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Kinetic and microstructural aspects of the reaction layer at ceramic/metal braze joints

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The formation and stability of the reaction layer when brazing non-oxide ceramic materials were studied. Si_3N_4–Si_3N_4, SiC–SiC and Si_3N_4–stainless steel braze joints were produced and investigated. Several filler metals, most Cu- and Ag/Cu-based, containing different amounts of titanium were used to evaluate the effect of titanium on the formation and growth of the reaction layer. Some braze joints were processed using filler metals containing precious metals for high-temperature and oxidation-resistant applications. It was established that the matrix composition of titanium-bearing filler metals affects the ceramic wetting characteristics and the reaction layer kinetics. In the Si_3N_4 braze joints, the reaction layer consisted of TiN and titanium silicides. An activation energy corresponding to the diffusion of nitrogen in TiN was calculated for the growth of the reaction layer. During fabrication of the braze joints with precious-metal-containing filler metals at 1250° C, Si_3N_4 decomposed and a sound joint could not be processed. Premetallizing the Si_3N_4 with an AgCuInTi filler metal resulted in the formation of the reaction layer and permitted the fabrication of sound braze joints at 1250 °C. Attempts to produce SiC braze joints with CuTi filler metals were unsuccessful owing to the decomposition of the SiC; a TiC reaction layer had developed, but this did not prevent the diffusion of copper into the ceramic substrate, nor did it slow down the decomposition of the SiC.

1. Introduction

The past 25 years have seen an increasing utilization of non-metallic materials, polymers, composites and industrial ceramics, because of some specific improved material property. Ceramics and metals exhibit a range of differing properties but, in general, ceramics are stronger, more refractory and less thermally expansive or conductive than metals. Furthermore, structural ceramics can provide strength and corrosion resistance at higher temperatures. Operations at elevated temperatures provide greater thermodynamic efficiency in energy-conversion devices and also efficiencies associated with decreased complexity and weight.

The inherent brittleness associated with ceramic materials, limits their application as structural components when complicated geometries need to be manufactured. However, in some cases, utilization of such ceramics can be expanded by joining the parts to shapes and tolerances not readily achieved otherwise. Complex internal passages for cooling flows, as in heat exchanges, can be achieved by joining. Perhaps one of the most important applications for ceramic joining is in the attachment of ceramic components functioning at high temperatures to structures of moving parts which must withstand stresses or temperature gradients too large for ceramics, and which must therefore be fabricated of metal. Design of systems with ceramic joining requires detailed information on the joints, including the materials in the layers of the joints.

The fabrication of ceramic joints is complicated by the fact that most metals would not wet the ceramic unless certain conditions are met. During brazing the liquid metal needs to make intimate contact with the solid ceramic surface to develop a metal–ceramic bond. Many theoretical models attempt to explain such bonding in terms of contact angle, θ, and work of adhesion, W. In the general case of a metal liquid drop in contact with the ceramic interface, the balance of surface tension forces results in the familiar Young equation

$$\gamma^{lv}\cos\theta = \gamma^{sv} - \gamma^{sl} \qquad (1)$$

where γ^{lv}, γ^{sv} and γ^{sl} are the corresponding surface energies of the liquid/vapour, solid/vapour and solid/liquid interface, respectively, and θ is the angle

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between γ^{lv} and γ^{sl}. The Dupree equation is derived from Equation 1

$$W = \gamma^{lv}(1 + \cos\theta) \qquad (2)$$

$\gamma^{lv}\cos\theta$ is defined as the wettability parameter and when this parameter is negative the system develops an obtuse angle and it is called a non-wetting system. On the other hand, a positive parameter implies that γ^{sv} is greater than γ^{sl}, an acute angle develops and consequently wetting results. A knowledge of the wetting behaviour of metals on ceramics is necessary for understanding the braze bonding interface between metals and ceramics [1–3].

It is established in the literature that it is necessary to develop a reaction layer at the ceramic interface to ensure wetting by the liquid metal [4–8] to produce a strong braze joint. One way to achieve this task is to metallize the ceramic surface before the actual brazing process. First attempts in this regard date back to the late thirties [9, 11], when the tungsten or moly-manganese metallization process was developed for joining alumina. This procedure has been developed to a degree where it is highly reliable, but the process is time consuming and requires a high degree of process control. A second way of joining ceramic to metal is by using an active brazing filler metal which is simple and needs minimum resources; furthermore, by promoting a chemical reaction at the interface, reliable metal–ceramic joints can be obtained. Most ceramic materials have primary ionic covalent atomic bonds and, consequently, will have a lack of delocalized bonding electrons needed to continue a metallic environment and hence create a low surface energy. Conventional brazing filler metals based on copper, silver, nickel or gold, cannot wet the ceramics [12]. To achieve the necessary decrease in γ^{sl} and the contact angle, the chemistry of the interface must be changed and hence some component of the braze must be active enough to alter the composition of the ceramic surface.

