaborators[8–10] have focused on developing joining strategies that combine a low joining temperature and the potential for subsequent high temperature use. To achieve this combination, a departure from the homogeneous interlayer structures typical of brazing and diffusion bonding was implemented. The partial transient liquid phase (PTLP) bonding method is an extension of the transient liquid phase (TLP) joining methods developed for the joining of Ni-based superalloys.[11] In both TLP bonding and in the PTLP method, the interlayer materials solidify isothermally at the joining temperature, however, there is an important difference in the interlayer design. TLP bonding uses homogeneous interlayers that melt completely, while the PTLP method uses inhomogeneous, multilayer metallic interlayers within which only a thin or partial layer melts at the bonding temperature. For example, a thin cladding layer (e.g. 1–5 μm thick) of a lower melting point metal, such as Cu, Au, Ag or their alloys, can be paired with a thicker core layer of a higher melting point metal, such as Ni, Pd, Nb, Pt, etc. The phase diagram for the core–cladding system is such that melting of the lower melting point component initiates at temperatures well below the melting temperature of the core layer. This allows joining to occur at a temperature well below the melting point of the more refractory core material. The core and cladding components must be selected and used in proportions that produce a homogenized alloy or compound with potential for high temperature use. This typically will limit the amount of liquid that is formed relative to that in TLP bonding. This feature has both advantages and disadvantages. The relatively thinner liquid layer places a premium on having well matched bonding surfaces; large interfacial gaps will be difficult to fill using a coated foil interlayer. On a positive note, when compared to TLP bonding, PTLP bonding has greater flexibility in interlayer design and much larger reductions in joining temperature are possible. Thus, metals that cannot be used in normal bonding processes can in some cases form the basis of the core layer in PTLP bonding.

The reactivity of the core and cladding material with the articles to be joined must, of course, also be considered. Ideally, thermodynamic information and phase diagrams can be used to assess the potential for interaction and reaction between the interlayer constituents and the materials to be joined at the joining temperature, at the intended use temperature, as well as during heat-up to and cool-down from the intended use temperature. In practice, the phase diagram base is often not adequate to allow a *complete* assessment of phase equilibria in the four (or more) component systems that result. Interesting and sometimes unanticipated complications can arise due to interactions between sintering additives in the ceramic and the metal, and between low levels of anion impurities (such as dissolved oxygen) in the foil, the foil metal and the ceramic.

2 BACKGROUND

Alumina is a widely used oxide ceramic, and alumina and sapphire have been the most commonly used vehicles for ceramic joining studies. A recent and extensive review of relevant joining studies can be found in Ref. 12. Interlayers used for diffusion bonding have included Nb, Pt, Ni, Cu, Au and Al. The more frequently used brazes include Al, Al alloys, Cu–O eutectics and Cu–Ag eutectic-based alloys. While the brazes provide substantially greater ease of processing, the brazed assemblies lack the high-temperature capability of diffusion bonded assemblies produced with Nb, Pt and Ni interlayers. Due to its widespread use and availability, alumina provided a convenient model system for PTLP bonding studies.

The potential of Si_3N_4 and SiC ceramics for high-temperature applications has prompted considerable interest in developing ceramic–ceramic and ceramic–metal joints involving these materials.[1,12] In general, metals react with silicon-based ceramics to form silicides. With Si_3N_4, nitrides may form; with SiC, carbide formation is possible. Recently, Schuster and co-workers examined phase equilibria in a wide range of Si–N–M and Si–C–M systems, where M represents a metal.[13] Their results confirm and extend the observations made in joining studies — at temperatures normally used for diffusion bonding and brazing, interfacial reactions between metals and these ceramics do occur, and the extent of reaction affects subsequent joint performance.[14] For example, the phase equilibria studies show that in vacuum, reaction between Ni and Si_3N_4 becomes rapid at $T \geq 1170\,°C$; joining studies show that vacuum brazing with pure Ni and Ni-rich brazes at high temperatures does not yield sound joints.[15]

The use of transient liquid phases for metal joining was developed to a high level of sophistication in efforts to mitigate problems in joining temperature-sensitive nickel-based superalloys for aerospace applications.[11] We are aware of relatively few efforts to utilize inhomogeneous interlayers to overcome some of the difficulties associated with high temperature ceramic joining.

Notable exceptions include the work of Iino and co-workers who used multilayer Ni/Nb/Ni and Nb/Ni/Nb foils for diffusion bonding Si_3N_4,[16] and subsequently, multilayer Ti/Ni/Ti interlayers for PTLP bonding[17] of Si_3N_4.

Our prior work has utilized Cu/Pt/Cu,[2] Cu/Ni/Cu[4] and Cu/Nb/Cu[5] interlayers designed to form thin or partial layers of a transient liquid phase to join alumina, and papers are available in the literature. In all three systems, it was possible to produce strong joints at temperatures well below the melting points of pure Pt, Ni or Nb, and below the temperatures generally required to form strong bonds between alumina and these interlayers by solid-state diffusion bonding.

