

Distribution and Chemistry of Phases Developed in the Brazing of Silicon Nitride to Molybdenum

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Abstract

Silicon nitride was brazed to molybdenum using two different nickel-based brazing alloys. The alloys used were AWS BNi-5 (Ni-18Cr-19Si at%) and an alloy with the same Ni/Cr ratio as BNi-5 but with 10 at% Si. Brazing experiments were carried out at 1220 and 1300°C for times ranging from 1 to 10 min. The quality and microstructure of the Si₃N₄/Mo couples were strongly influenced by the composition of the joining alloys, brazing time and temperature. Microchemical analysis revealed an elaborate joint microstructure with the formation of complex reaction products in the interface. Joint strengths of up to 50 MPa were achieved when these materials were brazed with an alloy containing 10% Si. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Silicon nitride, because of its superior mechanical properties at elevated temperatures and good resistance to corrosive environments is under active consideration for advanced structural applications such as gas turbines. However, improved joining techniques are required for these materials to meet the application requirements. The demand for ceramic joining arises from the fact that: (a) large or complicated ceramic components are difficult to manufacture in one piece, and (b) the brittle nature of ceramics may necessitate that these materials to be supported by metallic components.

Of all the joining techniques, high-temperature brazing, due to its simplicity, the small capital investment, and its potential as a mass-production process, is receiving extensive attention.^{1,2} However, brazing is a complex process affected by a number of factors simultaneously. One of the problems is the wetting behaviour of the base materials with the brazing alloy, particularly the ceramic, in order to achieve proper flow within the brazing gap. This is also a good indication of the reactivity of the brazing alloy with the base materials.³ Other requirements for the brazing alloy are (a) formation of a strong bond at the ceramic/filler metal interface and (b) stability at high temperatures and in severe chemical environments. Although a number of brazing alloys have been developed with good wetting and bonding behaviour with Si₃N₄, these alloys do not meet the high temperature requirement for many of the applications of Ceramic.^{4,5}

Due to the importance of Ni-based brazing alloys in high-temperature brazing and the reactivity of Ni and Cr with Si₃N₄,^{6–8} a commercially available brazing alloy, AWS BNi-5 (Ni-18Cr-19Si at%) and another alloy with the same Ni/Cr ratio as BNi-5, but with 10 at% Si were used as the filler metals (Table 1). The designations presented in Table 1, and used hereafter, refer to the Si content of the alloys. Previous studies showed that strong Si₃N₄ and SiC joints can form using these and other modified alloys based on BNi-5.^{9,10}

Mo, because of its low thermal expansion ($\alpha = 5.3 \times 10^{-6} \text{ K}^{-1}$), was selected as the metal member. In fact, Mo is usually used as an inter-layer in ceramic-to-metal joining. Since it alleviates stresses generated by the thermal expansion mismatch between the ceramic and metal.

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Table 1. Chemical analysis of the experimental brazing alloys

Designation ^a	Composition (at%)		
	Ni	Cr	Si
S10	69.61	20.35	10.04
S19 (BNi-5)	62.65	18.4	18.95

^aThe alloy designations refer to their Si contents.

2 Experimental

Sintered silicon nitride samples with Al₂O₃, Y₂O₃, and AlN as additives were prepared inhouse, by slip casting.¹¹ The green samples were sintered to $\geq 97\%$ of the theoretical density in a graphite element furnace at 1750°C for 2 h under a slight nitrogen overpressure (0.1 MPa). Joint specimens consisted of blocks of Si₃N₄ and Mo having approximate dimensions of 9×9×6 mm³ for joining experiments and 25×9×6 mm³ for fabricating a 50 mm long modulus of rupture (MOR) bars. All the 9×9 mm² surfaces of the joint specimens and 9×6 mm² surfaces of the MOR samples to be joined were mechanically ground and polished to a 1 μm finish and degreased in acetone ultrasonically prior to joining. Brazing experiments were carried out under a vacuum of 15 Pa in a graphite element vacuum furnace with a microprocessor controlled heating and cooling cycles. The brazing alloys, in quantities sufficient to form a layer of 100 μm thick upon solidification, were mixed with a water-based gel suspending agent (Nicrobraz Cement-S supplied by Wall Colmonoy Corporation) which provided a means of applying the filler metal in an easy-to-use thixotropic paste. A boron nitride brazing jig was used to insure sample alignment during the brazing process. After brazing, samples were sectioned perpendicular to the joint area and the resultant surfaces were polished for further examination.

