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The Brazing of Si$_3$N$_4$ with Ni–Cr–Si Alloys

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Abstract

The use of commercially available and laboratory made Ni–Si–Cr brazes for wetting and bonding Si$_3$N$_4$ has been explored. The microstructure and chemistry of brazed joints has been characterized by techniques such as optical microscopy, scanning electron microscopy, electron probe micro-analysis and X-ray diffraction. Si$_3$N$_4$ was wetted well by all the braze alloys at 1150–1200°C, but the joint quality obtained was poor because of the formation of brittle phases and solid solutions.

1 Introduction

The increasing interest in the application of structural ceramics such as Si$_3$N$_4$ and SiC is due to their high-temperature strength and creep resistance, excellent wear, corrosion and thermal shock resistance. However, reliable joining technologies are needed if ceramic inserts are to be used to exploit these properties or complex components are to be made from simple ceramic bodies.

Brazing is an attractive technique for joining ceramic–ceramic and, particularly, ceramic–metal systems. However to profit from the high temperature mechanical properties of ceramics, high temperature brazes have to be employed and several studies have suggested Ni-based alloys as suitable brazes for joining Si$_3$N$_4$ and SiC.

This paper describes an evaluation of the potential usefulness of some Ni–Cr–Si brazes for joining Si$_3$N$_4$, employing a material science approach based on phase stability and thermodynamic factors.

2 Background

Brazing is a versatile and cost-effective technique for joining both similar and dissimilar material systems. However, many of the brazes used for joining metal workpieces do not wet technologically important ceramics and hence a sub-class of brazes, active metal brazes, have been developed for the joining of ceramics. The distinctive feature of these active metal brazes is that they react to change the surface chemistry and wettability of the ceramics.

Commercially available active metal brazes are generally based on the Ag–Cu–(In, Pd)–Ti and Cu–Al–Si–Ti systems and can be used for applications that do not require service temperatures higher than 400°C. Si$_3$N$_4$ can be joined with these brazes and important applications have been found in the automobile industries. However, many of the proposed future uses of Si$_3$N$_4$ involve service temperatures in excess of 700°C. The selection of a high temperature active metal braze involves two tasks: (a) choice of a solvent and, (b), identification of a reactive component. The first task requires consideration of metallurgical and technological factors; the solvent must be sufficiently refractory and chemically inert with respect to the workpieces and the environment so that the joined structures can withstand service conditions such as high temperature oxidizing atmospheres. The development of brazes for high temperature metals such as super alloys can provide some guidance for solvent selection but the second task is often more difficult to accomplish. Identifying a suitable reactive component requires information about what type of products will be formed by the specific workpiece/braze combinations during the joining process. Equilibrium thermodynamics can provide insight about the chemistry of the products, but not about their formation kinetics or properties such as wettability or strength. Thus experimentation is almost always necessary to identify the optimum brazing materials and process conditions.

Several studies of the active metal brazing of engineering ceramics aimed to increase the service temperatures have been reported. In particular, Au–Ni–Ti and Pd–Ni–Ti alloys have been used to
The results obtained indicate that a major problem is the enhanced chemical reaction between the ceramic and the braze.

The present work focused on the utility of Ni–Cr–Si brazes. These are based on the Ni–21%Si eutectic which melts at 1143°C and were chosen for several reasons: their commercial availability, the expectation that the presence of Si will reduce the dissolution of the Si₃N₄, the successful use of Ni–Cr alloys to diffusion bond Si₃N₄, their potentially good high temperature mechanical properties, the ability of Cr to form bonding layers of CrN by reacting with Si₃N₄, and the good oxidation resistance of Ni–Cr alloys. However, a problem to be faced when using Si as a temperature depressant for Ni brazes is the brittleness of the joints caused by the formation of silicides if the Si content exceeds about 10%.

Thermodynamic modelling can be a useful design tool in predicting the behaviour of the ceramic-braze systems and predictions for the SiC/Ni–Cr–Si braze systems are in good agreement with the experimental results. Unfortunately Si₃N₄/Ni–Cr–Si systems are more complicated because the reaction processes are strongly influenced by the N₂ local partial pressure. Furthermore, to understand the behaviour of Si₃N₄/Ni–Cr–Si systems requires a thorough knowledge of the Ni–Cr–Si–N phase diagram. This is lacking but some data, cited below, are available for the Ni–Cr–Si and Ni Cr N systems. Furthermore, a few (Ni Cr Si)/N₂ nitridation experiments were conducted as a precursor to this brazing study, as discussed later.

