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Silicon nitride–stainless steel braze joining with an active filler metal

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Hot-pressed Si_3N_4 was brazed to 410-stainless steel using a Ag–Cu–Ti alloy foil in a vacuum. The occurrence of cracking due to processing was examined by systematically varying the brazing temperature and time between 840 and 900 °C and 6 and 60 min, respectively. Cracks were found in Si_3N_4 parallel to the bonding interface when the braze joints were processed at the lower temperatures (for all processing times at 840 °C and for times of 6 and 12 min at 860 °C). A reaction layer was observed to develop in the filler metal adjacent to Si_3N_4, rich in Ti and containing some Si. The thickness of this layer depended on brazing temperature and time. Microcracks were found in the reaction layer normal to the bonding interface in the joints processed at higher brazing temperatures (880 °C for 60 min and at 900 °C for 30 and 60 min). The low temperature cracks occurred, apparently, as a result of the incomplete relaxation of thermal stresses due to the presence of a hard continuous titanium strip in the filler metal; the high temperature microcracks seemed to be affected by the increase in thickness of the reaction layer and by the precipitation of intermetallic compounds. The compressive shear strength of the braze joints were evaluated and correlated with the cracking behaviour and microstructure changes in the joint. A strong braze joint was obtained when the reaction layer was relatively thin and no cracks were present in either the reaction layer or the Si_3N_4.

1. Introduction

In recent years, there has been an increase in the actual and potential uses of certain ceramics and of newer metal alloys. Techniques have been developed to produce joints for structural applications, where strength or vacuum tightness are often the primary requirements. Frequently these joints escape the notice of the casual observer because, when they are made well, there is a smooth transition from one material to the other with no obvious demarcation of the joint. Yet the technologies that are used to join ceramics are truly critical, because without them many uses of ceramics would be impossible or uneconomical. Some of these examples include cathode ray tubes, silicon nitride turbocharger rotors, valve guides and cam followers, etc.

A major anticipated application of ceramics in the automotive industry is in advanced heat engines; consequently, considerable research has been directed towards the joining of metals to ceramics [1–4]. One of the major problems in bonding these materials is whether a metallurgical joint can be developed, since conventional braze filler metals cannot wet ceramics because of the low surface energy of most ceramics. Studies investigating wetting phenomena and subsequent chemical reactions that occur along the ceramic-to-metal interfaces are valuable in order to understand the bonding mechanisms of joining ceramics to metals with excellent mechanical properties. Sessile drop experiments have been conducted and the contact angle estimated based on Young–Dupre's equation to evaluate wettability. For instance, it was found that for alumina (Al_2O_3), the contact angle of Sn + (0–5% Ti) filler metal with Al_2O_3 decreased significantly with the increase of titanium [5]. It has been found that braze metals containing an active metal, e. g. titanium or zirconium, are known to be effective in joining ceramic-to-metal [6–8]. Choh *et al.* [9] found that adding 1–5% cerium or calcium to liquid aluminium was extremely effective in improving the wettability between Al_2O_3–5% SiO_2 and the molten aluminum. They stated that cerium or calcium had a strong affinity for oxygen and appeared to increase the solubility of oxygen in liquid aluminum thereby improving wettability.

Another problem connected with ceramic-to-metal bonding is the thermal expansion mismatch between ceramics and metals which induces large residual stresses on cooling causing cracking of the ceramic substrate [9–11]. One way to overcome the residual stresses is to use ductile metal brazes or to introduce soft metal interlayers with the filler metal, such that the braze metal plastically deforms and by absorbing the thermal stresses, cracking of the ceramic is reduced [12, 13]. Another approach to reduce such stresses and improve the strength of the joint is the design of

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the joints. The designer must take into consideration the compensation of stresses and the way the stresses are to be distributed within the joint [14]. However, the chemical composition of the interface and the kinetics of formation of individual phases and compounds at the reaction layer, significantly influence the mechanical strength of the joint.

The objective of this investigation was to characterize microstructurally and mechanically the braze joint of silicon nitride to stainless steel by systematically varying the processing temperature and time. The development of reaction layers at either the metal or ceramic–braze metal interfaces were monitored. The microstructural and compositional changes of these regions are correlated with the occurrence of cracking and joint shear strength.

