Ceramics International 22 (1996) 527–533

0272-8842(95)00134-4
0272-8842/96 $15.00+.00

Joining Nitride Ceramics*

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(Received 21 June 1995; accepted 2 September 1995)

Abstract: Nitride ceramics are gaining importance in advanced technology applications. Examples include high temperature engine components of Si_3N_4, heat dissipating electronic substrates of AlN, and chemically inert cutting tools of cubic BN. The effective and widespread use of nitrogen ceramics in these and other applications, however, depends on the ability to bond them to metals, as well as to other ceramics.

Bonding ceramics to metals is inherently difficult because of their non-metallic characteristics, and this can be aggravated for nitride ceramics by their tendency to dissociate in vacua. The successful production of reliably strong joints by diffusion bonding and brazing with reactive filler metals is discussed. Reference will be made to the joining of AlN, BN and particularly Si_3N_4 using alloys containing reactive elements, and comments will be made on the influence of process and parameters such as temperature, environment and ceramic surface preparation on the microstructure, mechanical properties and high temperature stability of interfaces. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

There exists a large number of inorganic nitrides, but only those of a few of transition metals (Ti, Ta and Zr) and in particular those of B, Al and Si, are currently of technological importance for applications as varied as their physical and mechanical properties.[1] Thus, Si_3N_4 (SN) and its derivative SiAlON ceramics have excellent high temperature mechanical properties, wear, corrosion and thermal shock resistance, that make them suitable for components in near adiabatic engines, heat exchangers and wear resistant parts. AlN has received much interest in the electronics industry in recent years for applications where Al_2O_3 and BeO were once the choice, because of its high thermal conductivity and an expansion coefficient close to that of Si. Its potential applications range from substrates for hybrid circuits, heat spreaders to electronic ignition modules. It is also a viable material candidate in structural applications where electrical insulation, thermal conductivity and/or specialized thermochemical resistance is of consideration. Cubic BN, CBN, with a hardness second only to that of diamond and chemically inert is used for high-performance tool bits and in special grinding applications.

Many of the potential engineering applications of nitride ceramics require them to be fabricated as large and complex shaped components or more often to be functionally or structurally interfaced with otherwise metallic structures. Hence, the obvious alternative to fabrication techniques and the required development is that of reliable joining technologies, if the full potential of these ceramics is to be realised. Considerable effort has been devoted to the development of joining technologies in recent years and this article focuses on the materials science aspects that have proved of importance by referring to the bonding behaviour of AlN, BN and particularly to that of Si_3N_4.

*Research carried out within the Commission research and development programme.

2 JOINING PROCESSES

Many techniques can be used in principle to join ceramics to metals and those that have been employed in practice range from mechanical attachment to welding.[2] For nitrides, however, the range is more restricted; the most favoured technique is brazing, but diffusion bonding is advocated for joints that must withstand high service temperatures. For brazing it is essential that the molten filler metal wets the workpiece, but nitrides are generally not wetted by braze metals such as Ag or Cu and specialized procedures have to be used to ensure success. Conventional brazes such as the Ag–28Cu* eutectic can be used provided the ceramic surfaces have been metallized. Recent developments have led to new brazes that contain chemically reactive components such as Ti and do not require modification of the ceramic surface.[3] These active metal brazes wet in vacuum or inert atmospheres because the Ti reacts with the nitrides to form wettable reaction product layers. Ti activated Ag–28Cu eutectic brazes have been commercialized, but laboratory studies show that Ni brazes containing Cr and also Al and Al alloys can wet and bond with nitrides.[4,5]

Ceramic/metal (C/M) interfaces are created during diffusion bonding by the application of pressure at high temperatures. For nitride ceramics this must be done in vacuum or inert gas environments. Ceramics can be diffusion bonded directly to metals,[6] but it is often advantageous, if not necessary, to use foils of ductile metals as interlayers to promote bonding and accommodate some of the thermal and elastic mismatch between the workpieces. Such joints are produced by applying pressures of typically 10–100 MPa for up to a few hours at temperatures of 0.7–0.95 T_m of the foil.

Brazing, diffusion bonding and other joining techniques have been used in many laboratory studies, and some of the processes have progressed to production. At present the application of the techniques tends to be material and application specific, so each of the three nitrides of interest will be considered separately.