Some experimental data for Ni and Cr rich Ni–Cr–Si alloys have been published and Ansara et al. have assessed the data for Si lean alloys. The Ansara isotherms at 1027 and 1127°C are reproduced in Fig. 1. An obvious deficiency of this evaluation is that even the isotherm for 1127°C does not contain a liquid field, yet the commercial BNi-5, Ni–19Cr–18Si braze has a solidus of 1078°C. Hence, it became clear early on during this study that a more sound knowledge of this system was necessary if braze microstructures were to be interpreted, so a parallel programme was initiated to derive a full Ni–Cr–Si diagram and reference to its results will be made in the Discussion.

The stability diagram of nitride phases in various Ni–Cr alloys at 950, 1000 and 1125°C as a function of N₂ fugacity (partial pressure) is given in Fig. 2. More details concerning the thermodynamic calculations and experimental verification of this diagram can be found elsewhere. With decreasing temperature down to 1000°C a ternary phase, Cr₁ₓNiₓCr₄N₉, is stable in the Ni–Cr–N system. Nitridation of Ni alloyed with at least 28%Cr produced a π phase, Cr₁₀Ni₃N₁₇ or Cr₁₁Ni₈N₅₉, at 1000–1125°C which thermodynamic analyses demonstrated to be in equilibrium with the FCC Ni solid solution and Cr₂N at modest nitrogen activities.
3 Experimental

The ceramic used in this work was a commercial hot-pressed Si₃N₄ containing 1.8% Al₂O₃ and 5.1% Y₂O₃ as sintering aids. It was obtained from Ceradyne Inc., Costa Mesa, CA, USA, as a plate from which were cut samples measuring 7 x 15 x 3 mm. The faces to be bonded were polished, using a 1 μm diamond paste, to a final average roughness (Rₐ) of about 0.3 μm. The braze alloys used were 90 μm thick foils of a commercial BNi-5, obtained from Wesgo Inc., Belmont, CA, USA, and 500 μm thick foils of laboratory produced alloys. Their compositions are indicated in Fig. 1 and summarised in Table 1. Table 1 also includes their liquidus temperatures, which were determined by differential thermal analysis and ranged from 1135°C for BNi-5 to 1400°C for one of the laboratory alloys.

The ceramic pieces and the braze alloy foils were ultrasonically cleaned in methanol, rinsed in water and dried using an air blast immediately before being assembled as a sandwich and placed in the brazing furnace. The brazing experiments were performed under vacuum of 6 x 10⁻⁴ Pa (1 Pa = 1
times of 0.08–1 h and heating and cooling rates of 10°C/min. In accord with recommended practice for the BNi-5 alloy, each brazing cycle included a 1 h sub-solidus dwell at 1050°C during the cooling stage in an attempt to homogenize the seam microstructure. A slight uniaxial force of about 0.5 MPa was applied during brazing to maintain alignment of the workpieces.

Before commencing the main series of brazing experiments, the wetting behaviour of the brazes in vacuum at 1200°C was assessed. The alloy foils were placed on polished and cleaned Si₃N₄ substrates and heated at 10°C/min to 1200°C in a vacuum chamber evacuated to a pressure of less than 5 × 10⁻⁴ Pa. The samples were kept for 30 min at temperature and then cooled to room temperature at 10°C/min.

After being used in the wetting or brazing experiments, the samples were cross-sectioned, polished with diamond paste and finished with a 0.3 µm alumina slurry. The contact angles of wetting samples and the interfacial microstructures of brazed samples was characterized by optical microscopy and scanning electron microscopy. Electron probe microanalysis, (EPMA), and X-ray diffraction, (XRD), techniques were used to characterize the micro-chemistry of braze seams. The Vickers hardness of phases within the seams were derived using a 50 g load applied by Zeiss MHT-4 equipment.

