Joining mechanism in Si_3N_4 bonded with a Ni–Cr–B interlayer

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Abstract

A commercially available Ni–Cr brazing alloy foil with B infused at its surface layer was used to join silicon nitride ceramics. The joining region showed a diffusion zone at the middle of the interlayer and a reaction layer at the silicon nitride/brazing alloy interface. The reaction layer mainly consisted of CrN and BN while the diffusion layer was formed by $Ni_{[Cr, Si]}$ solid solution with some CrN precipitates. A reaction mechanism is proposed to explain the microstructure and phases observed in the bonding interlayer. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The practical use of silicon nitride ceramics for structural high temperature applications requires development of reliable joining techniques.[1–4] Among the joining methods, those involving liquid phase formation, such as brazing[5,6] and transient liquid phase bonding,[7–9] are receiving more attention because joints can be made in complex shaped parts using simpler tooling and mating surface preparation. Although Cu–Ag and Ti–Cu–Ag brazing alloys have been widely employed with good bonding results, these alloys can only be used for low service temperatures.[3,4]

The high thermal stability and corrosion resistance of Ni–Cr braze alloys make them good candidates for joining silicon nitride ceramic bodies as well as for joining silicon nitride with Ni based superalloys.[2,8,9] Due to the high melting point of Ni–Cr alloys (> 1345 °C[10]), the bonding of Si_3N_4 using Ni–Cr filler metal has been usually performed by solid state.[11–14] Generally, Ni–Cr or Ni–Cr–Si alloys with a Cr/Ni atomic ratio of 0.22–0.29 have been employed. These bonds showed a joining interphase formed by a continuous CrN reaction layer at the ceramic/metal interface and a metal layer consisting of $Ni_{[Cr,Si]}$ solid solution and/or Ni–Cr silicides inside the bonding interlayer.[11–14] Additionally, it has been shown that these alloys are quite sensitive to the joining conditions, such as joining temperature and N_2 partial pressure.[11,15,16] Although an increase in the joining temperature promoted wettability of these alloys, it also caused extensive reactions between the Si_3N_4 adherent and the Ni–Cr alloys.[11] The reactivity and wettability of Ni-based alloys were also improved by the addition of melting point depressants. Among the elements that decreased the melting point of Ni by forming low temperature eutectics, Si and B have been commonly employed.[9,7,17]

Ni–Cr–Si brazing alloys with different Si contents have been used for joining Si_3N_4 ceramics at 1220 °C and N_2 pressure of 15 Pa.[14,15] In this work, it was shown that Si additions > 25 at.% limited, or even stopped, the reaction between the filler and the Si_3N_4, resulting in poor joint strengths. The effect of Si additions and N_2 partial pressure on the wetting behaviour of silicon nitride ceramics by Ni–Cr–Si alloys have been investigated by Hadian and Drew,[15] using both thermodynamic modelling and experimental verifications. Although wetting occurred at 1220 °C for a N_2 partial pressure of 15 Pa, a transition to non-wetting behaviour was observed when pressure increased up to 10^5 Pa. Furthermore, a series of nickel silicides were formed that reduced the interfacial strength of Si_3N_4 joints with Ni based interlayers.[16–19]

Based on the Ni–B binary system,[20] it can be stated that small additions of B depress below 1100 °C the melting point of the Ni-alloys and therefore, it is more effective than Si. Consequently, for this study, a commercial Ni–Cr

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alloy sheet with B addition at its surface was selected as the filler metal to join silicon nitride ceramics. In this way, liquid forms at the interfacial layer at a much lower temperature than those required for conventional joining approaches.[7–9] This molten surface layer would promote diffusion and reaction with the Si_3N_4 adherent and may disappear during bonding by forming a more refractory phase.

The joint was characterised by analysing the microstructure, the chemical composition and the crystalline phases at the joining interlayer, as well as by measuring the interfacial shear stress. A joining mechanism is proposed to explain the microstructure of the bonding region. The results of the present work supply sound data that prove the suitability of Ni–Cr–B alloys for joining silicon nitride ceramics.