3 JOINING AND BONDING MECHANISMS

3.1 AlN

Since AlN has received primary interest in electronics applications as a substrate, its joining requirements are concerned with metallization and hermetic packaging.[7] Much of today's technical work on AlN addresses the metallization challenge.[8] The investigations range from studies on suitable glass compositions for glass-frit bonding of AlN to the suitability of the Mo–Mn process.[9–13] Another process which looks promising is DBC (direct bond Cu). Although the method and its acronym imply that Cu is bonded to AlN without any intermediary bonding layer, it is apparent that stronger bonding is achieved by preoxidizing the ceramic surface.[14,15] Obviously, joining takes place then via the gas–eutectic bonding route in a controlled partial pressure of O_2 environment.

*Unless otherwise specified, nominal compositions (wt%) are given.

Techniques for hermetic sealing of AlN using conventional and active metal braze alloys are also developed. Using *in situ* decomposition of TiH_2 or ZrH_2 [16] during the braze cycle to metallize the AlN surface, good quality AlN/AlN joints were obtained using Ag–22Cu–22Zn braze, with Ti_2N, Ti_3Al or ZrN and Zr_3Al identified as the reaction products. A sound bond was obtained when AlN was brazed to a low expansion Fe–Ni alloy ($\Delta\alpha \approx 2\times10^{-6}/°C$), but severe cracking occurred when the ceramic was brazed to Cu ($\Delta\alpha \approx 12.4\times10^{-6}/°C$).

Al does not wet at temperatures below 1000°C, but brazes based on the Ag–28Cu eutectic with 1–5% Ti or Zr additions [17–20] were found to wet AlN and react with it at temperatures as low as 800°C, as shown in Fig. 1. Detailed microstructural studies of the braze/AlN joint, which found TiN at the interface and a complex η-phase $(Ti, Cu, Al)_6N$ adjacent to it,[21] have clarified the role of the TiN formation in bonding, although the bond strength has not yet been evaluated. The only aspect that is sketchy at present is the formation of aluminides (e.g Ti_3Al) at the interface, reported by some but not all studies, and its role on the bond quality.[5,10,17] Using an Ag–Cu–Ti braze, AlN could also be bonded to Cu when a W intermediate layer was employed.[22] Bonding of Pt to AlN at high temperatures and in low PN_2 environments, when the ceramic will dissociate as given in Fig. 2, has been studied also.[26]

3.2 BN

There are few studies on the joining of CBN as compared to its hexagonal allotrope. However, the available information suggests that the two allotropes of BN generally interact similarly with

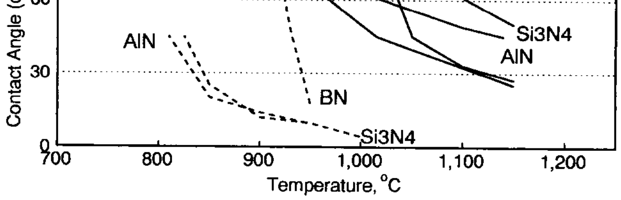

Fig. 1. Wetting behaviour of Si_3N_4, SiAlON, AlN and BN by Al and Ag–28Cu with 1–2% Ti additions. (After Refs 18, 19 and 20).

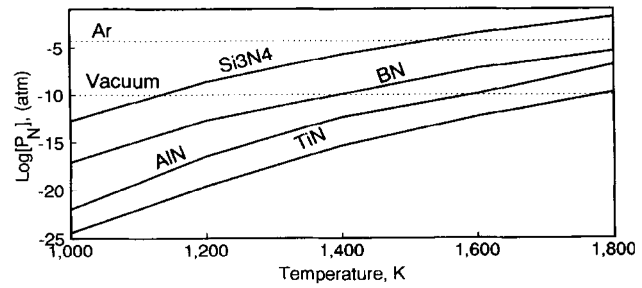

Fig. 2. Calculated partial pressures of N_2 as a function of temperature for the dissociation of Si_3N_4,[23] AlN,[24] BN[25] and TiN.[24] The PN_2 values for typical joining environments are shown as dashed lines.

metals.[27] CBN was found to be non-wetted by Cu, Ag, In, Sn and Au,[27] none of which forms a stable nitride, but it can be wetted by strong nitride formers such as Al and Ti, Fig. 2. Al wets well ($\theta < 45°$),[19] albeit as shown in Fig. 1 at the high superheat of 1000°C with AlN, or AlN and AlB_{12}[28,29] being formed as reaction products. Based on the Al–B–N phase diagram,[30] equilibrium between AlN–BN and BN–AlB_{12} exists at 900°C.