All compositions and phases within the braze layer were analyzed with wavelength dispersive X-ray spectroscopy (WDS) using an electron probe microanalyzer (EPMA) unit (CAMEBAX, Cameca, Courbevoie, France). The examination was carried out at an accelerating voltage of 15 kV using a beam current of 20 mA and a beam size of 2 μm. The standards used consisted of pure Ni (Ni-K_α), Cr (Cr-K_α), Mo (Mo-L_α), and SiO₂ (Si-K_α), Al₂O₃ (Al-K_α) and Drake & Weill No. 2* (Y-L_α), N was analyzed by difference. The program resident in the WDS system employed the PAP¹² correction method for converting the sample intensities to quantitative concentrations.

3.21Y–3.66La–16.25Al–12.68Si–18.11Ca–3.41Ce–3.79Pr–
= %38.890 wt

The four-point bend strength of the experimental joints were measured according to ASTM standard C 1161.¹³ Both the tensile and compressive faces of the MOR bars were longitudinally ground using a 240 grit diamond surface grinding wheel. The edges of the samples to be exposed to tensile stresses were bevelled. Specimens were then placed in a four-point bend jig with outer and inner span of 40 and 20 mm, respectively, and tested at room temperature on an universal testing machine (Instron model 1362) with a cross head speed of 0.5 mm min⁻¹. At least 10 specimens were tested for each set of measurements.

3 Results and Discussion

3.1 Si₃N₄/S19/Mo joints

The secondary electron image (SEI) micrograph of a typical Si₃N₄/S19/Mo joint brazed for 10 min at 1220°C is shown in Fig. 1. Selection of this temperature was based on the results of a previous investigation on joining Si₃N₄-to-Si₃N₄ using the same brazing alloys.¹⁴ The study showed that strong Si₃N₄ couples could form under the experimental conditions outlined in the previous section.

Figure 1 shows the presence of cracking at the ceramic/filler metal interface due to the thermal expansion mismatch between the joining materials. Figure 1 can be divided into four distinct zones labelled, A, B₁, B₂ and C. The values given in the figure are the mean of 10 measurements (all the values are in at%). The overall compositions of zone B₁ and B₂ indicate that zone B₁ is rich in Mo while, the concentration of Cr and N is higher in zone B₂. The micrograph shown in Fig. 2 indicates that zone B₁ consists of a light phase denoted as α and a matrix labelled E, with E being a eutectic structure. The microscopic appearance of zone B₁

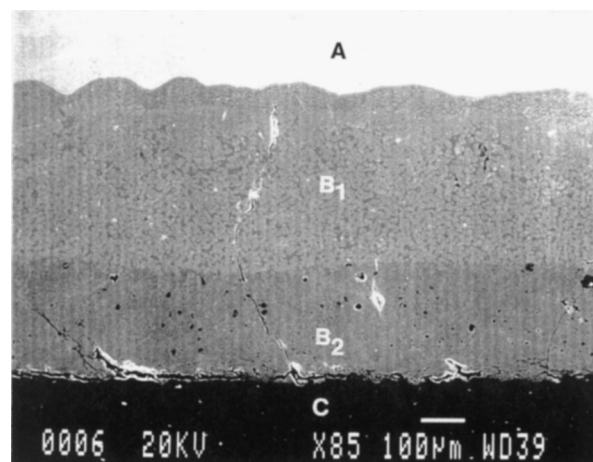


Fig. 1. SEI micrograph of a Si₃N₄/S19/Mo joint brazed for 10 min at 1220°C. A = Mo + <5%N; Cr and Si; B₁ = Ni–11Cr–19.5i–0Mo; B₂ = Ni–20Cr–11Si–10Mo–15N; C = Si₃N₄.