2. Experimental procedures

Si_3N_4 was prepared in house by pressureless sintering, at a maximum temperature of 1750 °C for 2 h in a flowing N_2 atmosphere of 0.1 MPa, a powder mixture of α-Si_3N_4 powders (SN-E10, Ube Co., Japan) with 4 wt.% Al_2O_3 (SM8, Baikowski Chemie, France) and 5 wt.% Y_2O_3 (Fine, H.C. Stark Co., Germany). The sintered material was formed by β-Si_3N_4 grains and Y-silicate grain boundary phases. It had a density of 3.2 g/cm^3, a fracture toughness of 6 MPam$^{1/2}$ measured by indentation, and a strength of 690 MPa, tested in four point bending.

A commercially available Ni–14.2Cr–3.3B (composition in wt.%) alloy foil of 50 μm thickness (Ni-Flex95, VBC Group Ltd, USA) was selected as the filler metal. The B is added into the surface layer of the alloy sheets by the Borofuse$^{(TM)}$ process. SEM micrograph of the foil cross-section and the corresponding X-ray diffraction pattern are shown in Fig. 1, where a 10 μm thick surface layer can be identified as the B-rich layer. From the XDR pattern, Ni_3B and CrB species besides Ni solid solution are identified in the foil. According to the Ni–B binary

phase equilibrium diagram,[20] Ni_3B forms an eutectic melt with Ni at 1045 °C, a much lower temperature than any of the melting points in the Ni–Cr system,[10] which is in consonance with the melting and optimum brazing temperatures recommended by the supplier, 1050 and 1163 °C, respectively.

The sintered Si_3N_4 billet was sawed and grounded using metal bonded diamond discs and wheels into specimens of 4×5×7 mm^3, being the 5×7 mm^2 the joining surface. The joint mating surfaces were grounded using a 540-grit diamond wheel to get a mechanical anchoring effect.[21] The Ni-alloy foils were cut into leaflets of 5×7 mm^2. Both the ceramic and alloy specimens were thoroughly cleaned before joining. Joining tests were done in a hot-press furnace at a maximum temperature of 1150 °C for 30 min, in a vacuum atmosphere of ∼20 Pa, applying a uniaxial pressure of 50 MPa.

Joined specimens were sectioned perpendicularly to the joint and then, polished with diamond suspensions of decreasing grain size up to 1 μm. The microstructure and chemical composition of the joint were analysed with a scanning electronic microscope equipped with an energy dispersive spectroscopy unit (SEM/EDS). Average analyses refer always to analyses performed using a window of 5×5 μm^2 while the rest are point analyses.

The strength of the joints was estimated by shear tests. After testing, the adhered metal foil was peeled off from one of the ceramic adherent, and analysed by the conventional θ–2θ X-ray diffraction configuration. Once the metal layer was removed, the mating ceramic surface was X-ray analysed by using both conventional θ-2θ focusing geometry and grazing incidence X-ray diffraction.

3. Results

A representative SEM micrograph of the joint region is shown in Fig. 2, where an important reduction in the thickness of the foil is evidenced. Two zones can be clearly distinguished in the interlayers: a middle layer of
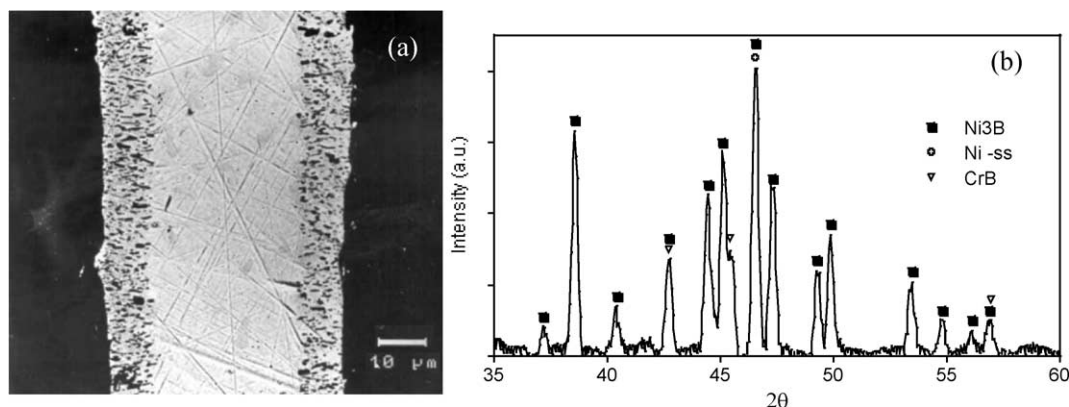