Cu alloyed with 7.5 and 10% Ti wets BN well,[19] as does the Ag–28Cu–2Ti alloy, although again at a relatively high superheat, Fig. 1. Ti-rich products, presumably TiN and TiB_2, were observed at the BN/Ti–active braze interfaces in accord with phase equilibria studies in the Ti–B–N system.[30] CBN grits were successfully brazed to a steel substrate using Ag–Cu–Ti alloy and survived preliminary grinding tests.[31] In contrast, Ni–Cr–P brazes failed to wet and bond CBN at 1100°C.[31]

3.3 Si_3N_4 and SiAlON

Research on SN ceramic joining has been significant and brazed SN components are in use, for example, in automobile engines.[32–34] Similarly, SiAlON brazed components are currently being evaluated for use in gas burners in industrial plants.[35]

Conventional and novel techniques, have been used for joining SN, SiAlON to itself or to metallic alloys. The range of approaches used reflects the severity of the problems encountered in joining ceramics for high temperature structural applications rather than the anticipated multiplicity of uses. A number of these approaches have produced strong joints, as summarized in Table 1. Active metal brazing is the more flexible and cost effective but, at present, lacks the ability to produce refractory SN joints. This has led to the development of non-conventional methods exploring either non-metallic bonding agents, such as oxides or oxynitride glasses, combined sintering with bonding, microwave heating and, very recently, by partial transient liquid phase bonding (PTLPB).

Active metal brazing has focused mainly on Al and Ti-containing alloys. Al wets and will react with SN ceramics to form AlN, as shown in Figs 1 and 2, provided a direct interfacial contact is established by disrupting or destabilizing the Al_2O_3 surface film. If the PO_2 in the joining environment is not very low, the Al_2O_3/SiO_2 films enter into the bonding mechanism and form SiAlON.[5,69,70] Additions of 1–5wt% Ti to Ag–28Cu, Cu and Ag–Cu–In alloys promote joining due to the strong reactivity of Ti with both Si and N_2. Ti-nitrides and Ti-silicides form at the interface, but microstructural studies have failed to offer a coherent picture as to whether hypo- or stoichiometric TiN is the bridging compound.[5,19,43,71] Although this question may sound academic it is fundamental in understanding wetting and spreading of reactive brazes on nitride ceramics and in designing new

Table 1. Silicon nitride joining*

Materials combination	Interlayer	Bonding route Liquid (L)/Solid (S)	Joint strength (MPa)	Reference
Sialon/Sialon	Cu–Ti	L	80–300	36
	Glass–Si_3N_4	L	70–690	37,38
Si_3N_4/Si_3N_4	Al, AlCu, AlSi,AlMg	L	20–600	39–42
	Ag–Cu–Ti	L	50–820	43–46
	Ti/Au–Ni–Pd, Pd–Ni–Ti, Ag–Cu–Hf, Cu–Si–Al–Ti, Ni–Cr–Si	L	0–510	47–52
	Ni, NiCr	S	100–550	53–57
	Fe,FeCr	S	200–780	58,59
	Mo, Nb, Ta	S	100–680	60,61
	Glass, Oxides, Oxynitrides	L,S	35–700	62–64
	None or SN	"Microwave"	105–390	65
	None or Y_2O_3/SN	"Sintering"	700–1000	66
	TiNi, Au–Cu–Ni,Au–Ni–Cr	"PTLPB"	100–1000	54,67,68

*Bending strengths are quoted unless specified otherwise. The indicated ranges, either of average strength or minimum and maximum values when a Weibull plot was reported, reflect differences between joining procedures and referenced studies.

brazes with minimum required active elements additions. Regardless of the interfacial details, both Al and, in particular, Ag–Cu–Ti brazes can form SN/SN joints with a strength distribution similar to that of the parent ceramic, as shown in Fig. 3.

Not surprisingly, direct brazing of the ceramic to high thermal expansion materials such as Ni-superalloys or steels is difficult because of residual stresses caused during cooling. Coping with residual stresses is a major problem, but insight can be gained from analytical and FEA calculations.[72–74] A large number of variables that control the level of residual stresses have been identified, but most of these can not be modified because of fixed joining practices and workpiece geometries. Instead, the use of intermediate or 'buffer' metal inserts of appropriate elastic/thermal properties and thickness that decrease the critical stresses in the ceramic has been proposed. This approach has been proven as indispensable in SN to metal joints, see Fig. 3, and it will remain so despite the search for more ductile braze alloys.