2. Experimental procedure

2.1. Production of braze joints

The silicon nitride used in this investigation was NCX-34 Si_3N_4 hot-pressed with Y_2O_3; it was sectioned into slices of $10 \times 10 \times 3.0\ mm^3$. A 410-stainless steel round bar, 15 mm in diameter, was used as a metal substrate which was sectioned into slices of 10.0 and 5.0 mm thick. A filler metal foil (0.13 mm thick) known as Ticusil (68.8 wt % Ag, 26.7 wt % Cu and 4.5 wt % Ti) was used, cut to dimensions of $10 \times 10\ mm^3$.

strates were ground manually using silicon carbide abrasive paper and polished on Nylon cloths dressed with 6 and 1.0 μm diamond pastes. Both base materials were cleaned ultrasonically in acetone following the standard metallographic preparation. The filler metal foil was sandwiched between the silicon nitride and stainless steel, and the whole sample was placed in a tube furnace. After loading, the furnace was evacuated to less than 6.66×10^{-3} Pa; the temperature was raised to 780 °C at a heating rate of 10 °C min^{-1} and then held at this temperature for 12 min. The samples were finally heated at a rate of 5 °C min^{-1} to the brazing temperature (840–900 °C) where they were held for different periods of time between 6 and 60 min. Afterwards the samples were cooled to 500 °C at a rate of 5 °C min^{-1}, followed by a rate of 2 °C min^{-1} to room temperature.

2.2. Metallographic and mechanical evaluation of braze joints

The braze specimens were cross-sectioned to study the microstructural and compositional changes in the filler metal foil as well as at the metal and silicon nitride interfaces. Standard metallographic procedures were also followed in preparing the samples. The filler metal foil was also mounted and metallographically analysed.

The microstructure, element distribution and phase identification in the joints were determined by means of light microscopy, scanning electron microscopy (SEM), energy dispersive microanalysis (EDX) and X-ray diffractometry (XRD). The shear strength was evaluated by submitting the braze joints to compressive shear tests using a special mechanical fixture and an Instron testing machine. The tests were conducted at room temperature applying a crosshead speed of 0.5 mm min^{-1}.

3. Results

3.1. Effect of brazing temperature and time on joint soundness

The soundness of the braze joints was assessed by considering the development of a crack during the processing cycle. Four brazing temperatures and four times per temperature were selected as the brazing parameters. Following processing, the braze joints were cross-sectioned and examined metallographically for cracks. A mapping was generated defining the regions of crackings (Fig. 1). Cracking was found in all samples processed at 840 °C and for processing times of 6 and 12 min produced at 860 °C. Cracking also occurred at higher temperatures and longer times. The shear strengths of the joints were determined for each of the processing temperatures and times selected, with the exception of those processed for 60 min. The results are summarized in Fig. 2, the shear strengths reported are an average of four test per processing condition. In the lower brazing temperatures the shear strength increased with longer brazing times, but at

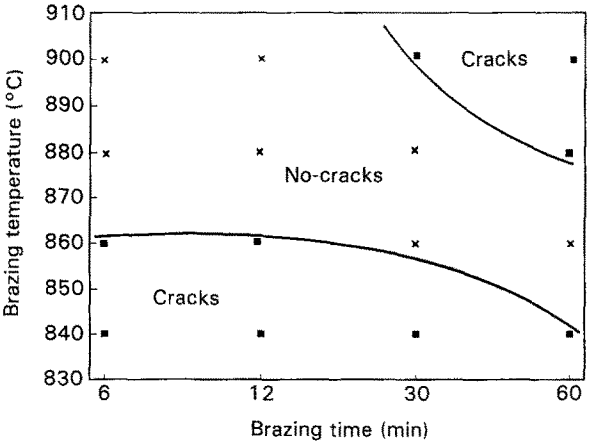

Figure 1 Cracking behaviour of Si_3N_4–stainless steel braze joints using Ticusil filler metal for different brazing times and temperatures.

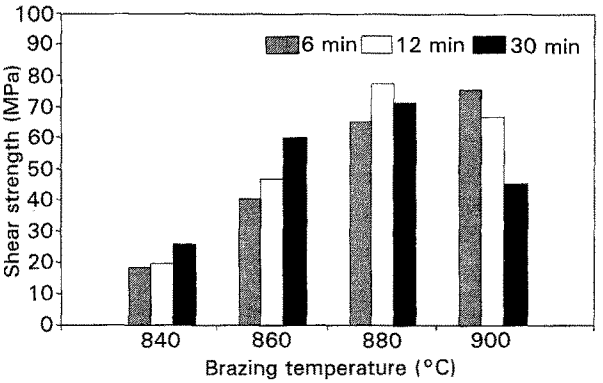

Figure 2 Shear strength of Si_3N_4–stainless steel braze joints as a function of processing time and temperature for a Si_3N_4 to steel thickness ratio of 0.3.

900 °C it was found that the strength of the joints decreased with increasing time. The braze joint produced at 880 °C for 12 min gave the highest shear strength values.

Most of the joints were produced using thicknesses of 3.0 and 10.0 mm for the silicon nitride and stainless steel, respectively. But there were few brazes produced by varying the ceramic-to-metal thickness ratio to assess its effect on cracks and joint strength. A brazing temperature of 880 °C and time of 12 min were selected as the optimum processing parameters for the evaluation of the ceramic-to-metal thickness ratio against joint strength. As expected, it was found that the shear strength diminished as this ratio increased, as shown in Fig. 3.