Naka *et al.* [6] found that brazes containing titanium can be used to join unmetallized ceramics and that wetting was achieved because the active metal reacts to change the chemistry of the ceramic surface.

In this study the active brazing process was used to investigate the formation and stability of the reaction layer when brazing Si_3N_4 to Si_3N_4, SiC to SiC and Si_3N_4 to stainless steel. The brazing was carried out under vacuum with several filler metals, all having titanium as active metal. The filler metals used contained different levels of titanium to evaluate its effect on the reaction layer kinetics and thickness. Furthermore, in some cases, the filler metal requirements, regarding exposure to corrosive environments and temperatures above 800 °C, cannot be met because their compositions are based on silver, which lowers the melting point of the filler metals. In this investigation, some of the filler metals selected contain precious metals, such as palladium and gold, to increase the melting temperature and oxidation resistance of the filler metal.

2. Experimental work

Experiments were carried out at the Materials Science Institute of the Aachen University of Technology (RWTH), Germany and at the Civil and Materials Engineering Department of the University of Illinois at Chicago (UIC), USA. The compositions of the substrates and filler metals used in these studies are shown in Table I. The Si_3N_4 stainless steel joints were fabricated at UIC at temperatures of 840, 860, 880 and 900 °C and times of 6, 12, 30 and 60 min in a vacuum of 10^{-5} torr (1.33×10^{-5} mbar). Ticusil and CB4 filler metals were used.

The braze samples produced at the RWTH were used to investigate the effect of titanium in the reaction layer as some of the base compositions of the filler metals were changed. Braze joints were also produced, to study the filler metal chemistries for high-temperature and corrosion-resistance applications. The joints that utilized silver-based filler metals were fabricated at 900 °C/10 min. A processing temperature of 1100 °C was employed when producing braze joints with the Copper-based filler metals. The high-temperature braze joints were processed at 1250 °C/10 min using filler metals containing precious metals.

All samples were prepared for microscopic evaluation using standard metallographic procedures. These examinations were conducted using optical and scanning electron microscopes. The compositional changes about the reaction layers were monitored using energy dispersion X-ray (EDX) and X-ray diffraction. Mass spectrometry was employed to detect compositional changes during brazing of some of the samples.

3. Results and discussion

3.1. Reaction-layer kinetics in the Si_3N_4 substrate

After brazing, the Si_3N_4/stainless steel specimens produced at UIC were observed in the scanning electron microscope for reaction layer formation. A braze joint cross-section produced with the Ticusil filler metal is shown in Fig. 1; the reaction layer, localized at the

TABLE I Base materials and filler metals

Base materials	
UIC-Si_3N_4	NCX-34 Si_3N_4 hot pressed with Y_2O_3
UIC-410 stainless steel	0.15 wt % C, 1.0 wt % Si, 1.0 wt % Mn, 12–13.5 wt % Cr, Fe.
RWTH-Si_3N_4	Pressureless sintered Si_3N_4 and hot-pressed Si_3N_4
RWTH-SiC	Hot-isostatically-pressed SiC
Filler metals	
UIC-Ticusil	68.8 wt % Ag; 26.7 wt % Cu, 4.5 wt % Ti
UIC-CB4	70.5 wt % Ag, 26.5 wt % Cu, 3.0 wt % Ti
RWTH-CB1	72.5 wt % Ag, 19.5 wt % Cu, 5 wt % In, 3 wt % Ti
RWTH-PNT	58 wt % Pd, 39 wt % Ni, 3 wt % Ti
RWTH-APT	91 wt % Au, 7 wt % Pd, 2 wt % Ti
RWTH-CuTi5	95 wt % Cu, 5 wt % Ti
RWTH-CuTi10	90 wt % Cu, 10 wt % Ti (melt-spin-foil)
RWTH-CuTi35	65 wt % Cu, 35 wt % Ti (melt-spin-foil)