Although Al and Ag–Cu–Ti brazed SN joints are usefully strong, the service temperatures which these joints can withstand in oxidizing environments are well below those required in a heat engine (e.g. 900°C).[34,35,75] This has led to laboratory studies of new braze alloys containing Au, Pd, Ni, Hf, etc., with higher solidus temperatures and better oxidation resistances and to the evaluation of Ni brazes originally developed for the joining of high temperature superalloys.[47–52] However, the use of more refractory brazes is limited by the dissociation of Si_3N_4 that can occur at $T > 1000$°C in low PN_2 environments, Fig. 2. Further, none of the new braze alloys can yet match the ease of handling and joint integrity achieved with the Ag–Cu–Ti filler metals.

These difficulties with brazing have led to interest in the PTLPB technique[76] in which a joint is fabricated by using an interlayer coated with a low melting temperature metal that is soluble in the substrate. The interlayer is heated to melt the coating and form a joint with the ceramic, and is then held at a temperature to permit the coating to form a refractory solid solution with its substrate. Thus the process is similar to brazing but the resultant structure is like that of a diffusion bonded joint.

Diffusion bonding itself has been used by several workers to bond SN and successes have been achieved by controlling the microchemistry and microstructure of the interfaces formed by using thin metal foils as indicated in Table 1. Ni–Cr foils (≤400 μm thick) can be used to produce Si_3N_4 joints that are strong, as shown in Fig. 4, and more oxidation resistant than those brazed with Ag–Cu–Ti.[77] Bonding was associated with the formation of solid solutions of Si by low Cr alloys or, for the strongest joints, of a reaction product layer of CrN that bridged the interfaces between the Si_3N_4 and high Cr alloys. The microstructural evolution and reaction kinetics of these systems are complicated because of their dependence on the activities of Si and N_2 at the interface, which in turn are affected by the chemistry of the bonding environment and the gas tightness of the Si_3N_4–interlayer interface.[78] Weak interfaces result if the reaction product layers are thick, as shown in Fig. 4, and the joint itself is degraded by the associated excessive ingress of Si to form brittle silicides. However, joints with strengths equal to that of the monolithic ceramic have been produced by using Fe and Fe–Cr alloys as bonding interlayers that remained strong at high temperatures, as shown in Fig. 5.

While strong joints can be produced by diffusion bonding, a perennial problem is the variation in strength from place to place within a bonded

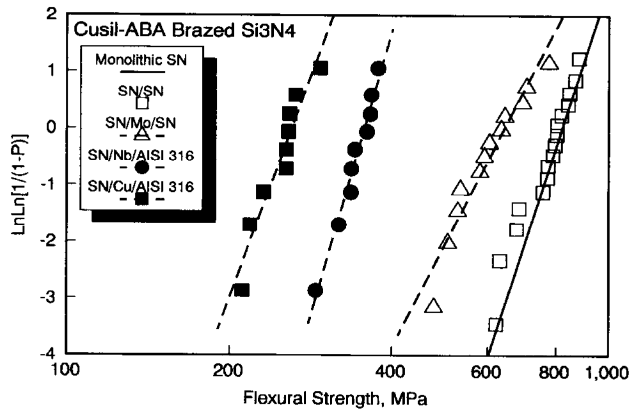

Fig. 3. Strength distribution of Si_3N_4 to Si_3N_4 and to AISI 316 brazed joints using commercial Cusil-ABA (Ag–34.7Cu–1.65Ti) filler metal.

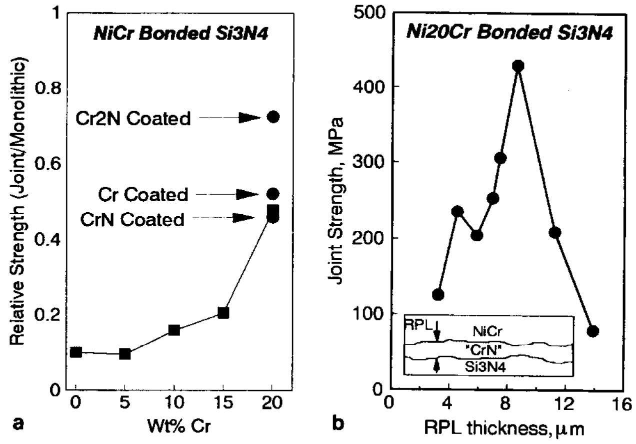

Fig. 4. (a) Joint strength (normalized to the monolithic ceramic strength, 904 MPa) of diffusion bonded Si_3N_4 with NiCr interlayers; (b) effect of the "CrN" interphase thickness on the strength of Ni20Cr bonded Si_3N_4 joints.