Fig. 1. SEM micrograph of a polished cross-section of the commercial Ni–Cr–B foil (a) and its corresponding XRD pattern (b).
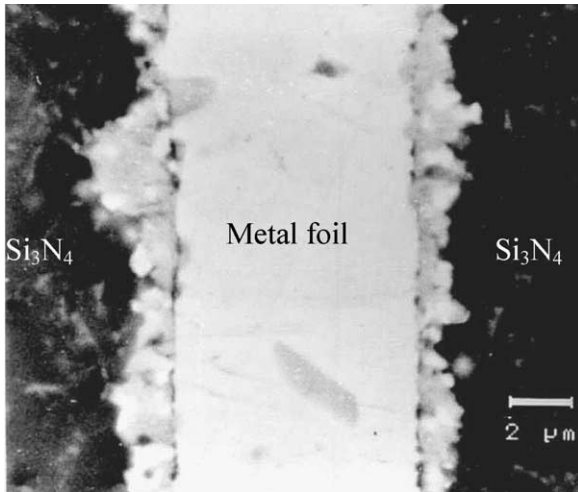
Fig. 2. SEM micrograph of a joining cross-section.

Table 1
Chemical composition of the joining interlayer (wt.%) analysed by EDS. Standard deviations of three analyses are shown

Zone	Ni	Cr	Si	Al	Y
Middle layer	85.7±0.6	6.3±1.0	8.0±0.3	–	–
Interfacial layer	7.7±1.4	83.8±2.0	7.1±3.1	1.5±0.4	–
Dark phases[a]	12.4–20.0	76.6–87.6	0.0–4.8	–	–
Light phases[a]	38.6	52.7	8.7	–	–

[a] Rather small for getting accurate analysis.

$\sim$8 μm thickness with a light colour and a darker layer of $\sim$1 μm, next to the ceramic adherent. Some darker phases dispersed within the middle layer and some lighter phases in the interfacial layer can be also observed.

The EDS data in the joining interlayer for the two regions are shown in Table 1. For comparison, EDS analyses were also done in the original foil giving average concentrations of 82.8 wt.% Ni and 17.2 wt.% Cr, as B cannot be detected. Therefore, after bonding, the Cr-content decreased to 6.3 wt.% while Si increased up to 8.0 wt.% in the middle layer. The dark areas observed in this region were rather small ($\sim$1–3 μm) for giving accurate analysis, nevertheless a significant increment in the Cr concentration ($\sim$76 wt.%), associated with a decrease in the Ni and Si contents, was evidenced.

The composition of the thin interfacial layer gave a high Cr content, 83.8 wt.% (see Table 1), with small amounts of Ni, Si and Al, the Si content being very close to that measured in the middle zone. Analyses of the light phases within this interfacial layer showed higher Ni contents ($\sim$43.2 wt.%) than the surrounding phase