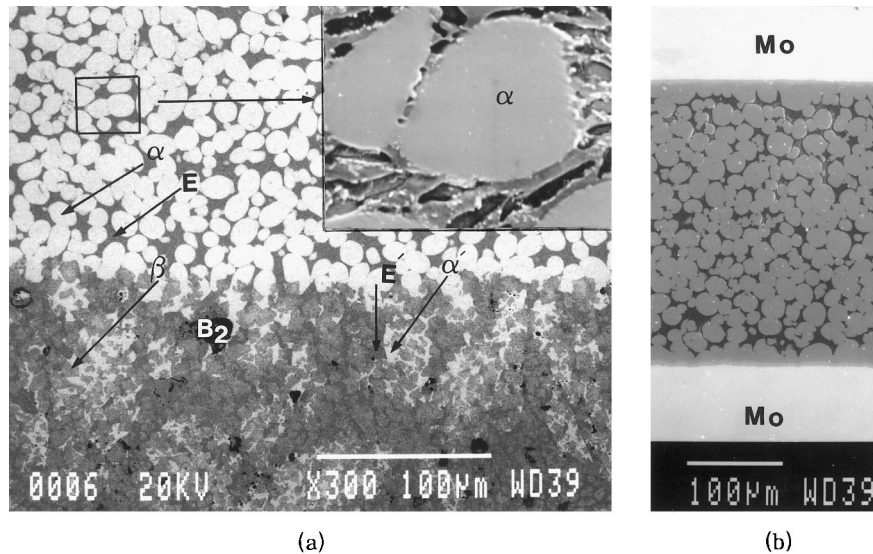


Fig. 2. (a) BEI micrograph of zone B_1 and B_2 and (b) SEI micrograph of a Mo/S19/Mo joint. α = Ni-8.5Cr-20Si-26Mo; α' = Ni-8Cr-19Si-26Mo-1N; E = Ni-19Cr-11Si; E' = Ni-Cr-9Si-8N; β = Ni-22Cr-13Si-12Mo-15N.

indicates a normal solidification with α as the primary solid phase. The chemical analysis of the phases in zone B_2 showed that this zone consisted of two phases, labelled α' and β and an eutectic E' . From the figure it can be seen that both E and E' have almost identical compositions in terms of Ni, Cr, and Si. However, some nitrogen dissolved in E' in zone B_2 . The higher concentration of N in E' than in α' is explained by the presence of more Cr in E' which has a higher solubility for N than any other constituent in the microstructure.¹⁵

The overall composition of the braze layer ($B_1 + B_2$) was determined as Ni-14Cr-16Si-15Mo-7N (at%). By performing a mass balance on the filler metal, an increase in Si content was observed. This observation along with the presence of nitrogen in the braze indicate that the filler metal had reacted with and decomposed the Si_3N_4 .

From the overall composition of the braze layer, it can be seen that the Mo content of the filler metal had increased from zero (starting alloy) to 15 at% (product alloy). Unfortunately there is no phase diagram available for the quaternary Mo-Ni-Cr-Si system, the presence of 15 at% Mo, with a melting temperature of about 2600°C, would have certainly increased the melting point of the braze alloy. In order to evaluate the approximate liquidus temperature of the braze, samples with the same composition of the product alloy (without taking into account the N) were prepared and heated up in the brazing furnace until melting occurred; the melting point was found to be $1270 \pm 10^\circ\text{C}$ which is significantly higher than the original S19 (BNi-5) alloy with a melting temperature of 1080–1140°C. Therefore, the brazing temperature of 1220°C was not suitable for this

