

SAND78-1341C
SAND-98-1341C

Recent Progress in Ceramic Joining

RECEIVED

JUN 30 1998

Ronald E. Loehman

Advanced Materials Laboratory
Sandia National Laboratories
Albuquerque, NM 87106

OSTI

CONF-980912

Keywords: Ceramic Joining, Ceramic Interfaces, High Temperature Joining, Ceramic-Metal Interfaces

Abstract

Both fundamental and practical aspects of ceramic joining are understood well enough for many, if not most, applications requiring moderate strengths at room temperature. This paper argues that the two greatest needs in ceramic joining are for techniques to join buried interfaces by selective heating, and methods for joining ceramics for use at temperatures of 800 to 1200°C. Heating with microwave radiation or with high-energy electron beams has been used to join buried ceramic interfaces, for example SiC to SiC. Joints with varying levels of strength at temperatures of 600 to 1000°C have been made using four techniques: (1) transient liquid phase bonding; (2) joining with refractory braze alloys; (3) joining with refractory glass compositions; and (4) joining using preceramic polymers. Joint strengths as high as 550 MPa at 1000°C have been reported for silicon nitride-silicon nitride bonds tested in four-point flexure.

I. Introduction

Techniques for joining ceramics have been under development for at least forty years and have led to many successful applications that are now in wide commercial use. There also have been many parallel advances in understanding of the fundamental processes related to ceramic joining, such as reaction mechanisms, diffusion kinetics, phase behavior, microstructure developments, etc. Because of its commercial importance and the level of research activity, ceramic joining has been the subject of a number of recent workshops, conferences, and special publications. It is beyond the scope of this paper to review all of these results; however, a few references [1-3] will give an idea of the level of activity and the state of knowledge in the field.

The term "advanced ceramics" is generally used to describe ceramics in high value-added, non-commodity applications where the properties of interest are pushed well beyond their typical values for ceramics. More specifically, in the context of ceramic joining, advanced ceramics frequently refers to ceramics for structural applications; that is, ceramics with high strength and toughness and good resistance to thermal shock and oxidation. Much of the research and development on joining such advanced ceramics has focussed on silicon nitride and silicon carbide. One particularly successful development that will be familiar to this audience is joining of a silicon nitride automotive turbocharger rotor to its steel shaft using active metal braze alloys [4].

Methods for joining advanced ceramics for uses at room temperature to possibly as high as 400°C are generally satisfactory for most applications. This is not to suggest that ceramic joining fundamentals are so well understood that any combination of ceramics and metals can be joined and exhibit acceptable properties on the first attempt. However, systematic approaches to joining are available and the number of options is broad enough [5] that a wide variety of ceramics and metals can be successfully joined. The two areas with the greatest need for advances in understanding and improvement in joining techniques are (1) methods for joining ceramics by selectively heating buried interfaces and (2) methods for making ceramic joints that will survive at high temperatures (100-1200°). This paper will discuss the need for such advances and will review recent results in both areas.

II. Joining by Selective Heating of Buried Interfaces

One limitation to conventional ceramic joining is that the entire assembly generally needs to be heated to the temperature where joining is accomplished. This requirement leads to many practical difficulties. For example, large parts need big furnaces, even though the volume of material that must be heated to the joining temperature is a small fraction of the total part volume. Heating large assemblies of heterogeneous materials, particularly those with substantial differences in

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

thermal expansion coefficients (CTEs) can lead to high thermal stresses that must be dealt with. Using selective heating, the volume of stressed material is minimized and the stresses therefore can be lower. The reason buried interfaces are an issue is that the desired joint frequently is in the interior of a volume of material. Further, some assemblies can contain heat-sensitive components, for example hermetic ceramic packages for microelectronic devices, and heating the entire device to the joining temperature can destroy its function. The two techniques for selective heating of buried interfaces that seem to have the greatest potential for selective heating of buried interfaces are microwave heating and heating using high-energy electron beams (e-beams).

1. Microwave Heating

Microwave heating is a technique for ceramic processing that has been the subject of research for more than a decade. The general status of the field was reviewed by the U.S. National Academy of Sciences in 1994 [6] and in a series of symposia sponsored by the Materials Research Society and the American Ceramic Society [7].

Absorption of microwave radiation by ceramics is generally low and thus microwave heating is inefficient for them. As a generalization, low loss dielectrics are transparent to microwave radiation, lossy dielectrics are absorbent, and metals reflect microwaves. Thus a lossy layer buried in a low loss dielectric would be heated preferentially.