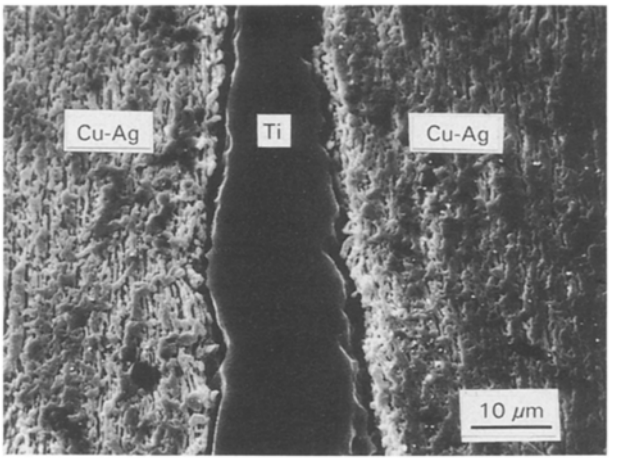

Figure 4 Scanning electron micrograph of the as-received filler metal.

3.2. Effect of brazing parameters on braze joint microstructure

The microstructure of the initial filler metal was examined and found to consist of two Cu–Ag eutectic layers compressing a Ti strip, as shown in Fig. 4. An EDX analysis was performed in each of these regions (Fig. 5) and found Ti present only in the central strip with none detected at the Cu–Ag eutectic regions, as seen in Fig. 5b. X-ray mappings of these regions were also obtained and these confirmed the initial element distribution.

The microstructural and compositional changes of the braze metal joint were monitored in terms of brazing temperature and time, samples were selected for cases where cracking occurred as a result of processing (30 min at 840 and 900 °C) and for a condition where no cracking occurred (30 min at 880 °C). Refer to Fig. 1 to locate these specimens on the map which illustrates the cracking activity.

Fig. 6 shows the microstructure of the joint produced at 840 °C for 30 min, with corresponding Ag, Cu and Ti X-ray maps. The Ti strip, apparently, did not undergo significant morphological changes (Fig. 6a); the X-ray map shows Ti localized at the centre of the braze metal, but some Ti also diffused to the interfaces with the silicon nitride and stainless steel substrates (Fig. 6c). Ag distributed uniformly in the eutectic matrix and Cu was sparsely found in the braze metal matrix and some had diffused to the Ti strip

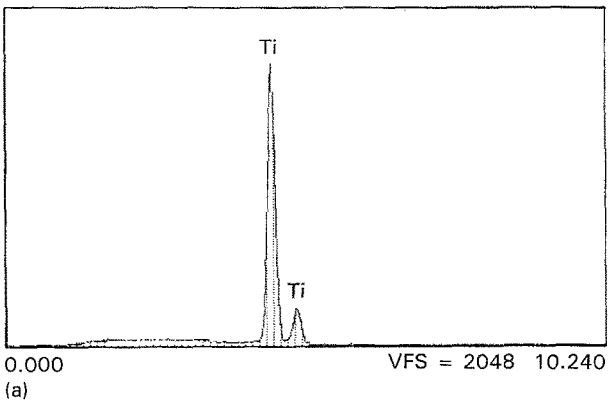

Figure 5 EDX analysis of (a) the Ti strip and (b) Cu–Ag eutectic matrix of the as-received filler metal.

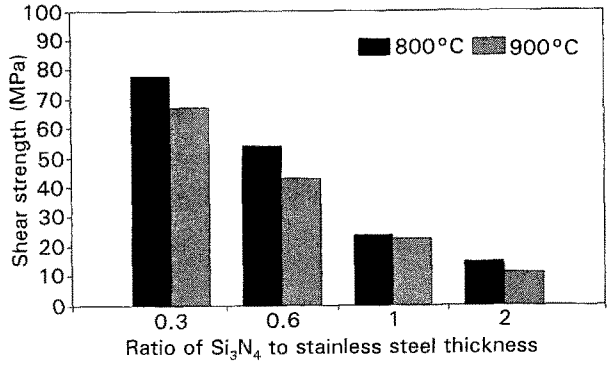

Figure 3 Shear strength of the braze joints as a function of Si_3N_4 to stainless steel thickness ratio. The joints were processed for 12 min at 880 °C and 900 °C.