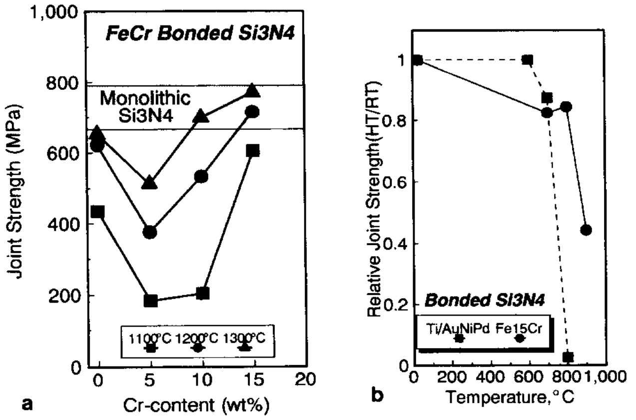

Fig. 5. (a) Strength of Si_3N_4 diffusion bonded at different temperatures with FeCr interlayers; (b) the normalized (to room temperature) high temperature strength of Si_3N_4 diffusion bonded with Fe15Cr or brazed Si_3N_4 with Ti/Au–Ni–Pd.[50]

assembly. The causes of this variability have been identified as the difference in reaction kinetics, and hence interphase formation, between the centres and peripheries of assemblies as in the SN/NiCr system, variations in the degree of contact between the mating ceramic/metal surfaces and, finally, variations in the severity of the tensile residual stresses in the ceramic edges.[79]

4 CONCLUDING REMARKS

It is clear that high integrity joints can be formed between nitride ceramics and metal workpieces and that successful joining depends on control of the chemical reaction that can promote wetting and the formation of bridging compounds. Nitrides are a well defined chemical family and there are many similarities in the reactions that benefit the joining of the three individual ceramics on which attention has been focused. Thus, bonding to and by Al, and by alloys containing Ti is associated with the formation of reaction product layers of mononitrides, AlN, TiN and, usually, also intermetallic compounds. The reaction path followed is ceramic→nitride product→intermetallic→metal and the logic of this can be seen for at least some systems by considering the chemical activities of the ceramic components in the metals along with thermodynamic predictions.

There are, however, differences as well. Thus, when analysing bonding to Cr containing alloys, thermodynamic models will fail unless they consider the N_2 pressure at the interface and its surroundings and also the diffusion of N_2 in the metal.[78] Again the wetting of BN by Al, Cu–Ti and Ag–Cu–Ti alloys required higher superheats than did AlN or Si_3N_4. The cause of this difficulty has not been established but it is plausible to relate it to the formation of a semi-metallic boride reaction product rather than a metallic aluminide or silicide. To understand such differences in the behaviour, and the similarities referred to above, requires more information and in particular detailed characterisation of the microchemistries of the nitride–metal interfaces supplemented by rigorous thermodynamic interpretation and kinetic considerations.[80]

Understanding the formation processes of nitride/metal interfaces is essential for reliable control of their fabrication, and thus for designing their fracture characteristics. Joints have been produced that are very strong when tested at room temperature, but Si_3N_4 in particular is receiving consideration as a high temperature structural material. Diffusion bonding can produce joints with good high temperature strengths but at temperatures which could degrade metallic workpieces, while none of the currently available braze families seem capable of satisfying the requirement for refractoriness. An ideal solution does not exist, but the wish for a simple low temperature process that produces refractory joints suggests that the applicability of partial transient liquid phase bonding techniques for the joining of Si_3N_4 in particular, may deserve serious study.

ACKNOWLEDGEMENTS

The author is deeply indebted to Dr M. G. Nicholas for his valuable contributions on several of the concepts and work presented here. He also thanks his colleagues, past and present co-workers (M. Nakamura, K. Suganuma, F. J. J. van Loo, A. Glaeser and A. Tomsia) for their contribution to the Institute work cited.