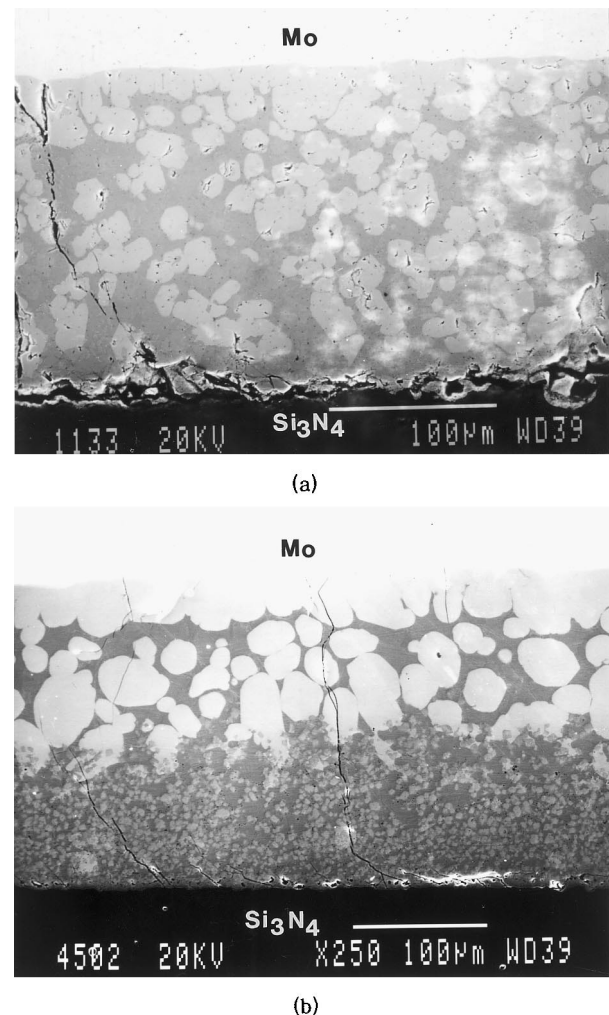


Fig. 3. SEI micrographs of Si_3N_4 /S19/Mo joints brazed for (a) 10 min and (b) 1 min at 1300°C.

system, mainly due to the higher liquidus temperature of the product alloy. Thus, further joining experiments were performed at a higher brazing temperature of 1300°C.

Figure 3 illustrates SEI images of $\text{Si}_3\text{N}_4/\text{S19}/\text{Si}_3\text{N}_4$ joints brazed at 1300°C for 10 and 1 min. A comparison of Figs 1 and 3(a) will show that the braze layer microstructure has been altered by the higher brazing temperature. The figure also shows a bond formation at the ceramic/filler metal interface. The strengths of these joints were measured using the four-point bend test and were found to be 25 ± 10 MPa. Most of the joints fractured at the ceramic/filler metal interface, however, in the case of the stronger joints, fracture occurred within the ceramic body near the interface. This was mainly due to edge cracking in the ceramic.

A comparison between the results of this study and previous investigations on joining Si_3N_4 -to- Si_3N_4 ¹⁴ where a strength of 120 MPa was achieved, indicates that the poor joining of Si_3N_4 to Mo is due to the presence of Mo in the product alloy and the reaction of this element with the ceramic at the Si_3N_4 /filler metal interface.

The reaction between Si_3N_4 and Mo has been investigated by several researchers.^{16–18} The investigation of Heikinheimo *et al.*¹⁷ in the study of Mo- Si_3N_4 diffusion couples at 1300°C showed that, independent of the nitrogen external pressure, only one phase, Mo_3Si , was formed at the interface. The reaction layer was very irregular and contained many cracks. At a N_2 partial pressure of 6×10^{-5} and 2 Pa they found layers of MoSi_2 , MoSi_3 and Mo_3Si in the Mo side of the joint.

The XRD pattern taken from the fracture surface of the joints brazed at 1300°C , on both the Si_3N_4 and the braze side, showed no identifiable spectra of any known compounds particularly of the phases expected in Mo-Si-N system. This is mainly due to the presence of Ni and Cr which make the system far more complex. Although, information exists concerning the ternary Ni-Cr-Mo¹⁹ and Ni-Si-Mo²⁰ systems, unfortunately no phase relationships about the quaternary Ni-Cr-Si-Mo system (even without taking the N into account) can be found in literature.