Example of the X-ray diffraction pattern of the metal foils removed from the fracture surface is shown in Fig. 3. Ni diffraction peaks were clearly identified with an indication of some solid solution, as seen by a small shift of the Ni peaks. In the enlarged pattern of Fig. 3b, traces of CrN are pointed out. In Fig. 4, X-ray diffraction patterns, done with an incident angle of 2°, of the mating Si_3N_4 side and the bulk Si_3N_4 specimen are depicted. The main difference between the spectra is the appearance of CrN and BN phases at the Si_3N_4 bonding interface. Diffraction peaks of Ni solid solution can also be detected. As is seen in Fig. 5, the XRD pattern obtained by the θ–2θ focusing geometry shows a
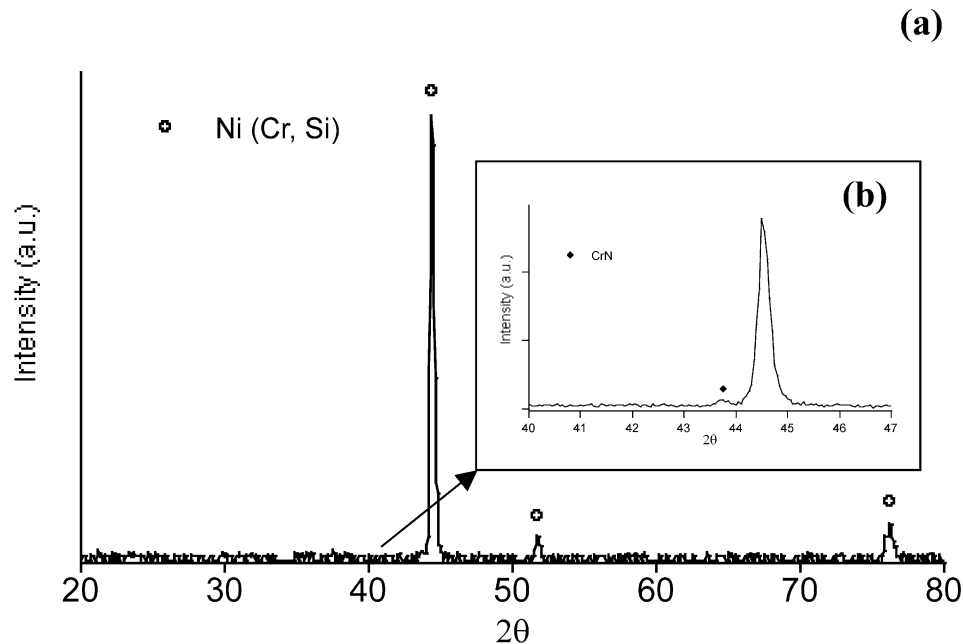

Fig. 3. XRD patterns of the metal foil peeled off from the fracture surface after the shear test: (a) complete pattern at 2°/min scan rate and (b) pattern obtained at 0.5°/min scan rate.
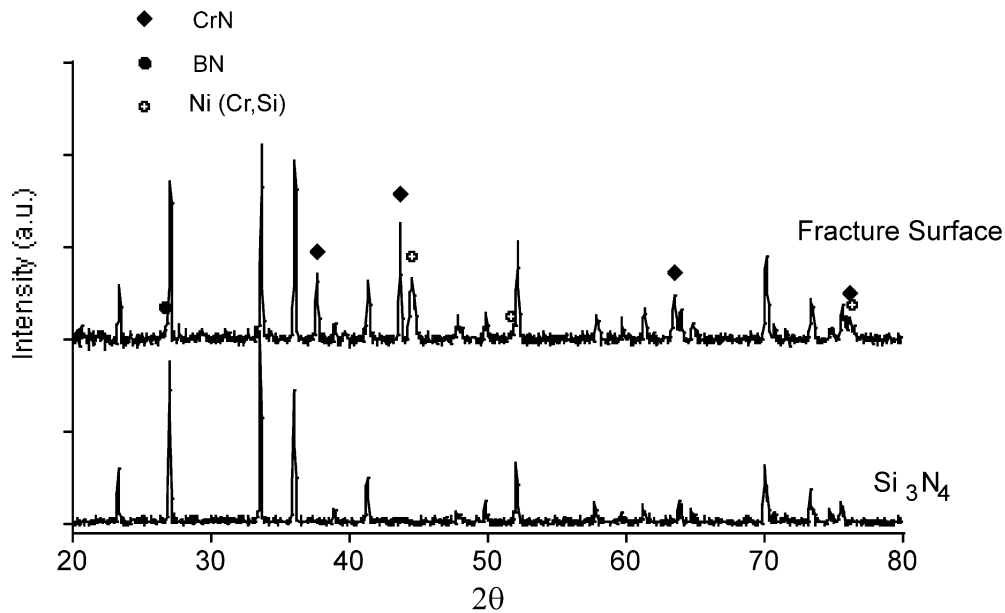
Fig. 4. Grazing incidence XRD pattern of the fracture surface of the joint on the Si_3N_4 side. Pattern of the bulk Si_3N_4, under same incident conditions, is shown for comparison.
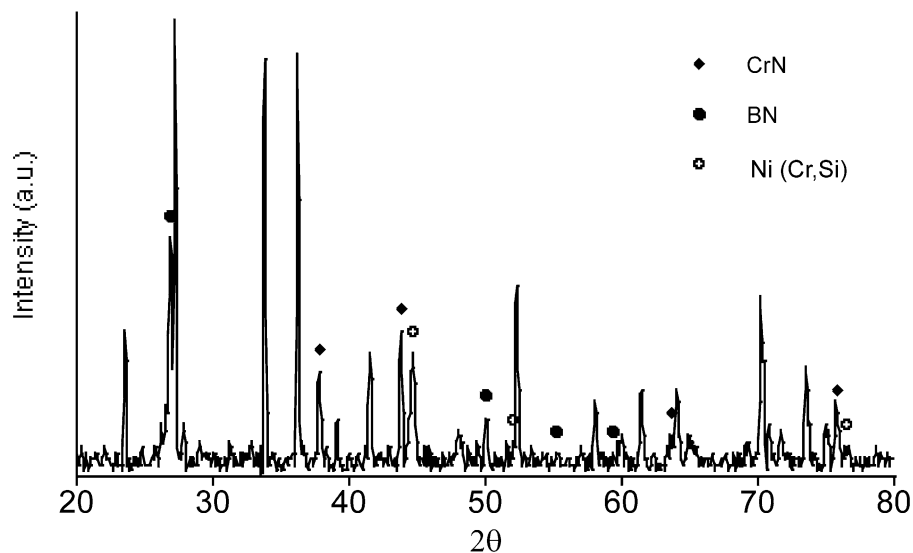