The penetration depth in a material at which the incident radiation energy is reduced to half its original value is given by [8]

$$D = 3\lambda_0/[8.686\pi \tan\delta (\epsilon/\epsilon_0)^{1/2}] \quad (1)$$

Where λ_0 is the wavelength, $\tan\delta$ is the dielectric loss factor, and (ϵ/ϵ_0) is the dielectric constant of the materials. The power, P , dissipated in a unit volume of material being heated by microwave absorption is [9]

$$P = (2\pi f \epsilon_r') (E^2/2) \tan\delta \quad (2)$$

where f is the microwave frequency and E is the electric field strength. An interface with high $\tan\delta$ (lossy material) sandwiched between two ceramics with low $\tan\delta$ would be selectively heated.

Microwave heating has not been widely studied as a technique for ceramic joining. Silberglitt, et al., [10-11] joined an assembly of sintered SiC to reaction bonded SiC (RBSC) using a 2.45 GHz multimode microwave cavity. The excess Si in the RBSC material probably enhanced power absorption. The joined part featured both a cylindrical lap joint and an end cap. The assembly was hermetic at room temperature after cycling to 1100°C.

2. E-Beam Heating

High-energy electron beams (e.g., 1 – 20 MeV) can deposit energy at depths of 1 cm or greater in ceramic materials. The differential absorption of electron beam energy in a material is given by [12]

$$dE/dx = -Sp \quad (3)$$

where S is the stopping power of electrons of energy V (in MeV-cm²/g), and ρ is the density (in g/cm³). For uniform stopping power S and an initial beam energy V_0 , the range for power deposition is given by

$$R = V_0/Sp \quad (4)$$

For 1-20 MeV e-beams, $S \approx 2$ MeV-cm²/g. A 10 MeV beam then has a range of about 1.5 cm in Si_3N_4 ($\rho = 10.2$ g/cm³). The temperature increase ΔT in a volume of material under e-beam irradiation is given by

$$\Delta T = \epsilon/Cp\alpha d \quad (5)$$

where ϵ = deposited energy density, Cp = heat capacity, ρ = density, a = area of material, d = thickness. Heating selectivity of a buried metal layer in a ceramic depends on the relative values of Cp and ρ . If $(Cp \cdot \rho)_{\text{metal}} < (Cp \cdot \rho)_{\text{ceramic}}$, the metal layer will be hotter than the surrounding ceramic.

Turman, et al. [12-13] have explored the use of a pulsed electron beam for localized heating to join buried ceramic interfaces in materials such as Si_3N_4 , SiC, Al_2O_3 , Al_2O_3 -Mo composites, and borosilicate glass. The beam was generated by a RF linear accelerator operating at 10-13 MeV. Varying the repetition rate of the beam between 8 and 120 Hz and the current between 8 and 120 μA gave a beam power of up to 1.5 kW. These operating conditions produced power densities between 0.2 and 2 kW/cm² for the beam, which were sufficient to melt Ag-Cu-Ti braze alloys placed between two 1x1x0.3 cm ceramic coupons. Heating times were as short as 5 sec and as long as 600 sec. In other tests 25 μm -thick Pt and Mo foils sandwiched between 1x1x0.3 cm pieces of Si_3N_4 were melted and bonded after 30-300 sec of irradiation with a pulsed e-beam (50-70 Hz) at 10-13 MeV and a beam power of 600 to 5000 w/cm² [12]. Too rapid heating was found to cause

deleterious thermal shock and lower heating rates were required for good joint strengths. Maximum shear strengths of 200 MPa were reported for SiN_4 - Si_3N_4 and Al_2O_3 - Al_2O_3 joints made with Ag-Cu-Ti brazes [13].

III. Ceramic Joints for High Temperature Use

A number of directions are being pursued for developing methods for joining ceramics for use at temperatures above the approximate 400°C limit for conventional joining techniques. In general, these approaches can be classified as (1) transient liquid phase bonding; (2) refractory braze alloys; (3) refractory glass bonding; and (4) joining using polymer-precursors to ceramics. What is common to these methods is production of a liquid phase at the interface that wets the ceramic to produce intimate contact. Presence of a liquid phase, at least initially, is important to avoid the need for high contact pressures that is characteristic of solid-state diffusion bonding. The requirement for high pressures makes solid-state bonding impractical for most applications. Of course, the liquidus temperature of the bonding material either must be above the desired use temperature for the joint or it can be present only as a transient phase during joining. The four approaches will be discussed separately below.