REFERENCES

1. BROOK, R. J., *Concise Encyclopedia of Advanced Ceramic Materials*. Pergamon, Oxford, UK, 1991, pp. 319–323.
2. NICHOLAS, M. G., Joining structural ceramics. In *Designing Interfaces for Technological Applications*, ed. S. D. Peteves. Elsevier, London, UK, 1989, pp. 49–76.
3. MIZUHARA, H. & MALLY, K., *Weld. J.*, **64** (1985) 27.
4. PETEVES, S. D. & NICHOLAS, M. G., Materials factors affecting joining of Si_3N_4 ceramics. In *Metal–Ceramic Joining*, ed. P. Kumar & V.A. Greenhut. TMS, Warrendale, PA, USA, 1991, pp. 43–65.
5. LOEHMAN, R. E., *Mater. Res. Soc. Proc.*, **8** (1989) 3.
6. SUGA, T., MIYAZAWA, K. & YAMAGATA, Y., *Mater. Res. Soc. Proc.*, **8** (1989) 257.
7. SHEPPARD, L. M., *Ceram. Bull.*, **69** (1990) 1801.
8. NORTON, M. G., *Mater. Res. Soc. Proc.*, **314** (1993) 223.
9. NORTON, M. G., STEELE, B. C. H. & LEACH, C. A., *Brit. Ceram. Proc.*, **41** (1989) 69.
10. NORTON, M. G., *J. Mater. Sci.*, **26** (1991) 2322.