(Fig. 6d). The microstructural changes were significant at the brazing temperature of 880 °C and time of 30 min, as seen in Fig. 7. The Ti strip completely disappeared; a reaction layer was observed at the bonding interface with the silicon nitride, and a much thinner reaction layer could be detected at the interface with the stainless steel. The bulk of the braze metal joint consisted of a light silver rich matrix with dark second phase particles, rich in Cu, uniformly dispersed. The X-ray maps corresponding to the Ti, Ag and Cu distributions are shown in Fig. 7b–d; Ti was absent from the bulk of the braze metal. The braze joint processed at 900 °C for 30 min showed larger

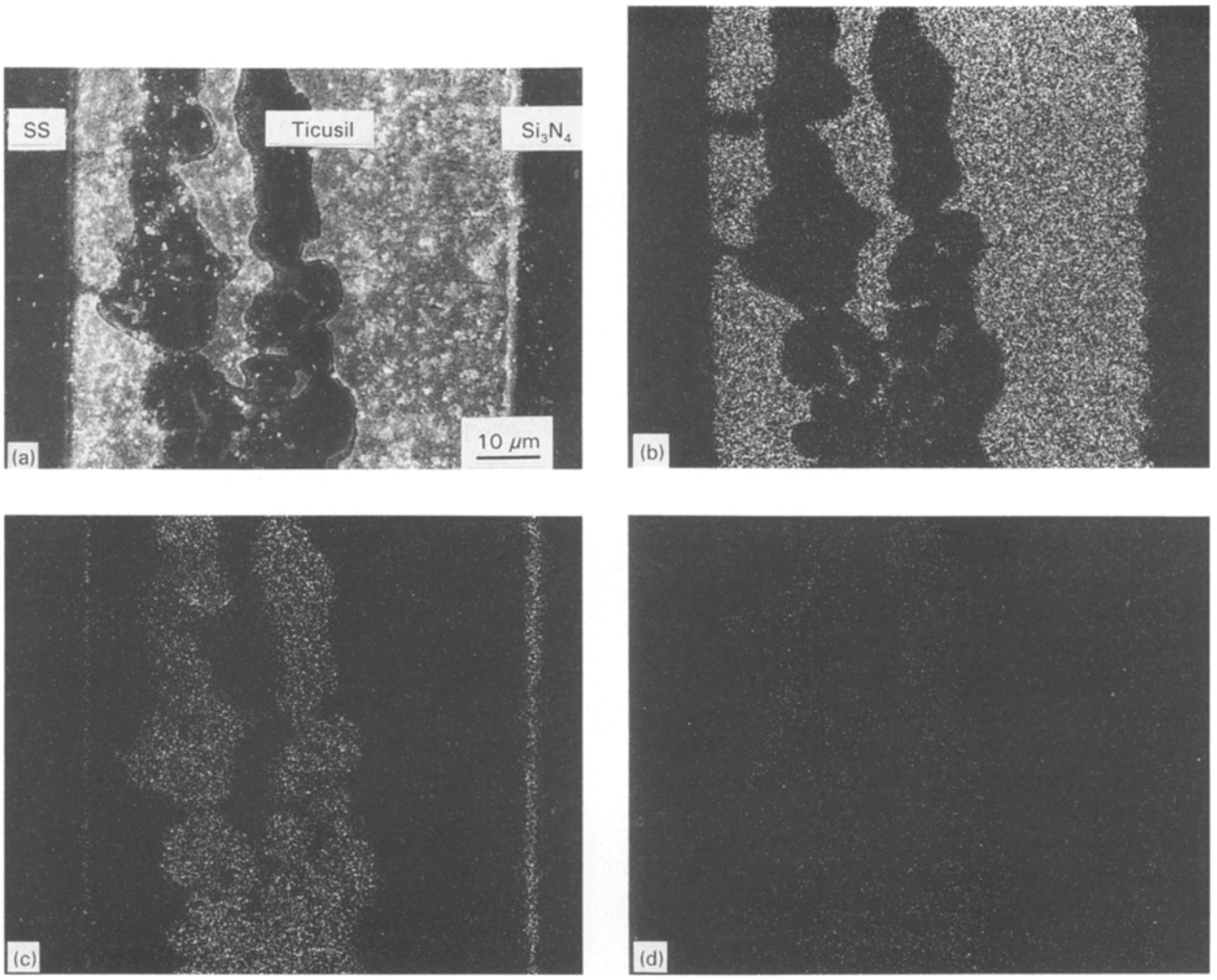

Figure 6 (a) Scanning electron micrograph of braze joint processed at 840 °C for 30 min. (b), (c) and (d) X-ray mappings corresponding to Ag, Cu, Ti, respectively, for the joint described in (a).

reaction layers at both bonding interfaces, but the silicon nitride end had the largest layer, as observed in Fig. 8a. EDX analyses were carried out at each of the reaction layers; Fig. 8b shows the results corresponding to the reaction layer adjacent to the stainless steel. Note that this region is rich in Ti and Fe, which lead us to speculate that Ti and Fe intermetallic compounds had developed. Fig. 9 shows the reaction layer at the Si_3N_4–filler metal interface and the EDX profile across this layer; it is seen that this region is rich primarily in Ti, with Si also present and Cu and Ag practically absent. From the X-ray diffraction pattern obtained from this interface (Fig. 10), TiN and Ti_5Si_3 peaks were identified in the spectra.