1. Transient Liquid Phase Bonding

As applied to ceramic joining this technique is a modification of one common in metals joining. In simplest terms, it uses alloys or layers of metals, one component of which initially melts to wet the ceramic surfaces. This transient liquid phase then disappears after it forms a higher melting alloy by dissolving the other metal components. The potential advantage is that the joining temperature in principle can be below the use temperature of the joint. Specific examples include Al_2O_3 joined to Al_2O_3 with interlayers of Cu/Pt/Cu, Cu/Ni/Cu, and Cu/Nb/Cu [14]. The principal disadvantage to this approach using metal alloys is that to date the number of alloy systems with the necessary combination of desired phase behavior, good wetting, and acceptable reactivity for joining have been very limited.

A variation of transient liquid phase bonding is being developed for SiC ceramics [15-16]. In this method the SiC surfaces to be joined are coated with a layer of carbon or "carbonaceous material". The coatings are heated at 110-120°C to make them adhere to the SiC surfaces. A layer of Si or Si alloy is then heated between the carbon-covered surfaces at a temperature above the melting point of the Si or Si alloy (1250-1450°C). The Si or alloy melts, wets the surfaces and reacts with the carbon to make a layer of SiC that bonds the two surfaces together. Joint strengths depended on the particular SiC being joined and on the part geometry. A four-point flexural strength of 267 MPa at 1350°C was quoted for joined Hexoloy-SA SiC [15-16].

2. Braze Alloys for Elevated Temperature Use

As stated above, Ag-Cu-Ti is the most common active metal alloy system for braze joining of ceramics. This system has liquidus temperatures in the 700-800°C range and use temperatures up to about 400°C. Braze alloys for making ceramic joints that can function at higher temperatures must have higher liquidus temperatures because the maximum use temperature of the joint will always be lower than the joining temperature. There have been a number of such studies reported [17-22]. Two examples will be described here that are typical of this approach to increasing the use temperature of ceramic braze joints.

Paulasto, et al. [17] reported brazing Si_3N_4 with an Au-Ni-V-Mo filler alloy. This alloy has a liquidus temperature 100-150°C higher than the more common Ag-Cu-Ti alloys. Vanadium serves as the active element that promotes wetting and interfacial reaction through formation of VN, VSi_2 , and V-Si-N phases [17]. Fracture tests of bonded specimens showed they retained their room temperature strengths (350-400 MPa) at 500°C. Strength decreased linearly with temperatures above 500° and was about 25% of the RT value (100 MPa) at 800°C.

Glass, et al. [18] and Loehman, et al. [19] discussed joining Si_3N_4 with Pd-Au-Ti and Pd-Au-V alloys. In the former case, the Ti was not part of the braze filler alloy, but was added as a coating to the ceramic before heating. In the latter case, the V was part of the 92Au-8Pd braze filler alloy at a level of 3-4 wt%. This alloy system was quite refractory, with a liquidus temperature of 1200-1240°C for the base 92Au-8Pd alloy [20]. Joining was done at 1300-1400°C in Ar. The active metal addition promoted wetting and bonding and, in the case of the Au-Pd-V alloy, formed a VN reaction layer at the interface and PdSi_2 in the residual Au-Pd alloy in the joint. The joining reaction was reported to be $\text{Si}_3\text{N}_4 + 4\text{V} + 6\text{Pd} = 4\text{VN} + 3\text{Pd}_2\text{Si}$ [19]. Four-point bend tests of Si_3N_4 joined with Au-Pd-M gave average joint strengths of 350 MPa at room temperature (M=V) and 200 MPa at 600°C (M=Ti) and 180MPa at 800°C (M = Ti) [18, 19, 21].