The current paper focuses on results from some more recently studied systems. We have again used multilayer Cu/Ni/Cu based interlayers to join alumina. However, as an extension of previous work, two methods of incorporating Cr were investigated to assess the role of "reactive" metal additions on the quality of joints prepared by PTLP bonding. The effect of varying the interlayer architecture has been examined, and the results compared to those obtained when alumina was joined with a commercial Cu–Ag based brazing alloy. To assess the effect of the cladding material on joint properties, Au has been substituted for Cu, and Au/Ni/Au and Au/80Ni20Cr/Au bonds have been assessed. In an extension of the method to non-oxide ceramics, Si_3N_4 and SiC ceramics were joined using a Cu–Au/Ni/Cu–Au based interlayer designed to form a liquid phase at $<950\,°C$. Changes in processing conditions were found to have a strong effect on Si_3N_4 joint properties. Work by Ceccone and co-workers[9,10] has explored the use of Au/80Ni20Cr/Au interlayers for bonding Si_3N_4.

3 EXPERIMENTAL PROCEDURES

Blocks of 99.5% Al_2O_3 (Coors, Golden, CO), Si_3N_4 (SN84-grade, NGK Insulators) and SiC (Hexoloy, Sohio Engineered Materials, Niagara Falls, NY) with typical dimensions of $19.5\times20.0\times22.5$ mm^3 (Al_2O_3) or $16\times16\times20$ mm^3 (Si_3N_4/SiC) were used as the ceramics in this study. The alumina has a density $\approx98\%$ with a bimodal grain size distribution (with the larger mode at ≈25 μm); the material contains a small amount of glassy phase. The Si_3N_4 material is pressureless sintered and contains Y_2O_3, MgO and ZrO_2 as sintering aids. The SiC material used is pressureless sintered α-SiC containing boron and excess carbon as sintering aids.

The bonding surfaces of the ceramic substrates were polished using successively finer diamond abrasive in an oil slurry, and finished with 1 μm grit size paste. To develop multilayer interlayers for joining, a thin layer of a relatively low melting point metal or alloy was deposited directly on to the polished and cleaned surfaces of a ceramic substrate. A thicker foil of a higher melting point metal was then inserted between the two coated substrate surfaces. The foil or core metal was selected on the basis of its physical properties (e.g. melting temperature, expansion coefficient and elastic modulus), the phase diagram of the coating-foil system, and the chemical compatibility of the foil and coating materials with the articles to be joined, as discussed previously.

The metal foils used for the core layer of the interlayers were typically commercially available and the pure metals were of high purity. Pure Ni foils (Puratronic grade; Johnson Matthey Material Technology, Hertfordshire, UK) of two thicknesses, 100 μm for alumina joining and 25 μm for Si_3N_4 and SiC joining, were used. This material is reportedly $\approx99.994+$ wt% pure with respect to metallic impurities. The 80Ni20Cr foil (Goodfellow, Malvern, PA) is 125 μm thick, and contains Si as its major impurity at an $\approx1.5\%$ level. The 90Ni10Ti foil was ≈100 μm thick and prepared at the Lawrence Berkeley National Laboratory from 99.9+ purity starting materials. For purposes of comparison, a commercial 50 μm thick Cu–Ag eutectic-based braze with Ti additions (Wesgo, Cusil ABA®) was also used.

Cu, Au and a Cu–Au alloy were used as the low melting point coating or cladding metals. Typically, the cladding layers were prepared by evaporation of high-purity source material(s) to generate a coating ≈3–4 μm thick. In some cases, 5 μm thick "microfoils" of high-purity Cu were used in place of a coating. The microfoils become progressively more convenient as the film or cladding thickness increases.

Substrate/interlayer/substrate assemblies were bonded in a vacuum hot press with an applied load of 5.1 MPa (Al_2O_3) or 8.8 MPa (Si_3N_4 and SiC). (These bonding loads were dictated by the limitations of the hot press used, and were not thought to be essential to the success of the joining. More recent studies by Mastumoto *et al.*[8] on Al_2O_3, and by Ceccone *et al.*[10] on Si_3N_4, have used bonding loads much more typical of brazing, and have produced successful joints as well.) During the bonding cycle, the vacuum in the press was in the range of 1.0–2.5×10^{-3} Pa. The bonding temperatures were selected to be somewhat above the melting temperature of the coating layer, and well