Fig. 5. XRD pattern of the fracture surface of the joint on the Si_3N_4 side, done using the θ–2θ focusing geometry.

decrease in the ratio between the CrN and BN peak intensities.

Shear strength of this joint was 40 ± 2 MPa. In most of the shear tests, fracture initiated at the interface and propagated within the Si_3N_4. In all the tests, the interfacial reaction layer remained adhered to the Si_3N_4 adherent (see Fig. 6).

4. Discussions

The metal foil removed after testing from the adherent surface corresponded to the core region of the joining interlayer (Fig. 2), as the reaction interface remained adhered to the Si_3N_4 side, as shown in Fig. 6. Comparing XRD and EDS data (Fig. 3 and Table 1), it can be stated that it is mainly Ni with 6.5 at.% Cr and 15.2 at.% Si in solid solution. The decrease in the Cr content compared to that observed in the original alloy indicates that there was Cr diffusion from the core to the interfacial reaction layer. The Si content in the middle layer is close to the solubility limit of Si in the fcc $Ni_{[Cr, Si]}$ phase at the joining temperature[16] ($\sim$15 at.%), nevertheless no nickel silicides were detected. According to Fig. 3, the dark phases observed in this layer (Fig. 2) should correspond to CrN. The formation of this phase
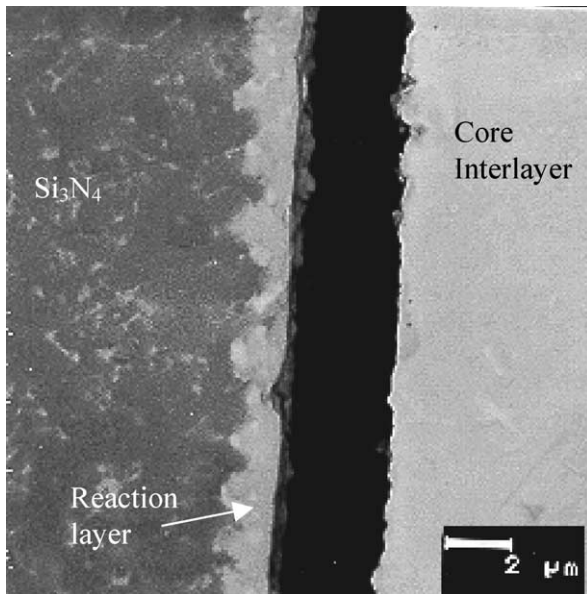
Fig. 6. SEM micrograph of the broken joint after shear testing, showing the reaction layer adhered to the Si_3N_4 side.