Nitridation of the Ni–Cr–Si alloys under total gas pressures up to 100 bars, took place in a sintering furnace (KCE, Germany). Temperature control was carried out with an optical pyrometer within ±5°C accuracy. All experiments were carried out in pure nitrogen (O₂ ≤ 10 ppm; H₂O ≤ 10 ppm). After nitriding under these conditions, formation of oxides was not detected at the surface of the samples. The surface of the alloys were examined after nitriding by XRD analysis with a cylindrical texture camera using nickel-filtered Cu-Kα radiation.

**4 Results and Interpretation**

### 4.1 Wetting

The contact angles derived from the 1200°C wetting studies are presented in Fig. 3. The commercial BNi-5 braze wetted well with an angle of 10°, while the laboratory produced braze alloys wetted even better with contact angles of virtually zero.

Also included in the figure are some contact angles reported for other Ni braze alloys. Using the criterion of a maximum contact angle of 30° for effective wetting of a ceramic suggested by Moorhead and Keating, it can be seen that all the Ni–Cr–Si brazes used in this study are adequate but some of the other compositions are unsuitable.

### 4.2 BNi-5 Microstructure

Comparison of the quoted Ni 19Cr 18Si composition of BNi-5 with the phase stability diagrams for both 1027 and 1127°C, Fig. 1, reveals that it lies within the solid–solid Ni₅Si₂–FCC Ni two phase field, yet very close to the boundary of the solid–solid–solid Ni₅Si₂–FCC Ni–Cr₃Ni₅Si₂ three phase field. It was surprising, therefore, that the microstructure of the as received BNi-5 braze, shown in Fig. 4, contained three phases. These were: (1) a matrix labelled M with a hardness of HV463, (2) a substantial amount of a hard irregular phase labelled A, and (3) a small amount of a hard angular phase labelled B.
Table 2. Phases identified in BNi-5 foils and braze seams. (Compositions are given in at%). The stoichiometry of the Q-phase was found to be Ni$_3$Cr$_2$Si$_6$N$_6$

<table>
<thead>
<tr>
<th>Condition</th>
<th>Phase M</th>
<th>Phase A</th>
<th>Phase B</th>
</tr>
</thead>
<tbody>
<tr>
<td>As -received foil</td>
<td>Ni s.s.</td>
<td>Ni$_3$Si$_2$</td>
<td>Q-phase</td>
</tr>
<tr>
<td>Melted foil, 1150°C, 15 min</td>
<td>Ni-24Cr-15Si</td>
<td>Ni$_3$Si$_2$</td>
<td>Ni-45Cr-15Si-3-5N</td>
</tr>
<tr>
<td>Braze seam, 1150°C, 15 min</td>
<td>Ni s.s.</td>
<td>Ni-27Si-7Cr</td>
<td>Q-phase</td>
</tr>
<tr>
<td>Braze seam, 1200°C, 15 min</td>
<td>Ni-24Cr-12Si</td>
<td>Ni$_3$Si$_2$</td>
<td>Ni-51Cr-15Si-3-5N</td>
</tr>
<tr>
<td>Braze seam, 1200°C, 30 min</td>
<td>Ni$_3$Si$_2$</td>
<td>Ni-28Si-2-8Cr</td>
<td>Q-phase</td>
</tr>
<tr>
<td></td>
<td>Ni-27Si-8.4Cr</td>
<td>Ni-32Si-3-5Cr</td>
<td>Cr-29Ni-14.9Si-7.3N</td>
</tr>
<tr>
<td></td>
<td>Ni-27Si-8.2Cr</td>
<td>Ni-32Si-4.3Cr</td>
<td>Cr-28Si12.2N</td>
</tr>
</tbody>
</table>

The compositions of the phases in this and other cross-sections are summarised in Table 2. Comparison of these compositions with the Ansara diagrams shown in Fig. 1 identifies the Ni-24Cr-15Si matrix, M as a Cr and Si saturated FCC Ni and the hard irregular Ni-26Si-10Cr phase A as a Cr enriched Ni$_3$Si$_2$. However, assigning an identity to the Ni-51Cr-15Si-3-5N composition of the angular phase B is difficult. The angular phase contains nitrogen and hence cannot be identified validly as any of the ternary compounds shown in the Ansara diagrams. Even if the N content is ignored, the normalised composition is not in accord with any of the phases shown in Fig. 1 but lies within the two phase field between Cr$_3$Ni$_2$Si$_2$ and the Cr$_3$Ni$_2$Si, or σ phase. Therefore, it was decided somewhat arbitrarily for the moment, (it will be justified later on), to regard the angular phase (B) as a quaternary compound, Q.