4. Discussion

4.1. Cracking due to processing

Cracking was found primarily in the silicon nitride adjacent to the interface with the filler metal in the brazes processed at low temperatures. Such cracks developed at the edge of the filler metal/ceramic contact (joint toe), propagated at an angle of ca. 45 °C, turning finally parallel to the filler metal–ceramic interface (Fig. 11). The cracks, as expected, most probably developed as a result of the stresses generated on cooling due to the thermal expansion mismatch between the stainless steel and the silicon nitride [15]. Naka *et al.* [16] calculated the stress distribution produced when Si_3N_4 was joined to stainless steel and indicated that the regions of maximum principal stress were almost perpendicular to the joint interface and that these stresses were greatest at the outer edges of the joint. It appears that the crack pattern found in the specimens produced at the lowest temperature in this study are consistent with these calculations. The crack most likely started due to a combination of radial and through-thickness stresses, normal to each other.

Cracking, in addition to differences in thermal expansions of the substrates, was apparently affected by the phase changes and microstructural modifications of the braze metal caused by variations in brazing temperature and time. The braze samples processed for 30 min at 840, 880 and 900 °C were selected to see if the microstructure appearance could be connected with crack occurrence. The microstructure of the 840 °C–30 min braze sample was found to have changed slightly, since the Ti metal remained as a continuous and relatively thick strip compared to the filler metal thickness (Fig. 6); a small increase in the microhardness of the titanium metal to about 220 VHN was observed but no microhardness change was