3. Joining Ceramics with Refractory Glasses

Some time ago, Loehman and co-workers [23, 24] discovered that silicon nitride can be joined using mixtures of oxides similar in composition to the grain boundary phases in silicon nitride ceramics. The oxide joining compositions were prepared as homogeneous glasses from oxides that have particularly high metal-oxygen bond strengths and thus are refractory and chemically stable. During bonding some of the silicon nitride dissolves in the molten glass to give a mixture of crystalline and amorphous oxynitride phases when cooled. Silicon nitride joined with thin layers of glass by heating to 1400 - 1700°C in Ar or N_2 had four-point bend strengths of 400 - 500 MPa at room temperature [25]. Recent work with refractory glass joining compositions based on the Y_2O_3 - Al_2O_3 - SiO_2 (YAS) and SrO - Al_2O_3 - SiO_2 (SAS) systems gave high

joint strengths at 1000°C [19, 26]. The average strengths of joined AS800 silicon nitride specimens at 1000°C were approximately 80% of the strength of the base Si_3N_4 and were higher even than the average of joined AS800 Si_3N_4 measured at room temperature. The increased strength at high temperature may have been due either to crystallization of the grain boundary phase after high temperature exposure or to the decreased thermal expansion mismatch strain between the joint phase and the base Si_3N_4 at 1000°C relative to that at room temperature. Cracks in the boundary phase perpendicular to the joint were consistent with the combination of a higher expansion oxynitride joint phase and the lower expansion of the base Si_3N_4 . This method of using refractory glass compositions is also being explored for joining SiC composites [26].

4. Joining Ceramics with Pre-ceramic Polymers

Pre-ceramic polymer is the name given to organo-silicon polymers that can be pyrolyzed to ceramics. Typical polymer compositions include polysilizanes, polycarbosilanes, polysilanes, and polysiloxanes, which can be transformed to silicon nitride, silicon carbide, silica, or mixed compositions. Because the bond rearrangement that occurs during pyrolysis can lead to adhesion of the polymer to ceramic surfaces, use of pre-ceramic polymers is a promising approach to ceramic joining [26]. In one example polycyclomethylsilizane blended with a powder mixture of Si_3N_4 , Y_2O_3 , and Al_2O_3 was used to join test bars of sintered silicon nitride [27]. Joining consisted of two-stage heat treatment of pyrolysis followed by bonding and consolidation of the joint region. This process yielded maximum four-point fracture strengths of 240 MPa at 1000°C, which were 44% of the strength of the monolithic bars at 1000°C. The authors stated that the strengths would have been higher if the joint region had been more completely filled with the polymer adhesive [27]. Other polymer compositions have been used for joining SiC ceramics [28].

Pre-ceramic polymers have several advantages for making ceramic joints that will be useful at high temperatures. One advantage is that, in principle, the composition of the joint can be tailored to match that of the ceramic. Before pyrolysis the material is like an organic adhesive or glue so coverage of microscopic surface roughness can be accomplished before heat treatment without high, applied pressures. Heat treatment converts the polymers to ceramics so the joint should be as refractory as the base material. The main problem to date has been the presence of porosity and incomplete filling of the joints because of insufficient wetting of the ceramic surface by the polymer and from gas evolved during pyrolysis.

IV. Conclusions

Both fundamental and practical aspects of ceramic joining are understood well enough for many, if not most, applications requiring moderate strengths at room temperature. This paper has reviewed progress in two emerging areas of ceramic joining: (1) techniques to join buried interfaces by selective heating, and (2) methods for joining ceramics for use at temperatures of 800 to 1200°C. Heating with microwave radiation or with high-energy electron beams has been used to join buried ceramic interfaces. Microwave heating requires careful choice of materials so that the joining medium preferentially absorbs the incident radiation. The best progress to date has been made in joining SiC. E-beam joining depends on the difference in heat capacity in the bonding medium and the surrounding ceramic that causes the joint region to be preferentially heated. Only small test specimens have been joined so far by this method.

Joints with varying levels of strength at temperatures of 600 to 1000°C have been made using four techniques: (1) transient liquid phase bonding; (2) joining with refractory braze alloys; (3) joining with refractory glass compositions; and (4) joining using preceramic polymers. Use of more refractory braze alloys requires the smallest departure from current commercial practice with active metal braze alloys. However, the potential for improvement in use temperatures is lowest for braze alloys. Joining with refractory glasses has given the highest strengths at high temperatures of all the techniques discussed. Four-point flexure strengths as high as 550 MPa at 1000°C have been reported for silicon nitride–silicon nitride bonded with a refractory glass composition. Joining ceramics with preceramic polymers has great potential for achieving desirable high temperature properties. However, problems with surface wetting and joint porosity from pyrolysis gases need to be solved to achieve this potential.