The microstructure of the BNi-5 foil was little changed by subjecting it to a simulated brazing cycle by melting in an Al$_2$O$_3$ crucible and holding at 1150°C for 15 min, Table 2. The microstructure contained three phases; 53% of the Ni-based solid solution matrix phase, 40% of Ni$_3$Si$_2$ and 7% of the quaternary Q-phase. However, major changes occurred when the alloy was subjected to braze cycles in contact with Si$_3$N$_4$.

4.3 Si$_3$N$_4$/BNi-5 interactions

The good wetting behaviour of BNi-5 ensured that brazed sandwiches were formed successfully at both 1150 and 1200°C. The wetting was so good that the braze also spread over the sides of the ceramic pieces, but the structures of the joints were poor. Optical microscopy revealed that there were voids within the brazed seam and that both the seam and the ceramic-metal interfaces were cracked, presumably due to stresses caused by the mismatch between the 9.5 × 10$^{-6}$ °C$^{-1}$ thermal expansion coefficient of the braze, and the 3.3 × 10$^{-6}$ °C$^{-1}$ of Si$_3$N$_4$.

After brazing at 1200°C (Fig. 5) it was found that the Vickers hardness of the braze matrix phase had been increased to about HV 1100 (Table 3), and that the composition of the braze seam had been changed (Table 2). The matrix became depleted in Cr but Fig. 6 shows that extending the brazing cycle caused the
Table 3. Hardness of the matrix phase in Ni-Cr-Si alloys before and after use in various experiments

<table>
<thead>
<tr>
<th>Alloy or System</th>
<th>Experiment</th>
<th>Hardness (Hv 50gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNi-5</td>
<td>None</td>
<td>463.5 ± 17.4</td>
</tr>
<tr>
<td>Si,NdBNi-5</td>
<td>Brazing at 1200°C</td>
<td>1090.3 ± 40.7</td>
</tr>
<tr>
<td>Si,NdNi-21</td>
<td>Brazing at 1200°C</td>
<td>1109.0 ± 34.0</td>
</tr>
<tr>
<td>Si,NdNi-35</td>
<td>Wetting at 1200°C</td>
<td>1061.5 ± 67.8</td>
</tr>
<tr>
<td>Si,NdNi-4</td>
<td>Wetting at 1200°C</td>
<td>1102.3 ± 31.6</td>
</tr>
</tbody>
</table>

Si content of the braze seam to increase progressively as more Si rich silicides were formed. With increasing the brazing time, the Ni,Si, phase identified in Fig. 4 as A was converted to Ni,Si, Fig. 7, and became very abundant. Finally, the EPMA studies showed that quite large amounts of a complex Ni–Cr–Si–N phase was formed, the N content of which increased with the brazing temperature and time. By comparison with the microstructure of the as received filler metal this phase was identified as the quaternary Q-phase.

The large amount of Si found in the braze seam clearly demonstrates that Si,N reacts with the liquid filler metal during the brazing process. The conclusion is reinforced by the fact that decreasing the brazing time to 5 min, still caused the conversion of the matrix to a brittle silicide. Rapid reaction of the ceramic with the molten braze is reported also by Hadian and his co-workers, who used the BNi-5 alloy for brazing Si3N4 to Mo at 1200°C. They measured a smaller increase in the Si content of the braze than it was observed in our study, but this difference may be explained by the higher partial pressure of nitrogen in their experiments (~8 Pa) compared to ours (~8 × 10^6 Pa), which leads to a lower chemical potential of silicon in Si3N4 and, therefore, to lower driving force for diffusion of silicon.

In some final experiments, the configuration of the joints was changed by the introduction of a 500 μm thick foil of Ni–22Cr, Fig. 8. In this case, 8-Ni,Si was not found within the braze seam after bonding at 1200°C for 30 min. However, there was an extensive formation of the Q-phase within a matrix of Ni-based solid solution and Ni,Si3. In places, the Q-phase was formed as spherical particles, that suggested it had grown in the molten matrix. Another reaction product worth noting was a layer of ‘CrN’ at the braze–ceramic interface that was observed exclusively in the central region of the joint.