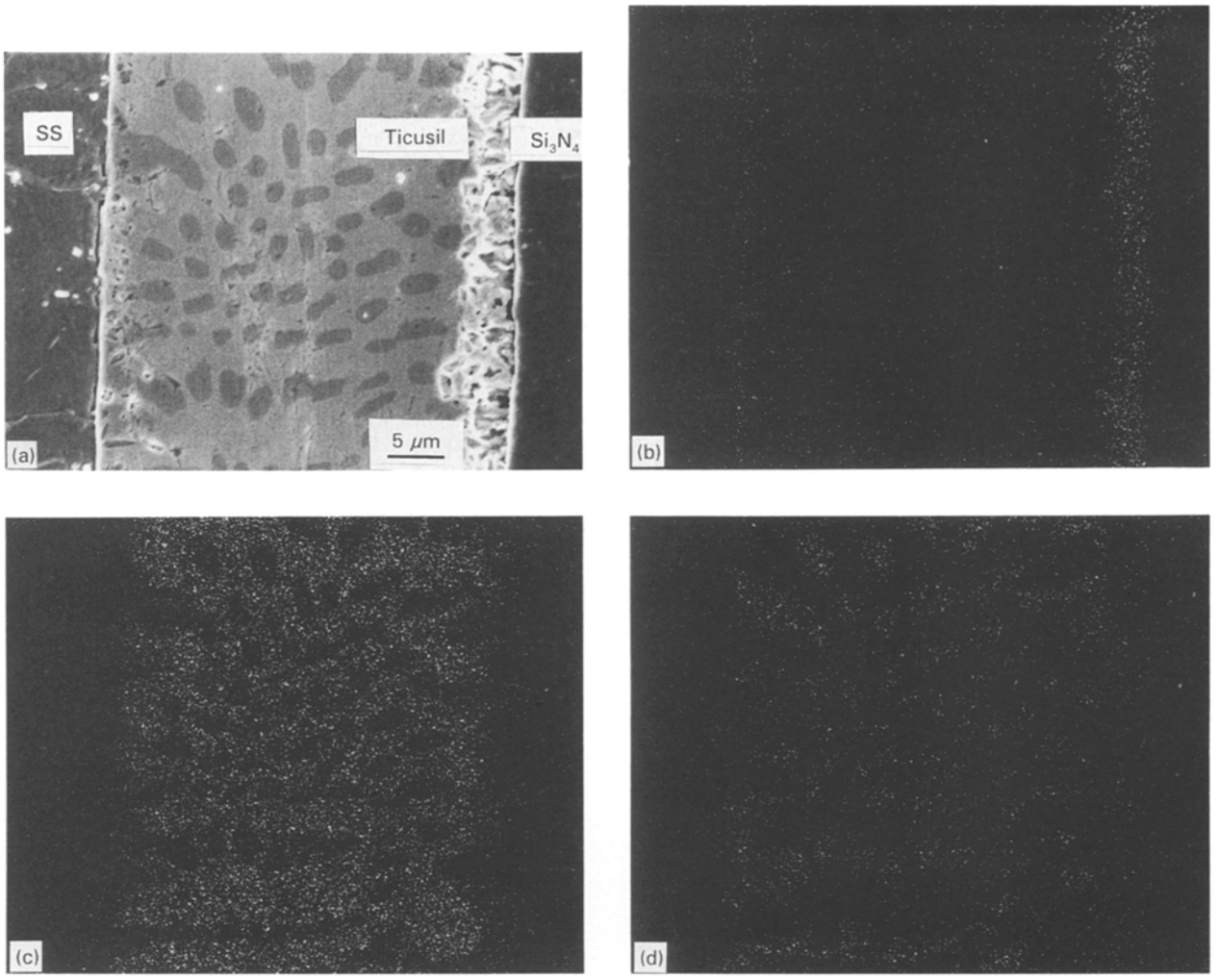

Figure 7 (a) Scanning electron micrograph of the braze joint processed at 880 °C for 30 min. (b), (c), (d) X-ray mappings of Ti, Ag and Cu, respectively, for the joint described in (a).

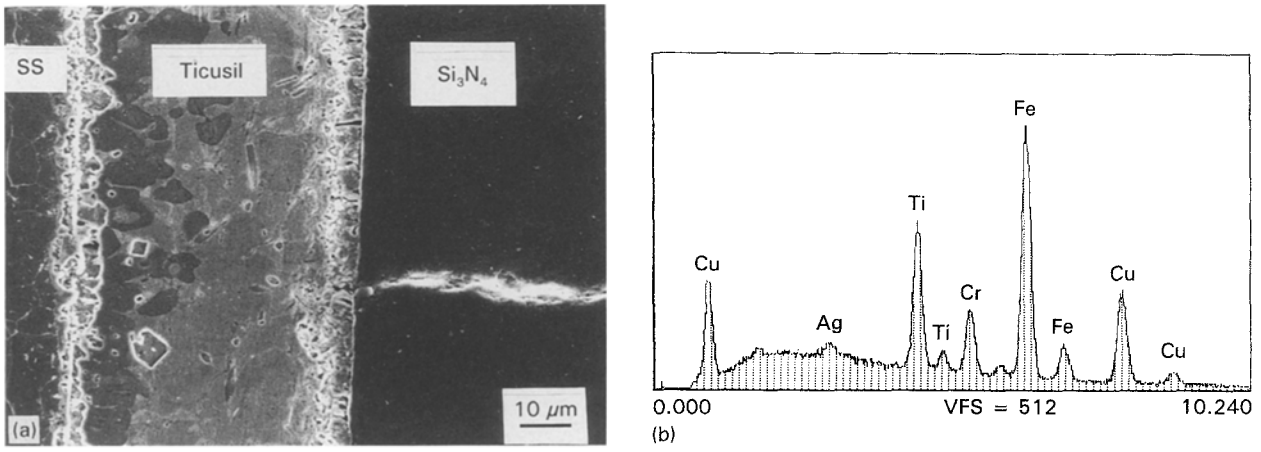

Figure 8 (a) Scanning electron micrograph of the braze joint processed at 900 °C for 30 min. (b) EDX analysis of the reaction layer at the stainless steel–filler metal interface.

noticed in the Cu–Ag matrix. Cu was detected to have diffused to the Ti strip, which lead us to think that a Cu–Ti intermetallic precipitated most likely due to the increase in microhardness of Ti. All these facts demonstrate a more brittle structure as a result of this brazing time and temperature compared to the initial filler metal. Microhardness measurements performed on the filler metal prior to brazing show a soft matrix of Cu and Ag of ca. 90 and 190 VHN, respectively, for the pure titanium component (Fig. 11).

Cracks were not found in the braze joints processed at 880 °C for 30 min nor was any titanium component present in the filler metal matrix. The microstructure consisted of a dark Cu rich phase (ca. 125 VHN)

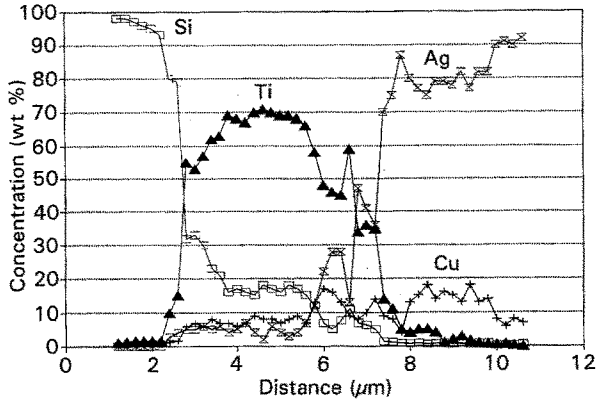

Figure 9 EDX profile across Si_3N_4–filler metal interface. Braze joint processed 900 °C for 30 min.

imbedded in the Ag matrix (100 VHN). The titanium was found to have segregated to the interfaces of the braze metal with both substrates. This reduction in microhardness, coupled with the elimination of the pure titanium as a continuous strip, apparently contributed to the relaxation of the thermal stresses. Similar microstructures and element distributions were observed in the braze joints processed at 880 and 900 °C for 6 and 12 min; no cracks were found in these specimens.