11. COX, C. V., HUTFLESS, M. J., ALLISON, K. & HANKLEY, D. L., *Int. J. Hybrid Microelectron.*, **10** (1987) 8.
12. HOHNE, D. & DUSDORF, W., Solder glass for joining AlN ceramics. In *Joining Ceramics, Glass & Metal*, ed. H. Krappitz & H. A. Schaffer. DGG, Frankfurt, Germany, 1993, pp. 76–84.
13. SCHWARTZ, M. M., *Ceramic Joining*. ASM International, Materials Park, OH, USA, 1990.
14. KLUGE-WEISS, P. & GOBRECHT, J., *Mater. Res. Soc. Proc.*, **40** (1985) 399.
15. CHIANG, W. L., TESSAROTTO, L. A. B., GREENHUT, V. A. & SHANEFIELD, D. J., Effect of substrate surface on bonding Cu–AlN by active metal thin film and gas–metal eutectic methods. In *Metal–Ceramic Joining*, ed. P. Kumar & V. A. Greenhut. TMS, Warrendale, PA, USA, 1991, pp. 247–261.
16. NORTON, M. G., KAJDA, J. M. & STEELE, B. C. H., *J. Mater. Res.*, **5** (1990) 2172.
17. LOEHMAN, R. E. & TOMSIA, A. P., *Acta Metall. Mater.*, **40** (1992) S75.
18. BROW, R. K., LOEHMAN, R. E., TOMSIA, A. P. & PASK, J. A., *Adv. Ceram.*, **26** (1989) 189.
19. NICHOLAS, M. G., MORTIMER, D. A., JONES, L. M. & CRISPIN, R. M., *J. Mater. Sci.*, **25** (1990) 2679.
20. LJUNGBERG, L., Joining of ceramics to metals by brazing. Ph.D Thesis, Chalmers University of Technology, Goteborg, Sweden, 1992.
21. CARIM, A. H. & LOEHMAN, R. E., *J. Mater. Res.*, **5** (1990) 1520.
22. NAKAO, Y., SAIDA, K. & MURABE, K., Brazing of AlN to Cu. In *Brazing, High Temperature Brazing & Diffusion Welding*, ed. E. Lugscheider. DVS, Dusseldorf, Germany, 1992, pp. 63–67.
23. HEUER, A. H. & LOU, V. L. K., *J. Am. Ceram. Soc.*, **73** (1990) 2785.
24. BARIN, I. & KNACKE, O., *Thermochemical Properties of Inorganic Substances*. Springer-Verlag, Berlin, Germany, 1973, p. 36 and 789.
25. *JANAF Thermochemical Tables*, 2nd edn. NBS, Washington, DC, USA, 1971.
26. KLOMP, J. T., van de VEN, A. J. C. & MONNERAYE, M., *Coll. de Physiq.*, **51-C1** (1990) 745.
27. NAIDICH, J. V., *Progr. Surface Memb. Sci.*, **14** (1981) 354.
28. XUE, X. M., WANG, J. T. & ZHAO, F. M., *J. Mater. Sci. Lett.*, **11** (1992) 199.
29. XUE, X. M., WANG, J. T. & QUAN, M. X., *Mater. Sci. Engng*, **A132** (1991) 277.
30. ROGL, P. & SCHUSTER, J. C., *Phase Diagrams of Ternary BN and Si_3N_4 Systems*. ASM International, Materials Park, OH, USA, 1992, pp. 3–5, 103–106.
31. CHATTOPADHYAY, A. K. & HINTERMANN, H. E., *J. Mater. Sci.*, **28** (1993) 5887.
32. TAGUCHI, M., *Adv. Ceram. Mater.*, **2** (1987) 754.
33. TANIGUCHI, M., NOZAKI, S., SUZUKI, O., ITO, M. & MATSUMOTO, S., SAE Technical Paper, Series 931934, 1993.
34. ITO, M. & TANIGUCHI, M., Metal/ceramic joining for automotive applications. In *Designing Ceramic Interfaces II*, ed. S. D. Peteves. CEC, Luxemburg, 1993, pp. 205–220.
35. FOLEY, A. G. & ANDREWS, D. J., Active metal brazing for joining ceramics to metals. Technical Review No. 13. GEC Alsthom, Stafford, UK 1994.
36. RAMSEY, M. J. & LEWIS, M. H., *Mater. Sci. Engng*, **71** (1985) 113.
37. WALLS, P. A. & UEKI, M., *J. Am. Ceram. Soc.*, **75** (1992) 2491.
38. WALLS, P. A., UEKI, M. & KUBO, H., *Mater. Res. Soc. Symp. Proc.*, **8** (1989) 35.
39. SUGANUMA, K., OKAMOTO, T., KOIZUMI, M. & SHIMADA, M., *Adv. Ceram. Mater.*, **1** (1986) 356.
40. NAKA, M., KUBO, M. & OKAMOTO, I., *J. Mater. Sci.*, **99** (1987) 4417.
41. NING, X. S., OKAMOTO, T., MIYAMOTO, Y., KOREEDA, A., SUGANUMA, K. & GODA, S., *J. Mater. Sci.*, **26** (1991) 2050.
42. KOHNO, A., YAMADA, T. & YOKOI, K., *J. Jpn Inst. Met.*, **49** (1985) 876.
43. LOEHMAN, R. E., TOMSIA, A. P., PASK, J. A. & JOHNSON, S. M., *J. Am. Ceram. Soc.*, **73** (1990) 552.
44. TANAKA, S. I., *Mater. Res. Soc. Symp. Proc.*, **8** (1989) 91.
45. PETEVES, S. D. & NICHOLAS, M. G., *J. Am. Ceram. Soc.*, **79** (1996) 1553.
46. PATTEN, D. O., TORTI, M. L. & CHARREYRON, P., *Ceram. Engng Sci. Proc.*, **10** (1989) 1866.
47. KANG, S., DUNN, E. M., SELVERIAN, J. H. & KIM, H. J., *Ceram. Bull.*, **68** (1989) 1608.
48. LUGSSCHEIDER, E. & TILLMANN, W., Interfacial reactions between new active filler metals and nonoxide ceramics. In *Designing Ceramic Interfaces II*, ed. S. D. Peteves. CEC, Luxemburg, 1993, pp. 499–517.
49. LUGSCHEIDER, E., TILLMANN, W. & WEISE, W., Heat- and oxidation-resistant joints by active brazing. In *Joining Ceramics, Glass & Metal*, ed. H. Krappitz & H. A. Schaffer. DGG, Frankfurt, Germany, 1993, pp. 99–107.
50. SANTELLA, M. L., Ceramic technology for advanced heat engines project. Semiannual Progress Report for October 1990–March 1991, ORNL/TMA-1859, Oak Ridge, TN, USA, 1991.
51. TILLMANN, W., Aspekte des Activiotens nichtoxidischer Ingenieurkeramiken, Dr Eng. Thesis. RWTH Aachen, Aachen, Germany, 1992.
52. CECCONE, G. & PETEVES, S. D., Joining of Si_3N_4 ceramics with metal interlayers. In *Euro-Ceramics III, Vol. 3*, ed. P. Duran & J. F. Fernandez. Faenza Ed. Iberica, Castellon de la Plana, Spain, 1993, pp. 337–342.
53. SUGANUMA, K., *J. Less-Common Met.*, **158** (1990) 59.
54. IINO, Y., *J. Mater. Sci. Lett.*, **10** (1990) 104.
55. NAKAMURA, M. & PETEVES, S. D., *J. Am. Ceram. Soc.*, **73** (1990) 1221.
56. MATSUSHITA, Y. & DERBY, B., Influence of nitrogen pressure on joint strength. In *Euro-Ceramics II, Vol. 1*, ed. G. Ziegler & H. Hausner. DKG, Cologne, Germany, 1993, pp. 695–699.
57. SUGANUMA, K., MORETTO, P. & PETEVES, S. D., *Mater. Sci. Forum*, **126–128** (1993) 567.
58. PETEVES, S. D. & SUGANUMA, K., *Ceram. Trans.*, **35** (1993) 229.
59. SUGANUMA, K., OKAMOTO, T., MIYATOMO, Y., SHIMADA, M. & KOIZUMI, M., *Mater. Sci. Tech.*, **2** (1986) 1156.
60. KOIZUMI, M., TAKAGI, M., SUGANUMA, K., MIYAMOTO, Y. & OKAMOTO, T., Solid-state bonding of Si_3N_4 to metals using HIP. In *High Tech Ceramics*, ed. P. Vincenzini. Elsevier, Amsterdam, The Netherlands, 1987, pp. 1033–1042.
61. SUGANUMA, K., TAKAGI, M., MIYAMOTO, Y., KOIZUMI, M., OKAMATO, T. & NAKATA, H. M., *Nippon-Seramikkusu-Kyokai-Gakujinsu-Ronbunshi*, **96** (1988) 1051.
62. BECHER, P. F. & HALEN, S. A., *Ceram. Bull.*, **58** (1979) 582.
63. JOHNSON, S. M. & ROWCLIFFE, D. J., *J. Am. Ceram. Soc.*, **68** (1985) 468.
64. IWAMOTO, N., UMEZAKI, N. & HAIBARA, Y., *J. Ceram. Soc. Jpn*, **94** (1985) 184.
65. FUKUSHIMA, H., YAMANAKA, T. & MATSUI, M., *Mater. Res. Soc. Proc.*, **124** (1988) 255.
66. BATES, C. H., FOLEY, M. R., ROSSI, G. A., SUNDBERG, G. A. & WU, F. J., *Ceram. Bull.*, **69** (1990) 350.