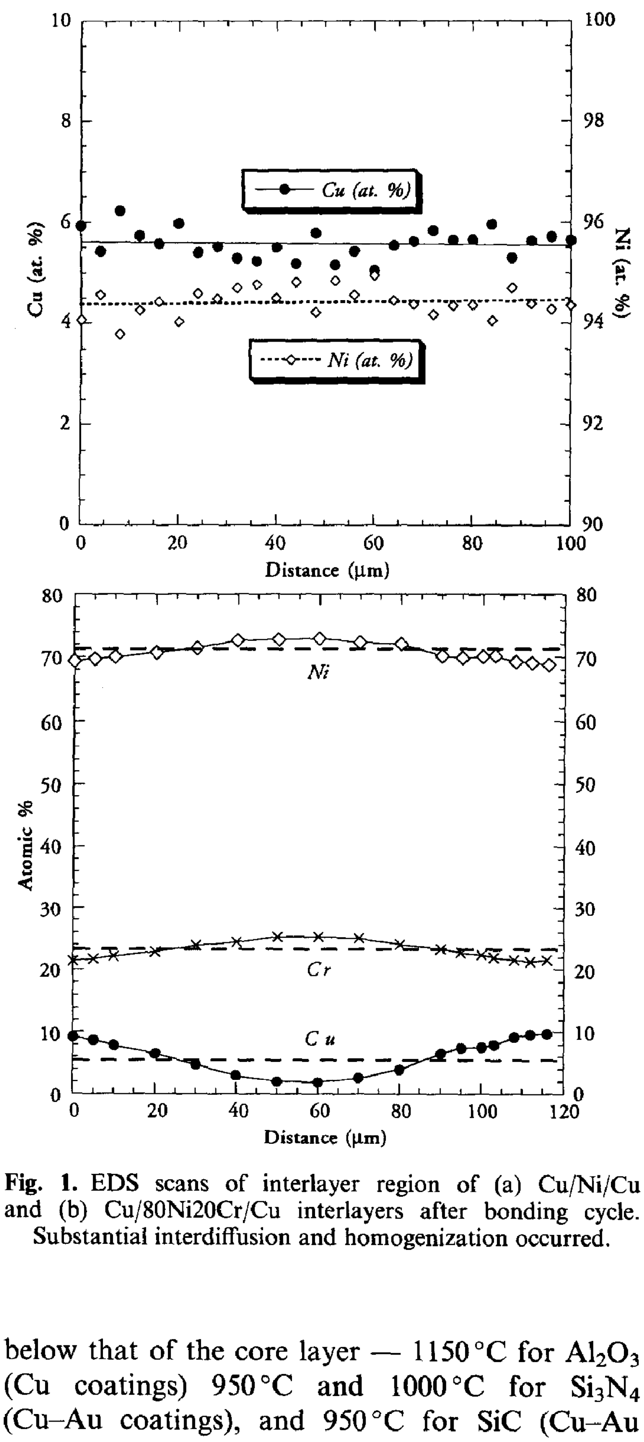

Fig. 1. EDS scans of interlayer region of (a) Cu/Ni/Cu and (b) Cu/80Ni20Cr/Cu interlayers after bonding cycle. Substantial interdiffusion and homogenization occurred.

below that of the core layer — 1150 °C for Al_2O_3 (Cu coatings) 950 °C and 1000 °C for Si_3N_4 (Cu–Au coatings), and 950 °C for SiC (Cu–Au coatings). These temperatures are all well below those normally used for diffusion bonding with the core metal. For Al_2O_3 bonding, heating and cooling rates to and from the bonding temperature are typically 4 °C/min and 2 °C/min, respectively, with a 6 h hold at the bonding temperature. For Si_3N_4, isothermal holds of 2 h at 950 °C and 4 h at 1000 °C were explored to vary the degree of interlayer homogenization during bonding, and cooling rates were varied (2 °C/min from 950 °C and 10 °C/min from 1000 °C) to impact the extent of phase separation in the Ni–Cu–Au alloy during cooling. A bond made with a 50 µm thick layer of Cusil ABA was prepared at 900 °C; the eutectic temperature for the Cu–Ag eutectic is ≈780 °C.

After bonding, the assemblies are cut into beams (typically 2.7×2.7×40 mm) that are polished and tested in the as-processed state at room temperature in four-point bend; a limited number of Al_2O_3 and Si_3N_4 beams were tested at elevated temperature. SEM, EDS and microprobe analysis have been used to characterize the microstructure and chemistry of the interlayer and fracture surfaces. More detailed discussions of the experimental procedures are available in the cited literature.

4 RESULTS AND DISCUSSION

4.1 Alumina bonded with Ni-based interlayers

Cu/Ni/Cu (and Au/Ni/Au) interlayers will evolve towards a homogeneous solid solution at elevated temperature. For the case of Cu/Ni/Cu, it is expected that at 1150 °C, a Cu-rich liquid film will coexist with Cu-saturated Ni. Interdiffusion ultimately causes the disappearance of the thin liquid film, and post-solidification annealing at 1150 °C should lead to the formation of a uniform Ni-rich Cu–Ni solid solution in the interlayer region. Similar behaviour is expected for the Au/Ni/Au interlayers. The Cu/Ni/Cu interlayers for alumina joining were designed to have an average interlayer composition of 94 at% Ni, 6 at% Cu. An EDS line scan perpendicular to the interlayer showed interdiffusion was substantial, and homogenization is essentially complete after processing [Fig. 1(a)]. The solidus temperature for the resulting interlayer is ≈1430 °C, which is within ≈23 °C of the melting temperature of pure Ni. Thus, the desired combination of a low processing temperature and the potential for a high ultimate use temperature was achieved. Similar results were obtained with Cu/80Ni20Cr/Cu interlayers, as shown in Fig. 1(b). We speculate that the somewhat thicker core layer, and resulting increase in diffusion distance, yielded an interlayer that was nearly, but not completely, homogenized.

Specimens bonded with Cu/Ni/Cu interlayers showed the potential for producing strong bonds — strengths as high as ≈270 MPa with ceramic failure were observed — however, the variability of the strength was substantial. As a result, the average strength of the as-processed beams (≈160 MPa) was well below that of the base ceramic (≈285 MPa), and the standard deviation (±63 MPa) was also large in comparison to that of the unbonded reference alumina (±25 MPa). A least squares fit of the data for Cu/Ni/Cu interlayer bonded alumina and for the unbonded alumina is included in Fig. 2. Fractographic analysis suggested that low strengths in this system were associated with regions of poor or incomplete Al_2O_3/interlayer contact. This in turn suggested that changes in interlayer chemistry that would improve the wetting characteristics of the transient liquid layer might lead to strength improvements. Spinel formation also occurred at the interlayer/Al_2O_3 interface, and may have affected the strength values. However, spinel layers were seen on both weak and strong bonds, and thus, did not appear to be the key or sole factor controlling strength.