Although the brazing temperature suggested for the commercial BNi-5 alloy ranges between 1150 and 1216°C, the present results demonstrate that a temperature of 1200°C is too high if it is to be used to join Si3N4. Hence, further brazing experiments at lower temperatures were performed.
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Fig. 9. Scanning electron micrographs of a Si$_3$N$_4$/BNi-5 joint brazed at 1150°C for 15 min.

Microstructure of a cross-section of a Si$_3$N$_4$/BNi-5 joint brazed at 1150°C for 15 min, shown in Fig. 9, is not significantly different to that produced at 1200°C, Fig. 5. Once more, three phases are present in the brazing seam. Quantitative electron probe micro-analysis of the braze seam, summarised in Table 2, showed that the Ni solid solution matrix was still present in the seam even though large amounts of Ni$_3$Si$_2$ had been formed, the amount of Cr dissolved in the Ni$_3$Si$_2$ was decreased from 8 to about 3%, and the angular Q-phase was even more deficient in nitrogen.

4.4 Interactions of Si$_3$N$_4$ with other Ni–Cr–Si brazes

The cross-section of a Si$_3$N$_4$/N-21 alloy (Ni–6Cr–22Si) joint bonded at 1200°C for 15 min, shown in Fig. 10(a), has features similar to those observed in Si$_3$N$_4$/BNi-5 joints. Once again, the results indicate a brazing temperature of 1200°C is too high because of excessive ingress of Si. This conclusion is supported by results obtained using the other Ni–Cr–Si laboratory alloys, N-4 (Ni–5Cr–10Si), N-5 (Ni–10Cr–10Si) and N-35 (Ni–10Cr–5Si). Melting occurred even though the liquidus temperatures of the alloys are 1350–1400°C, Table 1. The melting was associated with a matrix hardness increase, as shown in Table 3, and the formation of the brittle quaternary Q-phase.

A significantly different microstructure was produced when the laboratory alloy N-21 (Ni–6Cr–22Si) was used to braze at 1150°C for 15 min, as illustrated in Figure 10(b). In this case a reaction layer with an average thickness 2.4 ± 0.5 µm was formed at the ceramic/braze interface. A quantitative composition cannot be quoted for this reaction layer because of spatial resolution limitation of the electron probe micro-analysis technique, but from the optical appearance and morphology as well as from qualitative EDX elemental maps we may conclude that this layer is the quaternary Q-phase.

EPMA analysis of the braze seam revealed that the matrix was Ni$_3$Si$_2$ and that the angular inclusions shown in Fig. 10 had similar composition with the phases identified as Q in the other joint microstructures. Finally, cracks and voids were present in the seam, so the microstructure was unacceptable as in the case of the Si$_3$N$_4$/BNi-5 joints.

4.5 Nitridation of Ni–Cr–Si alloys

In general, as in the case of the Ni–Cr–N system, see Fig. 2, the activity of N$_2$ largely determines the stability of various phases in the Ni–Cr–Si–N system. Nitridation of Ni–15Cr–10Si alloy at 1125°C under 1 bar N$_2$ pressure or higher, produced a surface layer and internal precipitates of the
quaternary phase Q, Fig. 11. Careful EPMA analysis of equilibrated samples pointed out to a Ni$_{13}$Cr$_{10}$Si$_8$N$_6$ stoichiometry for the Q-phase. Additional nitriding experiments of different Ni–Cr–Si alloys (Ni–(20–35%Cr)–(2–5% Si)) have shown that the Q-phase exists as an equilibrium phase in the quaternary Ni–Cr–Si–N system over the temperature range of 1000–1250°C.

5 Discussion

It is clear that Si$_3$N$_4$ interacts strongly with Ni–Cr–Si brazes. Thus all the brazes wetted well at 1200°C, and the behaviour of the laboratory-made brazes (N-4, N-5 and N-35) is evidence of a melting temperature depression caused by the ingress of Si from the ceramic. Vigorous workpiece/braze interactions are often associated with good wetting, and all the brazes used in this study wetted very well. The least wetting braze was the commercial BNi-5 alloy which also has the highest Cr content. However, the correlation between Cr content and wetting behaviour is unclear because, for instance, the Ni–Cr–P brazes with the highest Cr contents also formed the lowest contact angles with Si$_3$N$_4$.