3.2 $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joints

Figure 4 illustrates a SEI micrograph of a $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joint brazed for 10 min at 1300°C . As was the case for the joints brazed with S19 alloy for the same time at the same temperature, no bonding occurred at the ceramic/braze layer interface. The lack of cracking in the braze layer indicates that debonding had occurred prior to complete solidification of the filler metal.

The morphology of the braze layer in Fig. 4 is somewhat similar to that of zone B₂ of Fig. 2(a). However, the β phase was difficult to identify in this case. The microstructure presented in the figure consisted of the α' phase and E' with almost the

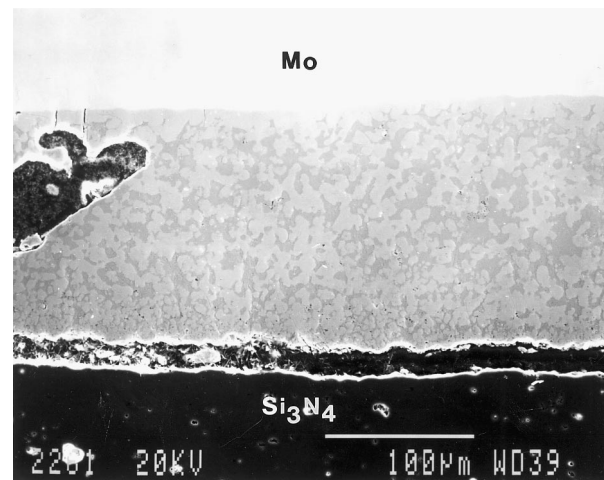


Fig. 4. SEI micrograph of a $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joint brazed for 10 min and at 1300°C . $\alpha = \text{Ni-8Cr-18Si-26Mo-4N}$; $E^1 = \text{Ni-15Cr-9Si-2.5Mo-8N}$;

identical composition as given in Fig. 2. However, in this case about 4% nitrogen and 3% Mo was found in α' and E' , respectively. A small amount of Al ($\approx 0.3\%$) from decomposition of Si_3N_4 were detected in the area close to the ceramic/metal interface. As was the case for the S19 joints, the XRD pattern taken from the fracture samples at both the ceramic and the braze layer side showed no identifiable peaks of any known compounds. With respect to the overall composition of the braze layer (Ni-13Cr-15Si-16Mo-8N) and by performing a mass balance on the product alloy composition, it was found that the Si content of the filler metal had increased from 10 to about 19 at%. This indicates a high reactivity between the ceramic and the S10 brazing alloy. Therefore, the brazing time was reduced to shorter times to alleviate these reactions.

Figure 5 shows a SEI micrograph of a $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joint brazed for 1 min at 1300°C . The figure provides evidence of bond formation at the ceramic/metal interface with no cracking in the braze layer. However, some minor porosity exists within the braze layer in the area close to Si_3N_4 /braze interface. This may indicate that, at the brazing temperature, the alloy near the interface was not completely liquid. Another possibility for the formation of porosity is N_2 gas evolution at the interface. Figure 5 also shows that the brazing time has a strong influence on reducing the interfacial reactions and consequently the joint quality.

An examination of Fig. 5 reveals that the braze layer microstructure is similar to that of the joint brazed for 10 min at the same temperature. The microchemical analysis showed that the product alloy consisted of α' phase and E' , with almost identical composition as the phases in Fig. 4. The overall composition of the braze layer was found to be Ni-14Cr-13Si-14Mo-7N which contains less Si,