In contrast, none of the specimens bonded with Au/Ni/Au interlayers were sufficiently strong to survive beam preparation.[18] Since beams with bend strengths as low as 50–60 MPa have survived the cutting, grinding and polishing procedures with other interlayer systems (with similar thermal expansion characteristics), this suggests that the strengths obtained in this system consistently lie below 50–60 MPa. There is again evidence of poor or incomplete Al_2O_3/interlayer contact in this system, and thus, additives that improve wetting might again lead to strength improvements. However, low strengths are also observed in samples where intimate contact between the metal and ceramic was achieved, suggesting that important differences exist in the nature of the bonding between Au and Al_2O_3 and, for example, Cu and Al_2O_3. Prior diffusion bonding studies[19] with alumina, that used gold as the interlayer, have shown that the properties are improved when bonds are prepared in oxidizing atmospheres. Similarly, Dalgleish *et al.*[20] have shown that when alumina/gold diffusion bonds are prepared in air, four-point bend strengths of up to ≈230 MPa are possible with samples of similar size to those prepared by PTLP bonding. The PTLP bonds in this study were prepared in a vacuum with either a refractory metal or graphite present, and thus, in low oxygen partial pressures. The bonding atmosphere, which is generally important, may play a particularly important role in this specific system.

Wetting experiments have shown that Cr additions[8,21] and additions of Ni–Cr alloys[8] to Cu reduce the contact angle of Cu-rich liquids on sapphire[8,21] and Al_2O_3 substrates[8] at 1150 °C. Cr is one of several metals often described as "reactive"; under the present conditions, Cr does not form a reaction product, and thus, changes in the contact angle are associated with beneficial changes in the ratio of interfacial energies at the three-phase junction along the sessile drop perimeter. Experiments were conducted to assess the effects of Cr additions to the transient liquid on the strength characteristics of bonded assemblies.

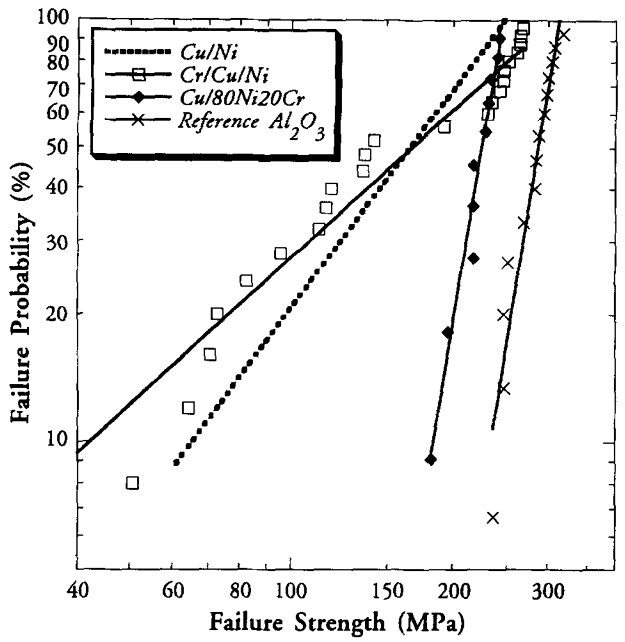

Fig. 2. Comparison of room temperature fracture behaviour of alumina bonded with Cu/Ni/Cu, Cr/Cu/Ni/Cu/Cr and Cu/80Ni20Cr/Cu multilayer interlayers. Note the cluster of high strength bonds achieved with the Cr coating, and the more consistently high strengths obtained using an 80Ni20Cr core layer.

For Cu-based TLP layers, two methods of incorporating Cr were examined. In the first, a thin (≈10 nm) pre-coat of Cr was applied to the alumina prior to depositing the 3 μm Cu coating, and a 100 μm thick Ni foil was used. In the second, no pre-coat was applied, but a 125 μm thick 80Ni20Cr alloy core layer was substituted for the 100 μm pure Ni interlayer. It was expected that at the bonding temperature, dissolution of the pre-coat or partial dissolution of the core layer would occur, and thereby introduce Cr into the TLP layer. These two methods of Cr incorporation yielded strikingly different results. When a Cr pre-coat was used, a large number of specimens exhibited strengths approaching those of the base ceramic, but overall, the average strength of assemblies was unchanged, and the standard deviation was increased. It is possible that this reflects a pre-coat that was too thin; at elevated temperature the pure Ni core layer will incorporate Cr, and thereby remove it from the liquid. Alternatively, the layer may not have been sufficiently uniform. In either case, the pre-coat did not consistently have the desired effect on bond strength. When the 80Ni20Cr core layer was used, the average strength increased to nearly 230 MPa, which represented at that time the highest average obtained (using PTLP bonding) for joined alumina assemblies. In these samples, failure occurred either entirely within the ceramic, or primarily in the ceramic with limited crack propagation along the