References

1. M. Santella, *Ceramic Bulletin* **71**, 947 (1992).
2. K. Suganuma, pp. 523-531, in *Engineered Materials Handbook*, Vol. 4 (S. J. Schneider, ed., ASM International, Metals Park, PA, 1991).
3. *Structural Ceramics Joining II, Ceramic Transactions* 35, (A. Moorhead, R. Loehman, and S. Johnson, eds, American Ceramic Society, Columbus, OH, 1993).
4. M. Itoh, N. Ishida, and N. Katoh, Tech. Paper Series, No. 88074, Society of Automotive Engineers, 1986.
5. E. Beauchamp and S. Burchett, pp. 532-41 in *Engineered Materials Handbook*, Vol. 4 (S. J. Schneider, ed., ASM International, Metals Park, PA, 1991).
6. *Microwave Processing of Materials, Publication NMAB-473* (National Academy Press, Washington, DC, 1994).
7. See for example, D. Clark, W. Tinga, and J. Laia, Jr., *Microwaves: Theory and Application in Materials Processing II, Ceramic Transactions* Vol. 36 (American Ceramic Society, Columbus, OH, 1994).
8. W. Sutton, *Ceramic Bulletin* **68**, 376 (1989).
9. J. Katz, *Ann. Rev. Materials Science* **22**, 153 (1992).

10. I. Ahmad, R. Silberglitt, Y-L Tian and J. D. Katz, *Ceramic Transactions* **80**, 455 (1997).
11. R. Silberglitt and G. Danko, *Proceedings of the 22nd Annual Conference on Composites, Materials and Structures* Cocoa Beach, FL, January 25-30, 1998 (in press).
12. B. Turman, S. Glass, J. Halbleib, D. Helmich, and R. Loehman, *Sandia Report* SAND95-0595 (NTIS, Springfield, VA, 1995).
13. B. Turman, S. Glass, P. Yang, F. Gerstle, J. Halbleib, T. Voth, B. McKenzie, J. Clifford, and K. Habiger, *Sandia Report* SAND97-2785 (NTIS, Springfield, VA, 1997).
14. M. Schalz, B. Dalglish, A. Tomsia, and A. Glaeser, *Ceramic Transactions* **35**, 301 (1993).
15. M. Singh, *Scripta Materialia* **37**, 1151(1997).
16. M. Singh, S. Farmer, and J. Kiser, *Ceramic Sci. and Eng. Proc.* **18**, 161(1997).
17. M. Paulasto, G. Ceccone, S. Petevs, R. Voitovich, and N. Eustathopoulos, in *Ceramic Microstructures '96* (A. Tomsia, ed., Plenum, New York, NY, to appear 1998).
18. S. Glass, F. Hosking, R. Loehman, F. Mahoney, J. Pollinger, J. Stephens, and P. Vianco, *Int. J. Materials and Product Technology*, to be published 1998.
19. R. Loehman, S. Glass, B. Quillan, F. Mahoney, F. Hosking, J. Stephens, P. Vianco, and J. Pollinger, Proc. NATO Advanced Workshop on Interfacial Science in Ceramic Joining, Bled, Slovenia, Klewer, Netherlands, to be published 1998.
20. H. Okamoto and T. Massalski, *Binary Alloy Phase Diagrams*, ed. T. Massalski, ASM International, Metals Park, OH, 1986.
21. J. Stephens, P. Vianco and F. Hosking, *JOM* **54**(1996).
22. A. Hadian and R. Drew, *J. Am. Ceram. Soc* **79**, 659(1996).
23. R. Loehman, U.S. Pat. No. 4347089, Aug. 31, 1982
24. M. Mecartney, R. Sinclair, and R. Loehman, *J. Amer. Ceram. Soc.* **68**, 472 (1985).
25. S. Johnson and D. Rowcliffe, *J. Amer. Ceram. Soc.* **68**, 468 (1985).
26. S. Glass, F. Mahoney, B. Quillan, J. Pollinger, and R. Loehman, *Acta Materialia*, to appear 1998.
27. S. Johnson, Y. Blum, G. McDermott and M. Gusman, *Scripta Metall. et. Materialia* **31**, 1025 (1994)
28. Z. Zheng, O. Unal, and M. Akinc, paper SXV-026-97, *Ceramic Bulletin* **76**, 236 (1997).

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.

M98005922



Report Number (14) SAND--98-1341C
CONF-980912 --

Publ. Date (11) 199809
Sponsor Code (18) DOE/EE, XF
UC Category (19) UC-1404, DOE/ER

19980720 072

DOE