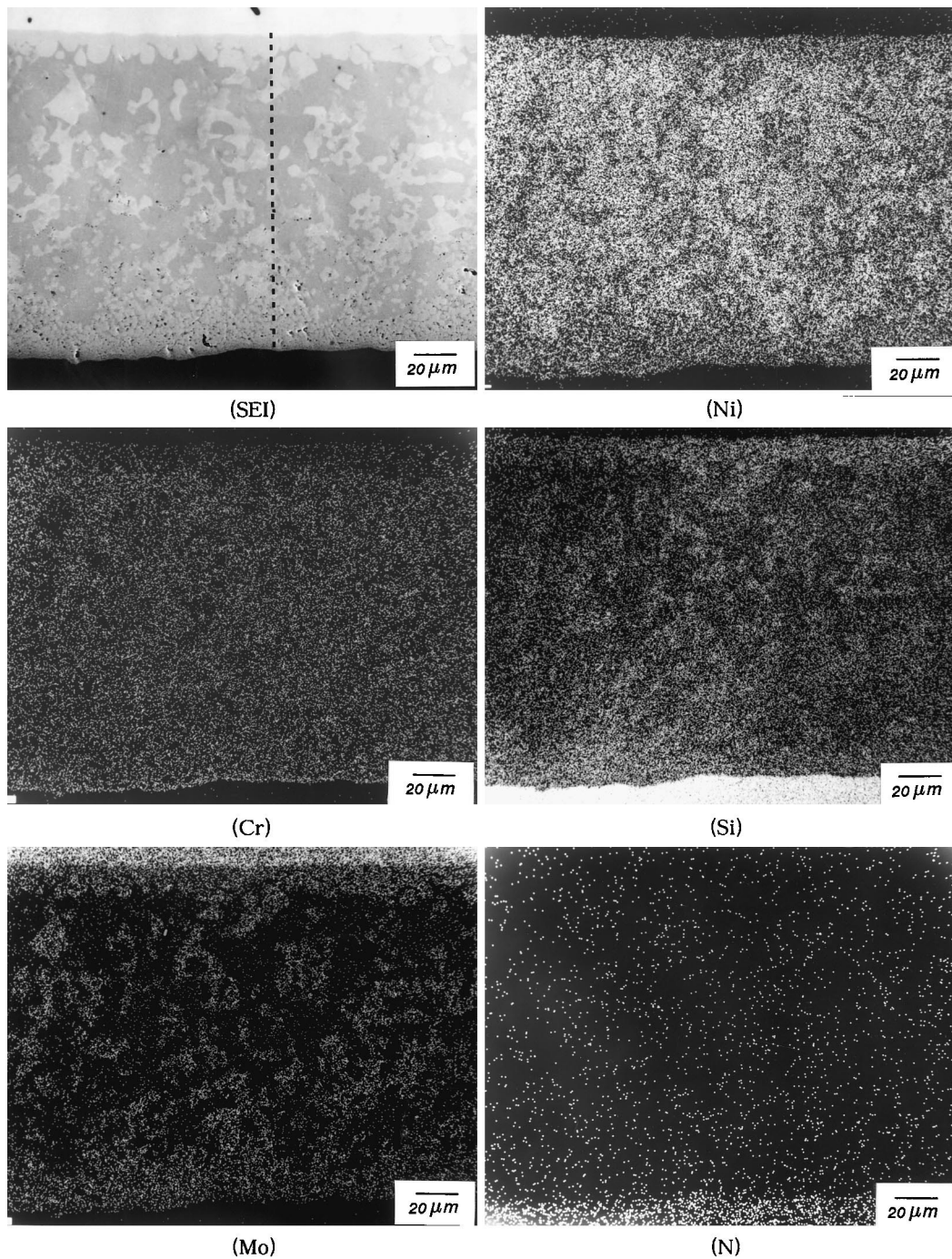


Fig. 5. SEI and WDS compositional dot maps for a $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joint brazed for 1 min.

Mo and nitrogen than the joint brazed for 10 min. This is mainly due to the shorter brazing time.