While braze/ceramic interactions promote wetting, the resultant microstructures are excessively brittle and none of the Ni–Cr–Si brazes used in this study can be considered satisfactory joining materials for Si$_3$N$_4$, not even the commercially developed BNi-5.

Upon brazing at 1200°C the liquid filler metal reacts with the ceramic leading to an ingress of Si and nitrogen into the braze. Since the melting point of the Q-phase is higher than 1250°C, as determined by the nitridation experiments, the interaction of the nitrogen with the liquid Ni–Cr–Si filler metal is as follows:

$$\text{Si}_3\text{N}_4 + L ⇔ Q + L'$$

where L' is the remnant Cr-depleted liquid filler metal. The second eutectic isotherm in the binary Ni–Si system (L' ⇔ Ni$_2$Si$_2$ + δ-Ni$_3$Si) lies at 1215°C. Chromium that is still present in the liquid may depress the temperature of this eutectic. However, the significant ingress of silicon from Si$_3$N$_4$ into the molten braze leads to the formation, inside of liquid, of precipitates of δ-Ni$_2$Si (or its high temperature modification θ-Ni$_3$Si) having a higher liquidus temperature. Then, these precipitates grow through the liquid. Such a mechanism seems to be confirmed by the resultant morphology of the reaction zone after brazing at 1200°C for 15–30 minutes (Fig. 5(a), (b)).

At 1150°C the interactions between the ceramic and the braze are less severe. Still the liquid filler metal is enriched with Si and depleted from Cr. Besides the formation of the quaternary Q-phase, excess of Si within the molten filler metal result in the precipitation of Ni$_2$Si at the brazing temperature rather than upon cooling.

In order to decide whether any other Ni–Cr–Si braze might be suitable, it is necessary to understand the reaction paths followed by the ceramic/braze systems, especially the formation of the nitride phases inside the braze seam. For instance the formation of a continuous layer of CrN at the interface is desirable because this could impede the ingress of Si, whereas the formation of the brittle Q-phase in the seam deteriorates the joint quality. Quantitative understanding of the reaction paths cannot be achieved because of the lack of phase equilibrium data for the Cr–Ni–Si–N system but some qualitative guidance can be obtained from considering the recent Ni–Cr–Si phase diagram study in parallel with this brazing work.

The ineffectiveness of the Si contents of the brazes in inhibiting further detrimental ingress of Si from the ceramic is further illuminated by these studies. Figure 12 displays two experimentally determined isothermal sections for 1050 and 1125°C that should be relevant to phase structures of molten and solidified brazes. Comparison of this new information with the assessments for Si lean alloys shown in Fig. 1 reveals both similarities and differences which impinge on our observations. There is agreement about the phase structure of the laboratory made alloys: N-4, (Ni–5Cr–10Si), N-5, (Ni–10Cr–10Si) and N-35, (Ni–10Cr–5Si), lie within the Ni solid solution and N-21, (Ni–6Cr–22Si), lies within the two phase field between Ni$_3$Si$_2$ and the FCC or γ-Ni solid solution. The ineffectiveness of the Si contents of the brazes in inhibiting further detrimental ingress of Si from the ceramic is further illuminated by these studies. Figure 12 displays two experimentally determined isothermal sections for 1050 and 1125°C that should be relevant to phase structures of molten and solidified brazes. Comparison of this new information with the assessments for Si lean alloys shown in Fig. 1 reveals both similarities and differences which impinge on our observations. There is agreement about the phase structure of the laboratory made alloys: N-4, (Ni–5Cr–10Si), N-5, (Ni–10Cr–10Si) and N-35, (Ni–10Cr–5Si), lie within the Ni solid solution and N-21, (Ni–6Cr–22Si), lies within the two phase field between Ni$_3$Si$_2$ and the FCC or γ-Ni solid solution.
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Similarly, there is agreement that any \( \sigma \)-phase present in the as-received BNi-5 will have been a nonequilibrium or a quaternary phase.