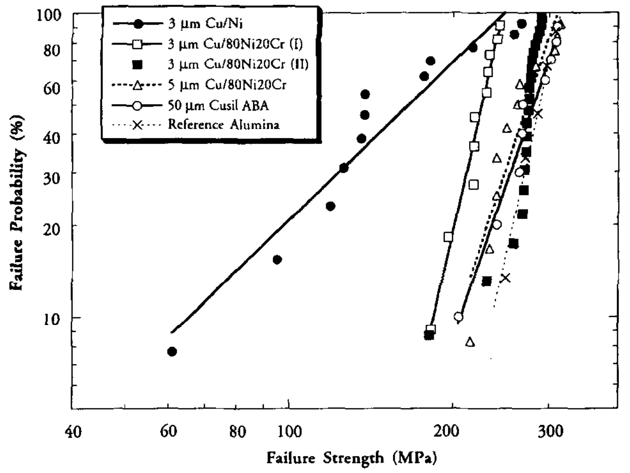

Fig. 3. Comparison of room temperature fracture behaviour of alumina bonded with Cu/Ni/Cu, Cr/Cu/Ni/Cu/Cr and Cu/80Ni20Cr/Cu multilayer interlayers. Note the cluster of high strength bonds achieved with the Cr coating, and the more consistently high strengths obtained using an 80Ni20Cr core layer.

alumina/interlayer interface, suggesting that Cr "strengthens" the interface. The standard deviation in strength (± 19 MPa) is comparable to that characteristic of the unbonded alumina. The results and failure mode suggested that the strength distribution reflects the flaw population of the ceramic, and use of a higher strength alumina might shift the strength distribution of bonded assemblies to correspondingly higher values. Subsequent work by Locatelli[18] using an in-house fabricated alumina with an average bend strength of ≈440 MPa has confirmed this expectation.

When 80Ni20Cr interlayers were used in conjunction with Au-based TLPs, the samples were more tolerant of cutting and handling, but it was still not possible to produce joints with measureable strengths. Initial results of studies using Cu-based TLPs with 90Ni10Ti core layers have been promising. In contrast to Cr, Ti at sufficiently high activity can and does react with alumina, and thus, changes the nature of the ceramic surface. If the weakness of Au/Al_2O_3 bonds is due to intrinsically weak bonding, the use of true reactive elements in the interlayer may be necessary to allow the use of Au-based TLPs. Work on this topic is in progress.

More recent work has examined the effect of Cu–Ni–Cr interlayer architecture on the resulting joint properties. The thickness of the Cu layer was varied somewhat, and slight changes in processing conditions were made. Increasing the thickness of the Cu layer will increase the amount of liquid formed, and thus, should reduce the demands on surface preparation. However, the solidification time will also be increased, and the ultimate temperature capabilities of the joint are diminished if the core foil thickness is held constant. The results are summarized in Fig. 3, and compared with fracture results obtained when the bond is made with a commercial braze alloy. The results show that when the process is optimized, results equivalent to those obtained with commercial brazes are possible, and strength is limited by the strength of the ceramic. Nakashima *et al.*[8] have shown that bonds can be produced using Cu/80Ni20Cr/Cu interlayers while applying substantially lower contact pressure (≈10 kPa) than that used in this study, i.e. similar to those used in conventional brazing. This enhances the attractiveness of the process. Recent mechanical testing by Locatelli[18] on Cu/80Ni20Cr interlayer bonded alumina confirms that these samples retain useful levels of strength to temperatures of up to 1000 °C. We note that these tests were performed using samples with 230 MPa average room temperature strength, and thus, were not processed under optimum conditions. Although more work addressing high temperature mechanical properties is clearly needed, the results collectively indicate that the PTLP method has the potential to provide joints for systems and applications where high processing temperatures are particularly troublesome and deleterious, where high-temperature performance is the end goal, or where both are factors.

4.2 Si_3N_4 and SiC bonded with Ni-based interlayers

The thermal expansion mismatch between Si_3N_4 and SiC ceramics and even refractory metals such as W is significant. As a result, there was a desire to minimize the yield stress of the interlayer, and thereby maximize the potential for the relaxation of thermal expansion mismatch stresses by plastic flow. Since phase diagram and chemical compatibility studies[13] indicate that reaction between Si_3N_4 and Ni becomes observable in vacuum at temperatures of ≈1170 °C, it was thought desirable to reduce the melting temperature of the TLP layer on a Ni core layer relative to that of pure Cu. A TLP layer based on Cu–Au alloys was selected because Cu and Au are compatible with Si_3N_4 to at least 1085 °C and 900 °C, respectively, and the Cu–Au binary exhibits a melting point minimum. To retain the ductility of the core layer, and to improve wetting, ≈4 at% Ti was added only to the Cu–Au layer. The overall composition of the interlayer is < ≈80 at% Ni, ≈10 at% Cu, ≈10 at% Au, with < 1 at% Ti. We note that a braze alloy of this composition would require a higher processing temperature, and use of such a braze would likely lead to excessive interfacial reaction. To compensate for the reduced processing temperature (950 °C or 1000 °C), the reduced processing