can be explained assuming that N_2 liberated from the Si_3N_4 decomposition does not escape, building up a high N_2-pressure at the Si_3N_4/alloy interface[22]. Based on the calculated stability diagrams of nitride phases in Ni–Cr alloys as a function of nitrogen fugacity,[16,23] for the present Ni–19Cr (at.%) alloy, CrN precipitates can

be formed at $\sim 1150\ ^\circ C$ when the N_2 fugacity is higher than 5 bar. In spite of the reportedly low values for N_2 solubility in Ni (see review by Kodentsov et al.),[23] nitrogen diffusion and formation of CrN precipitates in Ni–Cr alloys were evidenced in several papers.[23,24]

From the XRD pattern of the joint ceramic side (Fig. 4), it can be stated that the adhered reaction zone (Fig. 6) mainly consists of CrN and BN. X-ray penetration depth in Si_3N_4 is $\sim 2\ \mu m$ for the 2° fixed scanning conditions and $\sim 25\ \mu m$ for the θ–2θ focusing geometry. Therefore, the higher CrN/BN intensity ratio for the XRD peaks observed at low incident angle (Figs. 4 and 5) would indicate that CrN is located closer to the fracture surface, i.e. BN phase would be adjacent to the Si_3N_4 side of the interface.

In most of the shear tests, fracture initiated at the interface and propagated within the Si_3N_4, which has been associated to the lack of relaxation of the residual tensile stresses, developed in the adherents at the interface free edge, because of either a low plasticity of the metal or a poor load transfer across the interfacial reaction layer.[19,25] The shear strength values and the crack propagation during fracture were both similar to those observed for Si_3N_4/Ni/Si_3N_4 joints done at $1150\ ^\circ C$, under similar experimental conditions.[19]

A mechanism for describing the overall joining process can be proposed based on the above experimental data. The initial brazing foil is a Ni $_{[Cr]}$ solid solution with a
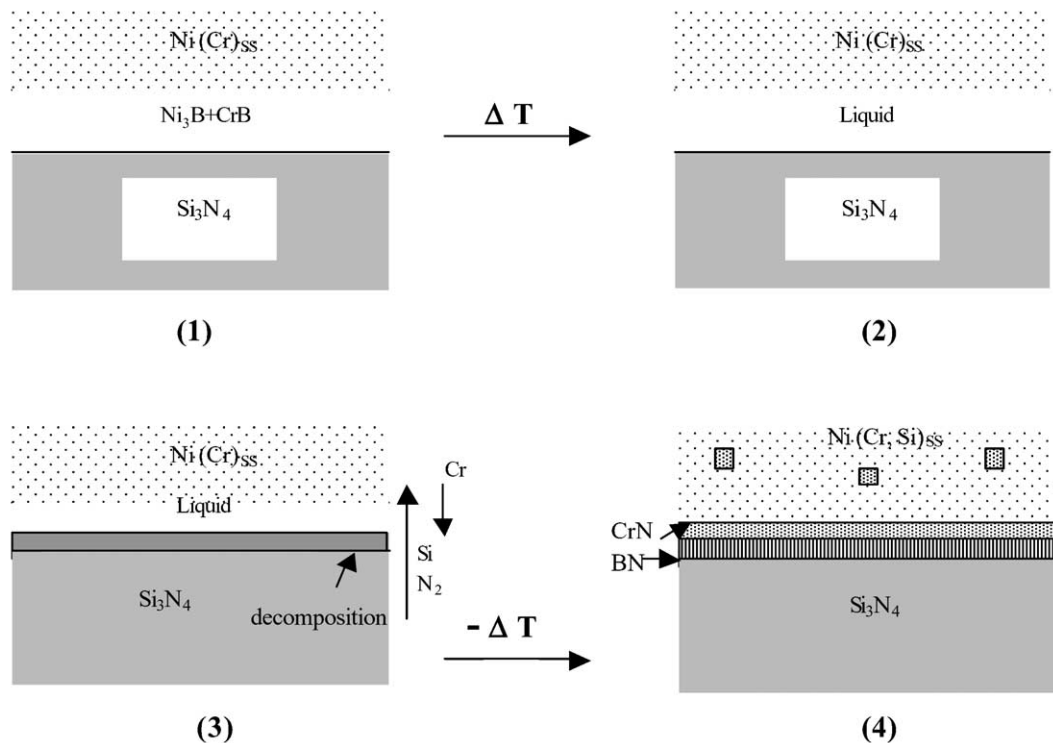