Cracks developed again when the braze joints were processed at 880 °C for 60 min and at 900 °C for 30 and 60 min. These cracks, as explained before, apparently developed first as microcracks in the reaction layer at the braze metal side adjacent to the interface with the silicon nitride. However, it was found in most cases that only one major crack propagated into the silicon nitride as extension of a microcrack (Fig. 8). This suggests that most of the residual stresses were relaxed by the propagation of a single crack into the ceramic substrate. The orientation of the crack normal to the braze metal–silicon nitride interface was probably influenced by the development of the reaction layer coupled with the precipitation of brittle intermetallic compounds, (Fig. 10), and most importantly

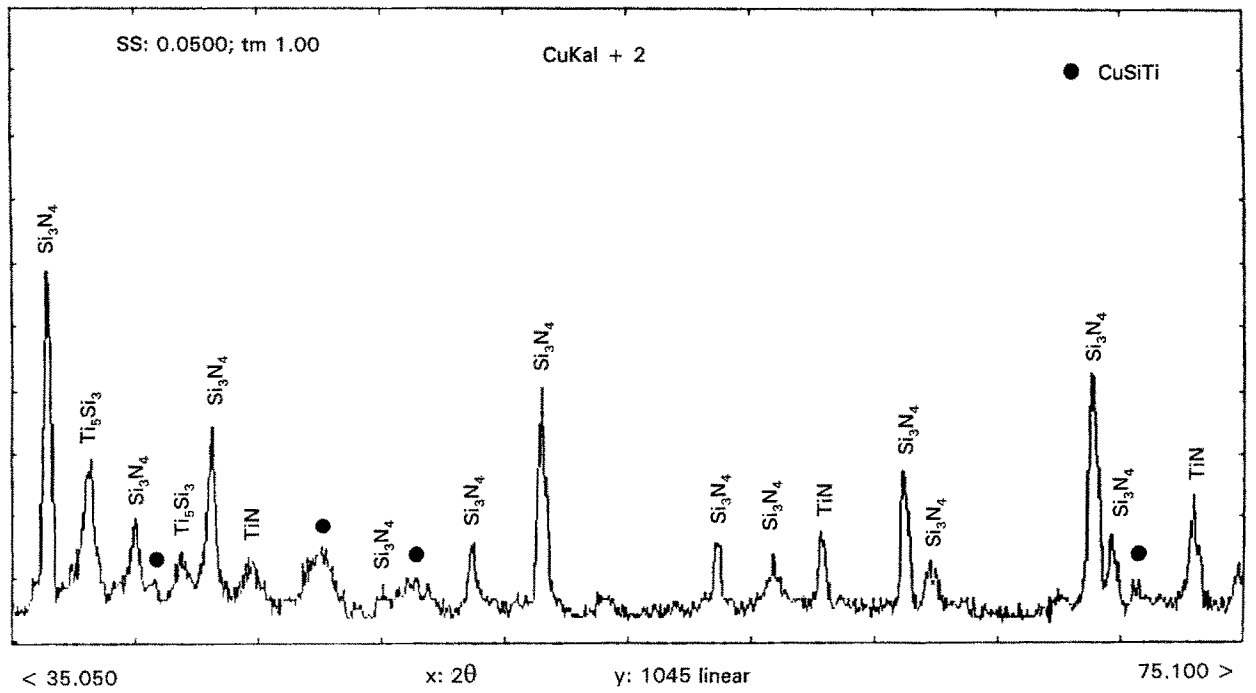

Figure 10 X-ray diffraction pattern of the reaction layer at the Si_3N_4–filler metal interface.

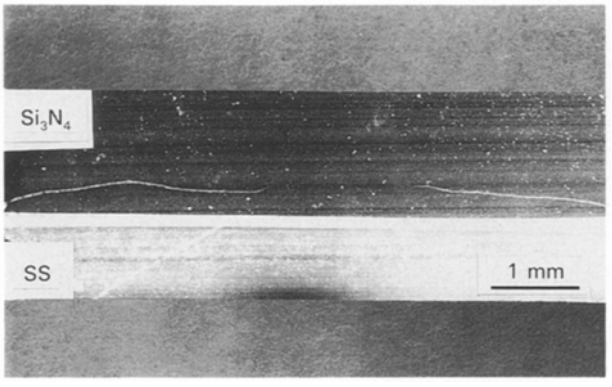

Figure 11 Cracking in the Si_3N_4 adjacent to the filler metal–ceramic interface for braze joints processed at low temperatures.