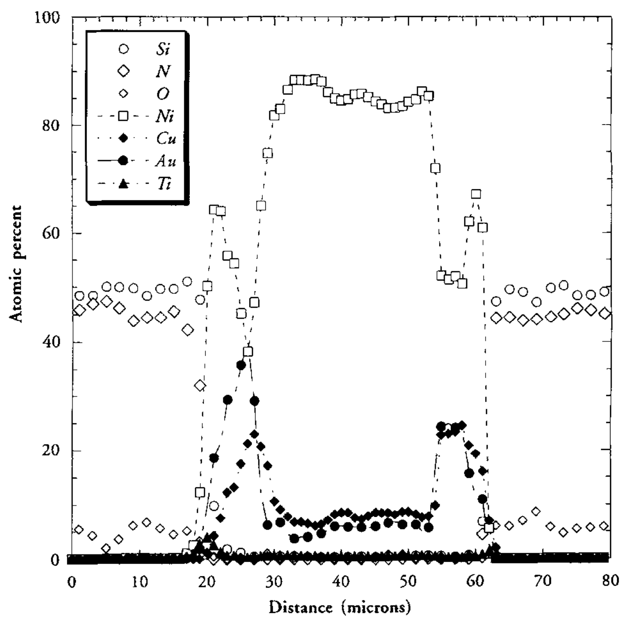

Fig. 4. Microprobe scan results of the interlayer region of Si_3N_4 bonded with a Ni–Cu–Au–Ti interlayer after completion of the bonding cycle.

time (2 h or 4 h), and in an effort to reduce the residual stresses, the Ni foil thickness was reduced from 100 µm to 25 µm.

The results of a microprobe line scan perpendicular to the Si_3N_4/interlayer interface of a sample bonded at 950 °C and slowly cooled to room temperature are provided in Fig. 4. At the left and right extremes, Si, N and O (from sintering additives) are the dominant components, and the composition is, to a good approximation, independent of position. There is a slight enhancement of the Ti concentration near the Si_3N_4/interlayer interface; this is consistent with observations in other systems, where reaction layers containing Ti, e.g. TiN, are formed. In contrast to more typical reactive metal braze formulations, the amount of Ti is quite limited, and thus, the amount of Si liberated by the reaction of Ti with the Si_3N_4 is also reduced. There is a roughly 40 µm thick central region corresponding to the interlayer, within which the composition varies. Some homogenization is evident, with Au and Cu concentrations reaching 5–10 at% at the core. However, there is also a region nearer the Si_3N_4 where the Au and Cu concentrations are higher. A more detailed analysis shows that there are oscillations in the Ni content, with local values as low as 40 at% Ni. The overall profile suggests a process that is more complex than that evident in the Cu/Ni/Cu interlayers.

The phase diagram provides some clues as to the origin of the compositional modulation. The Ni–Cu–Au ternary system has a miscibility gap at $T \leq 970\,°C$,[22] and tie-lines are reported to extend from the Ni-rich corner to the Au–Cu binary. The fully homogenized interlayer has a composition that would lie within the miscibility gap at temperatures below ≈900 °C. As the Ni content is decreased, the onset of phase separation occurs at higher temperatures. Thus, incomplete homogenization coupled with slow cooling from the 950 °C bonding temperature could be expected to lead to a complex two-phase interlayer structure. Figure 5 shows the microstructure of the interlayer. A two (or more) phase structure in the interlayer region is indicated by the contrast difference in SEM. Near the Si_3N_4 interface, the region expected to have the highest Au and Cu content if homogenization is incomplete, a relatively coarse two-phase structure has developed. EDS analysis indicates that the regions of light contrast have a composition of ≈40 at% Ni, ≈39 at% Au and ≈21 at% Cu, while those of darker contrast have a composition of ≈70 at% Ni, 15 at% Au and 15 at% Cu. The respective liquidus temperatures are between 1000–

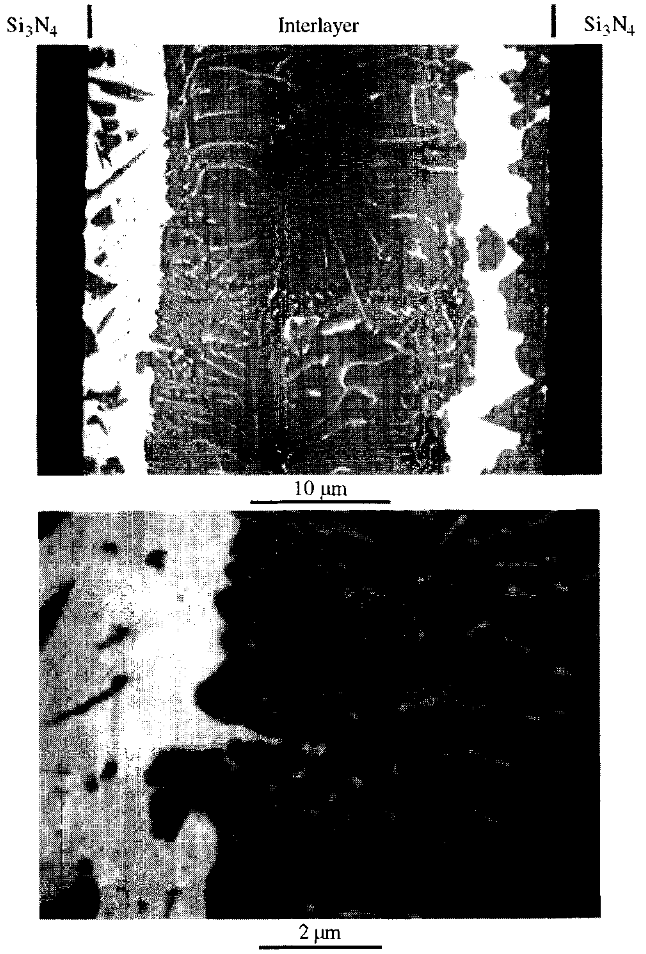

Fig. 5. (a) Low magnification and (b) higher magnification SEM micrographs of interlayer microstructure of bonded Si_3N_4 sample subjected to a short anneal time at 950 °C and slow cooling to room temperature, conditions that promoted phase separation within the interlayer.