Figure 5 also illustrates the X-ray elemental dot mapping within the braze layer. As can be seen from the figure, the distribution of Ni, Cr, Si, and N is fairly uniform within the braze layer. However, Mo and Si are more concentrated in the α and α' phases and the area close to the ceramic/braze layer interface. The EPMA performed along the interfaces shown in Fig. 5 are presented in Fig. 6 and provides additional information on the elemental distribution within the braze layer. The figure clearly indicates that there is no large concentration gradient for Ni, Si, and particularly Cr

and N in the braze layer and in the area close to ceramic/filler metal interface.

The bend strength of the $\text{Si}_3\text{N}_4/\text{S10}/\text{Mo}$ joints brazed for 1 min were 55 ± 10 MPa. From the comparison of this strength value with those presented in literature it was revealed that most of the available data centre around the application of solid-state bonding rather than brazing for joint fabrication. Depending on the filler metal used and joining conditions, strength values ranging from 19 to 313 MPa have been reported.^{21,22}

The fractography examination of the $\text{Si}_3\text{N}_4/\text{Mo}$ MOR bars revealed that most of the bars fractured through the braze layer at the ceramic/braze layer

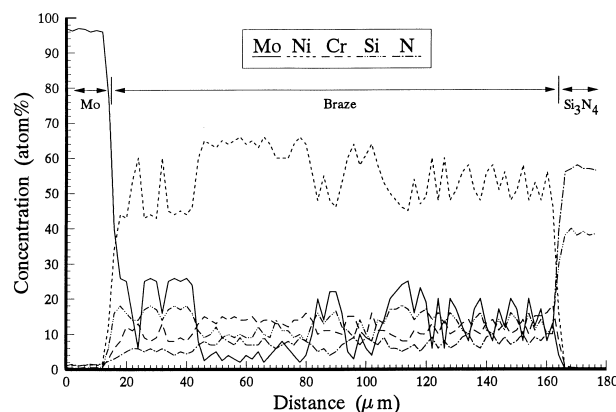


Fig. 6. EPMA microanalysis line profiles across the joint area in Fig. 5.

interface which is apparently the plane of weakness in the joints. In some cases the cracks, which had initiated at the edge of the sample due to the residual CTE mismatch stresses, propagated under the bending load and fracture occurred in the Si_3N_4 near the interface. In fact the influence of edge cracks in determining the joint quality is stronger than the interfacial bond strength by itself.

It is worth mentioning that one of the problems observed in all the joining experiments was blushing of Mo by the filler metals (wetting of unwanted area of parent materials by a filler metal), mainly due to the high reactivity between them. This problem, in many cases, resulted in the depletion of the filler metal from the braze gap. An attempt to paint the Mo sides with a so-called 'stop-off' agents* (a suspension of fine ZrO_2 powder in a lacquer) failed to prevent the Mo from blushing and the filler metal crept beneath the coated layer.

4 Conclusions

1. Couples brazed with Ni-18Cr-19Si (S19) at 1220°C , no bonding occurred at the ceramic/filler metal interface. A two zone microstructure resulted from competition between Mo diffusion from the metal side and Si and N from the ceramic side of the joint. The microchemical analysis revealed extensive diffusion of Mo into the liquid brazing alloy altering its chemistry and melting behaviour. Thus, the alloy was no longer entirely liquid and therefore bonded inadequately to the ceramic.
2. Brazing at a higher temperature (1300°C) resulted in a more uniform microstructure. However, after heating for 10 min, no bonding occurred at the ceramic/filler metal interface

because of severe reaction between the mating materials. However, reducing the time to 1 min resulted in bonding.

3. The Ni-20Cr-10Si (S10) alloy exhibited the same behaviour as S19. However, strong bonding was observed only upon brazing at 1300°C for 1 min, whereas the 10 min joints showed no bonding or mechanical strength.
4. The microchemical analysis revealed that the joint microstructures were strongly influenced by the diffusion of Mo, Si and N from the parent materials. Although the reaction products could not be identified at the interfaces, it is believed that the formation of complex Mo compounds was responsible for debonding at the ceramic/filler metal interface for the 10 min-brazed joints.
5. Flexural strengths of up to 55 MPa were achieved when brazing was performed with the S10.

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