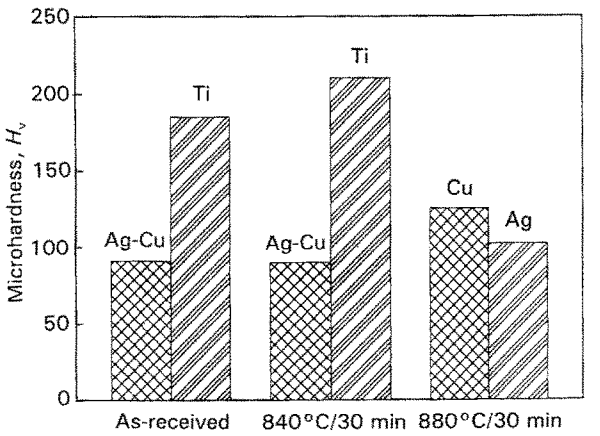

Figure 12 Microhardness of the filler metal in the as-received condition and two processing temperatures.

by its thickness. Apparently, the initial radial stresses of the stainless steel on cooling possibly placed the reaction layer in compression; but silicon nitride, which did not contract fast enough, put the interface of the reaction layer in tension causing microcracks. Further propagation of one of the microcracks into the silicon nitride occurred on further cooling and was caused by the bending stresses experienced by the ceramic substrate due to the radial and through-thickness contraction stresses.

4.2. Strength

The mechanical strength of the braze joint was necessarily affected by the occurrence of cracking during processing. Fig. 2 summarized the results of the shear tests; a quick observation of this figure implies that increasing the temperature and time of brazing improves the joint strength. But, studying Fig. 2 in conjunction with Fig. 1 it can be seen that the presence of cracks in the braze joint was an important factor in its strength. All the braze joints produced at 840 °C had low strength values and all contained cracks. A significant improvement in shear strength was observed when the specimens were processed at 860 °C for 30 min, and it was found that no cracks developed. A significant drop in strength was found in the braze welds produced at 900 °C for 30 min, but cracks were again found in these joints.

The strength of the braze joint also depended, apparently, on the nature and/or size of the reaction layer. Even for the specimens processed at 840 °C, a slight increase in shear strength was observed despite the presence of cracks, which is evidently connected with a reaction layer seen when titanium was detected at the braze metal–silicon nitride interface. Titanium is known to improve the wettability of ceramics, thus its diffusion to this interface marks the first step in the formation of the reaction layer.

It was observed that even in the absence of cracks, the longest brazing time at a given temperature did not necessarily mean improved strength, as in the case of the samples processed at 880 °C for 6, 12 and 30 min. Note that there was an increase in strength between the 6 and 12 min processing, but then a slight decrease followed for samples processed at 30 min. The same drop in strength was found as the brazing time was increased from 6 to 12 min in the specimens processed at 900 °C. For a fixed brazing time of 12 min, the increase of temperature from 880 to 900 °C also resulted in a drop in strength. All of these results dealing with joint strength could be explained in terms of the thickness or nature of the reaction layer. Systematic studies are underway to correlate the morphological changes and thickness of the reaction layer with the strength of the braze weld; available data points to the fact that either a thin layer or a thick reaction layer would weaken the joint strength.

Another aspect investigated was the effect of the substrate thickness ratio on joint strength. As expected, the increase in this thickness ratio resulted in lower strength values, as observed in Fig. 3. One cause for this decrease can be attributed to the processing cracks at the interface resulting from the thermal expansion mismatches and reaction layer developments, however, a drastic change in joint strength was seen for the thickness ratio of 1.0. This significant reduction has to be attributed to the geometry or large thickness of the Si_3N_4 compared to the stainless steel; as a matter of fact, in the thickness ratio of 1.0 and 2.0, bending was observed in the free Si_3N_4 surface implying large tensile stresses at this surface, which would promote cracking in the ceramic substrate.

5. Conclusions

The influence of processing temperatures and times on the morphological changes of the braze metal as well as on the development of the reaction layer was examined. The strength of the Si_3N_4–stainless steel joints was evaluated in conjunction with the microstructural changes in the braze metal. The following conclusions were drawn from this study.

1. Cracks in Si_3N_4 were found for all joints processed at 840 °C and for times shorter than 12 min at 860 °C. Cracks were also found at the braze welds processed at the longest times at 880 and 900 °C.
2. The low temperature cracks were parallel to the bonding interface, while the high temperature joints had microcracks in the reaction layer normal to the bonding interface with a major crack propagating into the Si_3N_4.
3. The low temperature cracks were apparently a consequence of residual stresses and the presence of a hard continuous titanium strip. The high temperature cracks were apparently affected by an increase in size of the reaction layer and precipitation of intermetallic compounds.
4. The strength of the joint was affected by the reaction layer thickness. A stronger bond was obtained when the reaction layer was relatively thin. The optimum brazing parameters were 12 min at 880 °C.

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