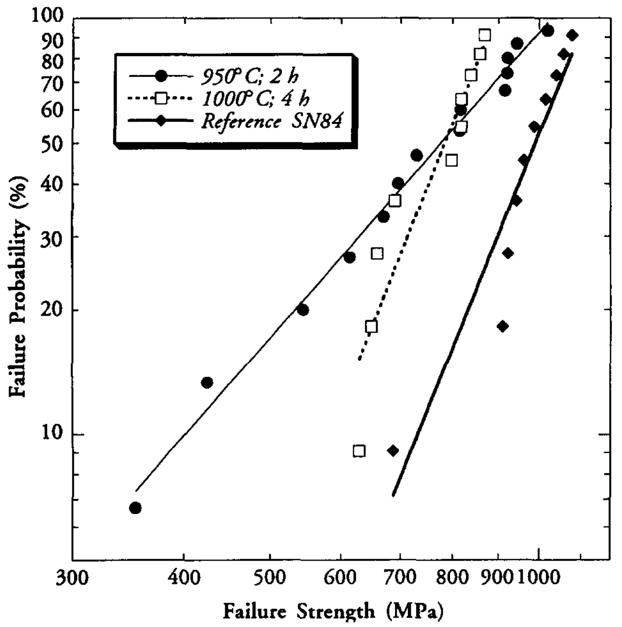

Fig. 6. Plot of failure probability vs failure strength for Si_3N_4 bonded with a Cu–Au–Ni based interlayer, and for the base ceramic. A change in processing conditions led to a substantial change in the scatter in strength values.

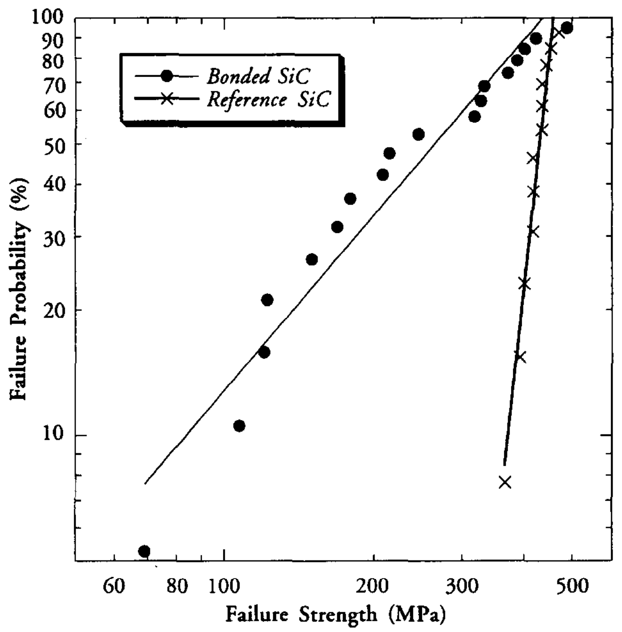

Fig. 7. Plot of failure probability vs room temperature failure strength for unbonded and Cu–Au/Ni/Cu–Au interlayer bonded silicon carbide. As was the case for silicon nitride bonded with the same interlayer, a useful level of strength was obtained in many specimens, however, the scatter in strength is a concern for engineering applications, and steps to narrow the strength distribution are being explored.

1050 °C and 1200–1250 °C. Moreover, the line connecting these compositions extends roughly from the Ni-rich corner to the Au–Cu binary as expected for a tie-line. Nearer the mid-plane of the interlayer, phase separation also occurs, but on a finer scale. The Ni-rich regions contain ≈80–85 at% Ni, while the Ni-poor regions contain as little as 40 at% Ni. Interlayer microstructures in bonded SiC assemblies were not examined in detail, but incomplete homogenization would also be expected. Although the residual inhomogeneity may have little effect on room temperature strength, the regions of lower Ni content can be expected to degrade the joint properties at elevated temperatures.

Room temperature bend tests were performed on both bonded Si_3N_4 and SiC assemblies prepared at 950 °C, and on unbonded reference specimens of comparable dimensions. Results are summarized in Fig. 6 (Si_3N_4) and Fig. 7 (SiC). In both cases, the strongest beams had strengths approaching those of the reference ceramic (960 ± 110 and 420 ± 30 MPa for Si_3N_4 and SiC, respectively). Although the average strengths (770 MPa and 260 MPa for Si_3N_4 and SiC, respectively) were sufficiently high to be useful, the scatter, as measured by the standard deviation (±200 and ±130 MPa), was larger than desirable.