67. DALGLEISH, B. J., TOMSIA, A. P., NAKASHIMA, K., LOCATELLI, M. R. & GLAESER, A. M., *Scripta Metall. Mater.*, **31** (1994) 1043.
68. CECCONE, G., NICHOLAS, M. G., PETEVES, S. D., DALGLEISH, B. J., TOMSIA, A. P. & GLAESER, A. M., *Acta Mater.*, **44** (1996) 657.
69. PAN, W. X., OKAMOTO, T. & NING, X. S., *J. Mater. Sci.*, **29** (1994) 1436.
70. NING, X. S., OKAMOTO, T., MIYATOMO, Y., KOREED, A. & SUGANUMA, K., *J. Mater. Sci.*, **26** (1991) 4142.
71. SUEMATSU, H., PETROVIC, J. J., MITCHELL, T. E. & YANO, T., *Ceram. Trans.*, **35** (1993) 59.
72. STEPHENS, J. J., BURCHETT, S. N. & JONES, W. B., Stress relaxation of braze joints. In *Advances in Electronic Packaging, Vol. 1*, ed. W. T. Chen & H. Abe'. ASME, New York, NY, USA, 1992, pp. 363–372.
73. FOLEY, A. G. & WINTERS, C. G., *Brit. Ceram. Soc. Proc.*, **48** (1991) 107.
74. PINTSCHOVIUS, L., PYKA, N., KUBMAUL, P., MURIZ, D., EIGENMANN, B. & SCHOLTES, B., *Mater. Sci. Engng*, **A177** (1994) 55.
75. KAPOOR, R. R. & EAGAR, T. W., *J. Am. Ceram. Soc.*, **72** (1989) 448.
76. SHALZ, M. L., DALGLEISH, B. J., TOMSIA, A. P. & GLAESER, A. M., *Ceram. Trans.*, **35** (1993) 301.
77. PETEVES, S. D., Improved joining of surface modified silicon nitride ceramics. In *Ceramics Today — Tomorrow's Ceramics*, ed. P. Vincenzini. Elsevier, Amsterdam, The Netherlands, 1991, pp. 1469–1477.
78. KODENTSOV, A. A., KIVILAHTI, J. K., van LOO, F. J. J. & PETEVES, S. D., *Ceram. Trans.*, **35** (1993) 135.
79. HE, M. Y. & EVANS, A. G., *Acta Metall. Mater.*, **39** (1991) 1587.
80. HEIKINHEIMO, E., KODENTSOV, A., van BEEK, J. A., KLOMP, J. T. & van LOO, F. J. J., *Acta Metall. Mater.*, **40** (1992) S111.