Fig. 7. Scheme proposed to explain the joining process: (1) initial state, (2) formation of a transient liquid phase, (3) reaction and diffusion processes and (4) final state.

surface layer of about 10 μm, composed of Ni_3B and CrB. During the joining process, the eutectic temperature of the Ni_3B–Ni subsystem is reached and a thin liquid layer is formed at the Si_3N_4/Ni-alloy interface, which improves the intimate contact at the joining interfaces and promotes reaction between the ceramics and the alloy. This liquid reacts with the Si_3N_4 adherent liberating N_2 that builds up at the interface. This nitrogen will react with both B and Cr atoms present in the eutectic melt to form the BN/CrN interfacial reaction layer, reducing the amount of liquid at the interface. Moreover, the nitrogen atoms will diffuse through the BN/CrN layer into the $Ni_{[Cr]}$ interlayer, reacting with Cr atoms to form CrN precipitates. On the other hand, Si will also diffuse through the reaction zone forming the $Ni_{[Cr,Si]}$ middle diffusion layer whereas Cr counter diffuses from the core to the interfacial zone. As no gradient in the Si and Cr concentrations were observed through the middle layer, the diffusion of Si atoms from the interface may be limited by the BN/CrN interfacial layer, avoiding a larger reaction among the Si_3N_4 and the alloy.

The overall joining process is represented in Fig. 7 and can be summarised by the following reaction:

$$Si_3N_4 + \{Ni_3B + CrB\}/Ni_{ss}(Cr) \rightarrow BN + CrN$$
$$+ Ni_{ss}(Cr, Si) + CrN_{precipitates}$$
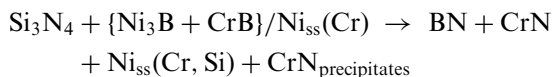
5. Conclusions

A uniform joint between silicon nitride ceramics with a good mechanical resistance, 40 MPa of shear strength, is achieved by using a Ni–Cr–B alloy as the bonding interlayer. The joining mechanism is described by the formation of an eutectic liquid at the ceramics/metal filler interface that reacts with the Si_3N_4 adherent liberating N_2 and Si. Si diffuses through the liquid to form a $Ni_{[Cr,Si]}$ diffusion interlayer, and N_2 reacts with the B and the Cr of the eutectic liquid to form the BN/CrN reaction interfacial layer. Nitrogen also diffuses across the liquid to the $Ni_{[Cr,Si]}$ interlayer precipitating inside the Ni–Cr–Si alloy as CrN. Diffusion of Cr from the middle to the interfacial reaction layer is also observed.