Fractographic analysis of the Si_3N_4 assemblies prepared at 950 °C showed some amount of ceramic failure in virtually all bonded samples, and a trend towards an increasing degree of ceramic (as opposed to interfacial) failure and fragmentation as the fracture strength increased. In some intermediate strength joints, failure involved extensive tearing of the metal foil, and there were instances in which the interfacial debonding switched from one ceramic–metal interface to the other, resulting in the formation of metal ligaments that bridged the crack. For samples with bend strengths above ≈800 MPa, failure was primarily in the ceramic, and crack branching was extensive. This caused fragmentation of the ceramic, and secondary cracking was evident in many samples. The large amount of stored energy in the highest strength samples leads to an "explosive" failure of the specimen. For SiC, the lowest failure strength (69 MPa) was observed in a sample in which a large unbonded region was present along the interface. In some samples, comparisons of exactly corresponding positions on the fracture surfaces again showed that tearing of the metal interlayer occurred. However, for SiC, failure appeared to be dominated by crack propagation within the ceramic. This does not preclude failure initiation at or near the interlayer in the region of most intense residual stress. Further work will be required to identify failure origins, and to understand the cause of the wide strength distribution that is observed.

A specific objective of the present work was to develop an interlayer with high-temperature use capability. A limited number of elevated temperature bend tests were conducted on the Si_3N_4 bonds prepared at 950 °C. The results suggested that at 650 °C, the strength was approximately half the room temperature value; at 800 °C, failure occurred in a ductile manner at very low stress. Thus, a considerable softening of the interlayer occurs in this temperature interval. We believe that this is entirely consistent with the phase diagram, and the observed microstructural and microchemical characteristics of the interlayer. In an effort to eliminate or reduce the softening of the interlayer, processing conditions were modified in a direction that would facilitate more complete homogenization (4 h at 1000 °C), and suppress phase separation during cooling (10 °C/min cooling). The increased homogeneity was expected to improve the high temperature performance of joints. An assessment of the interlayer microstructure and microchemistry is in progress and will be reported elsewhere.

The high temperature properties of the joints produced at 1000 °C have not yet been investigated, however, the room temperature properties of these joints are included in Fig. 6. It was expected that the change in processing temperature would change both the amount and the composition of the transient liquid phase layer, and possibly the contact angles. As is evident in comparing the properties of joints produced at 1000 °C and at 950 °C, the change in processing condition has changed the room temperature properties significantly. Although the average strength is unchanged, the scatter has been reduced significantly, the standard deviation decreasing from 200 MPa to 90 MPa, similar to the standard deviation for the base ceramic. This is an important result, indicating that as was the case for alumina, manipulation of the processing conditions can lead to the development of specimens with reproducibly high bond strengths. It remains to be determined whether with further refinement of the procedure the properties will more closely approach those of the base material.

A number of potential interlayer systems for joining Si_3N_4 systems suggest themselves. Collaborators at the Institute for Advanced Materials (Petten, The Netherlands) have explored the joining of Si_3N_4 with Au/80Ni20Cr/Au interlayers.[9,10] The alloy foil used in this study was 80Ni20Cr with a thickness of either 125 or 25 μm. The Si_3N_4 used for the bonding experiments was a Kyocera material that contained Al_2O_3 and Y_2O_3 as sintering additives. Measurements performed at Petten identified the average strength of monolithic Kyocera Si_3N_4 as 710 MPa, and thus, the strengths of the bonded assemblies can be expected to be somewhat lower than those obtained with the higher strength Si_3N_4 material. The thickness of the Au coating used was 2.5 ± 0.1 μm. A range of bonding temperatures spanning 960–1100 °C was examined.

An assessment of a cross-section prepared after bonding showed that bonding conditions involving a 4 h hold at 1000 °C resulted in acceptable levels of interlayer homogenization, and avoided deleterious reactions. Under these conditions, a reaction product layer of CrN was formed at the interlayer/Si_3N_4 interface. Such joints had average strengths of 272 MPa. These strengths are similar to those achieved by diffusion bonding using 80Ni20Cr foils and optimized procedures.[23]

One particularly significant aspect of the Petten study involves the bonding conditions. The bonding pressure in this work was no more than 0.5 MPa, pressures comparable to those used in conventional brazing processes, and thus well below the levels used in most of the Berkeley work. Experiments at Berkeley duplicating the time–temperature conditions but with an imposed bonding pressure of the order of 5 MPa yielded nearly identical four-point bend strength results. Thus, the results imply that the imposed pressure is not necessary to produce bonds. In the Au/80Ni20Cr interlayer system, most, if not all, failures occurred along the Si_3N_4/interlayer interface. Thus, further refinement of the TLP chemistry and bonding conditions is required, and can be expected to increase the average strength.

5 SUMMARY AND CONCLUSIONS

New approaches to joining ceramics for high-temperature applications using multilayer interlayers have been explored, and the capability of forming strong Al_2O_3–Al_2O_3, Si_3N_4–Si_3N_4 and SiC–SiC joints has been demonstrated. The methods rely on a thin TLP layer that allows joining at relatively low temperature while reducing only slightly the temperature capability of the interlayer relative to that of the pure core layer. As in conventional brazing, reactive metal additions appear to have a beneficial impact on strength characteristics; the use of a Cr-, Ti- or Zr-containing core layer appears to be a viable alternative to deposition of Cr or Ti. A more complete understanding of the factors that lead to interfacial flaws and incomplete wetting is required to allow the more consistent development of strong joints. The recent observation that the bonding pressure can be reduced to levels comparable to those in brazing is promising and merits further study. Finally, the high temperature properties of the joined assemblies must now be characterized to assess the potential of PTLP bonded assemblies for service in high-temperature high-stress applications.

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