In contrast, the isothermal sections due to Ansara et al., shown in Fig. 1 predict that the commercial BNi-5, Ni-18Cr-19Si, lies on the edge of a solid–solid two phase field between FCC Ni and Ni₄Si₂. This is not confirmed by the new isotherms shown in Fig. 12. In these, the BNi-5 composition lies close to the edge of the \( L_2 \) liquid field at 1125°C and presumably will lie on the actual edge of an expanded \( L_2 \) liquid field at the braze liquidus of 1135°C. Even more informatively, the new diagram for 1050°C casts light on the microstructure of the solidified braze seams produced by the equilibrium of the brazes and the dissociating ceramic. Ingress of Si will cause the Ni solid solution braze matrix to be replaced progressively by silicides and we have observed the formation of Ni₄Si₂ and Ni₅Si₃.

The same considerations apply to the interaction of solid Ni–Cr alloys during the diffusion bonding of Si₃N₄, but the approach to equilibrium will be much slower. The diffusion coefficient of Si in Ni–22Cr at 1200°C is \( 4.9 \times 10^{-14} \text{ m}^2\text{s}^{-1} \), probably 10 000 times slower than in the molten braze because the self diffusion coefficient for molten Ni lies in the range \( 10^{8}–10^{10} \text{m}^2\text{s}^{-1} \).

A substantial displacement Cr is caused by the conversion of the Ni–24Cr–12Si matrix of the braze to Ni₄Si₂ and Ni₅Si₃ containing only 8% of Cr. The ingress of Si from the ceramic that causes this displacement of Cr is accompanied also by a release of nitrogen and our experimental results show the displacement to result in a formation of a Cr rich nitride, Ni₃Cr₃SiN₆, which can be in equilibrium with the Ni-solid solution and Ni₄Si₂ or Ni₅Si₃. The presence of Ni₃Cr₃SiN₆, therefore provides proof of one logical step in the progress of a reaction path in the uncharted Ni–Cr–Si–N system created when a Ni–Cr–Si alloy is used to braze Si₃N₄.

The 1050°C isotherm in Fig. 12 shows that one or more of the Cr–35Ni–25Si (T), Cr–30Ni–10Si (\( \sigma \)) or Ni–30Cr–20Si (\( \sigma' \)) phases will be in equilibrium with the \( \gamma \)Ni braze matrixes and that the \( T \) and \( \sigma' \) phases will be in equilibrium with Ni₃Si₂ matrices. Experimental measurements of the Cr enriched angular \( Q \)-phase in solidified BNi-5 seams with both \( \gamma \)Ni and silicide matrices yielded compositions of approximately Ni–42Cr–16Si–12N, intermediate in metal stoichiometry between that of the \( T \) and \( \sigma \) phases. The \( \sigma \)-phase is not in equilibrium with the Ni₄Si₂ present in all the solidified braze seams, but there are tie lines between the \( T \)-phase and both \( \gamma \)Ni and Ni₃Si₂. Thus the designation of the angular \( Q \)-phase in BNi-5 braze seams, and possibly the reaction product layer formed by N–21, as a \( \gamma \) modified T phase is a logical, albeit tentative, outcome of the Ni–Cr–Si phase diagram studies.

It is clear that the prospects of improving the joint characteristics by varying fabrication conditions such as time and temperature are bleak. Diffusion barriers will need to be applied to the ceramic surfaces to prevent Si and nitrogen ingress when using Ni–Cr–Si braze alloys.

6 Conclusions

Ni–Cr–Si braze alloys wet and adhere to Si₃N₄ and in some cases spreading is observed. Despite
the large range of brazing conditions explored, the joint quality obtained was very poor. Unbonded areas, cracks and voids were observed in almost all the samples.

Contact between the molten Ni–Cr–Si brazes and Si₃N₄ caused ingress of Si and nitrogen from the ceramic. In the case of the commercial BNi-5 alloy, the relatively ductile γNi matrix of the braze was converted to brittle Ni,Si, or Ni,Si. Other changes caused by the ingress of Si were the formation of a Ni–Cr–Si–N compound as inclusions or a reaction product layer.

The difficulties encountered when using the Ni–Cr–Si alloys are related to fundamental materials science effects rather than inappropriate choice of brazing conditions. None of the Ni–Cr–Si brazes can offer direct resistance to the embrittling ingress of Si and nitrogen from the ceramic.

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