References

1. Loehman, R. E. and Tomsia, A. P., Joining of ceramics. *Am. Ceram. Soc. Bull.*, 1988, **67**(2), 375–380.
2. Nicholas, M. G. and Mortimer, D. A., Ceramic-metal joining for structural applications. *Mater. Sci. Technol.*, 1985, **1**, 657–665.
3. Suganuma, K., Miyamoto, Y. and Koizumi, M., Joining of ceramics and metals. *Ann. Rev. Mater. Sci.*, 1988, **18**, 47–73.
4. Santella, M. L., A review of techniques for joining advanced ceramics. *Am. Ceram. Bull.*, 1992, **71**(6), 947–954.
5. Moorhead, A. and Keating, H., Direct brazing of ceramics for advanced heavy-duty diesels. *Weld. Journal*, 1986, **65**(10), 17–31.
6. Loehman, R. E., Tomsia, A. P., Pask, J. A. and Johnson, S. M., Bonding mechanisms in silicon nitride brazing. *J. Am. Ceram. Soc.*, 1990, **73**(3), 552–558.
7. Duvall, D. S., Owczarski, W. A. and Paulonis, D. F., TLP bonding: a new method for joining heat resistant alloys. *Weld. Journal*, 1974, **53**, 203–214.
8. Glaesser, A. M., The use of transient FGM interlayers for joining advanced ceramics. *Composites Part B*, 1997, **28B**, 71–84.
9. Locatelli, M. R., Marks, R. A., Chapman, D. R., Nakashima, K. and Glaesser, A. M., Transient liquid phase (TLP) routes to the joining of structural ceramics. In *Interfacial Science in Ceramic Joining, NATO ASI Series*, ed. A. Bellosi, T. Kosmac and A. P. Tomsia. Kluwer Academic Publishers, Netherlands, 1998, pp. 111–134.
10. Nash, P., The Ni–Cr system. *Bull Alloy Phase Diagrams*, 1986, **7**(5), 466–476.
11. Nakamura, M. and Peteves, S. D., Solid-state bonding of silicon nitride ceramics with nickel-chromium alloy interlayers. *J. Am. Ceram. Soc.*, 1990, **72**(5), 1221–1227.
12. Peteves, S. D., Moulaert, M. and Nicholas, M. G., Interface microchemistry of silicon nitride/nickel-chromium alloy joints. *Metal. Trans. A*, 1992, **23A**, 1773–1781.
13. Kodentson, A. A., Kivilahti, J. K., van Loo, F. J. J. and Peteves, S. D., Interphases in Si_3N_4/Ni–Cr alloy joints. In *Ceramic Trans., Vol. 35, Structural Ceramics Joining II, American Ceramic Society*, ed. A. J. Moorhead, R. E. Loehman and S. M. Johnson. American Ceramics Society, Weterville, OH, 1993, pp. 135–144.
14. Hadian, A. M. and Drew, R. A. L., Strength and microstructure of silicon nitride ceramics brazed with nickel-chromium-silicon alloys. *J. Am. Ceram. Soc.*, 1996, **79**(3), 659–665.
15. Hadian, A. M. and Drew, R. A. L., Thermodynamic modelling of wetting at silicon nitride/Ni–Cr–Si alloy interfaces. *Mater. Sci. Eng. A*, 1994, **189**, 209–217.
16. Ceccone, G., Nicholas, M. G., Peteves, S. D., Kodentson, A. A., Kivilahti, J. K. and van Loo, F. J. J., The brazing of Si_3N_4 with Ni–Cr–Si alloys. *J. Eur. Ceram. Soc.*, 1995, **15**, 563–572.
17. Nash, P., The Ni–Si system. *Bull. Alloy Phase Diagrams*, 1987, **7**(5), 6–14.
18. Esposito, L., Bellosi, A. and Celotti, G., Silicon nitride-nickel joints through diffusion bonding. *Acta Mater.*, 1997, **45**(12), 5087–5097.
19. Osendi, M. I., De Pablos, A. and Miranzo, P., Microstructure and mechanical strength of Si_3N_4/Ni solid state bonded interfaces. *Mater. Sci. Eng. A*, 2001, **308**, 53–59.
20. Brandes, E. A. ed., *Smithell's Metals Reference Book*, 5th edn. Butterworths, London, 1976, pp. 472, 468 and 735.
21. Mohandas, T., Murthy, V. S. R., Dutta, A. and Mallesham, P., The role of surface finish in contact brazing. *J. Mater. Sci. Lett.*, 1999, **18**, 167–169.
22. Heikinheimo, E., Kodentsov, A., Beek, J. A. V., Klomp, J. T. and Loo, F. J. J. V., Reactions in the systems Mo–Si_3N_4 and Ni–Si_3N_4. *Acta Mater.*, 1992, **40**, S111–S119.
23. Kondentsov, A. A., Van Dal, M. J. H., Cserhati, C., Daroczi, L. and Van Loo, F. J. J., Permeation of nitrogen in solid nickel and

deformation phenomena accompanying internal nitradation. *Acta Mater.*, 1999, **47**(11), 3169–3180.

24. Rubly, R. P. and Douglass, D. L., Internal nitridation of nickel-chromium alloys. *Oxidation of Metals*, 1991, **35**(3/4), 259–278.

25. Kovalev, S. P., Miranzo, P. and Osendi, M. I., Finite element simulation of thermal residual stresses in joining ceramics with thin metal interlayers. *J. Am. Ceram. Soc.*, 1998, **81**(9), 2342–2348.