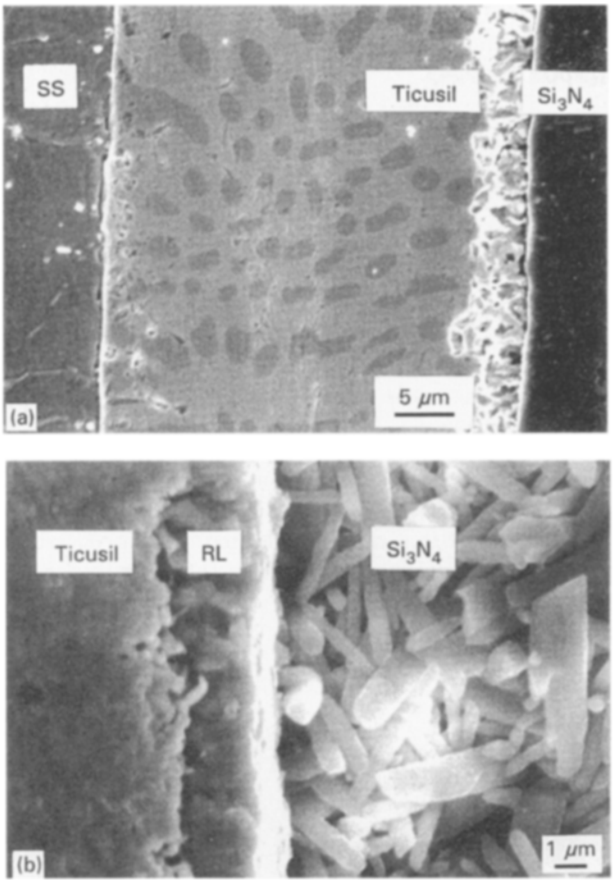

Figure 1 Scanning electron micrographs of Si_3N_4/Ticusil/stainless steel joints processed at 860 °C for 30 min, etched in molten NaOH at 350 °C for 8 min.

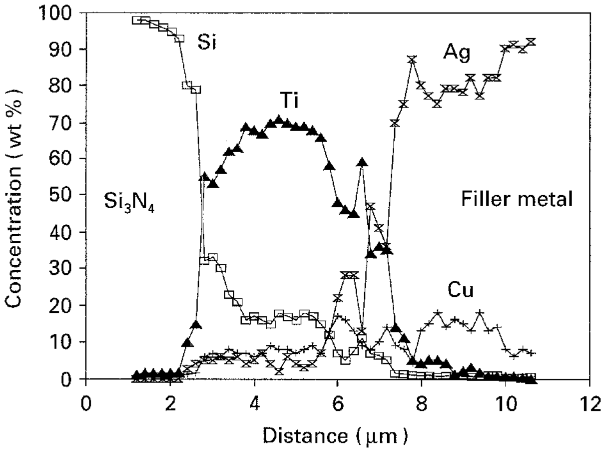

Figure 2 EDX profile across Si_3N_4–Ticusil filler metal interface, for the braze joint processed at 880 °C for 30 min.

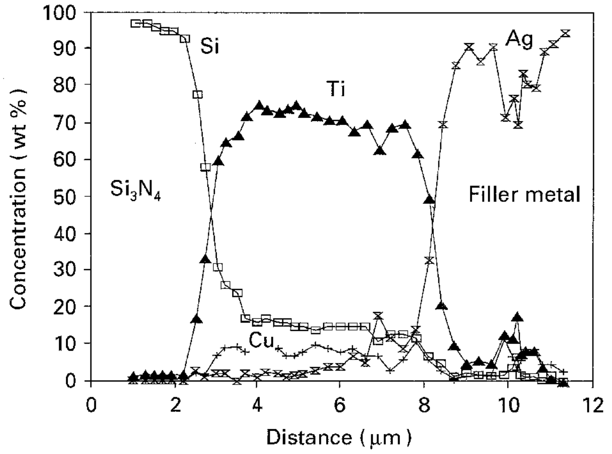

Figure 3 EDX profile across Si_3N_4–CB4 filler metal interface for a braze joint specimen fabricated at 880 °C for 12 min.

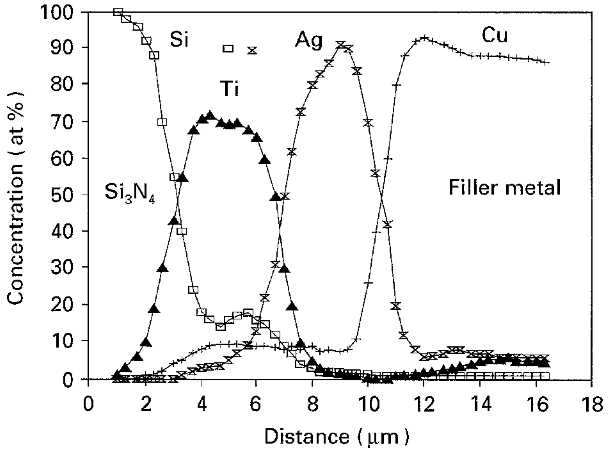

Figure 4 EDX profile across Si_3N_4–AgCuTi3 filler metal interface for an Si_3N_4/Si_3N_4 specimen processed at 900 °C for 10 min.

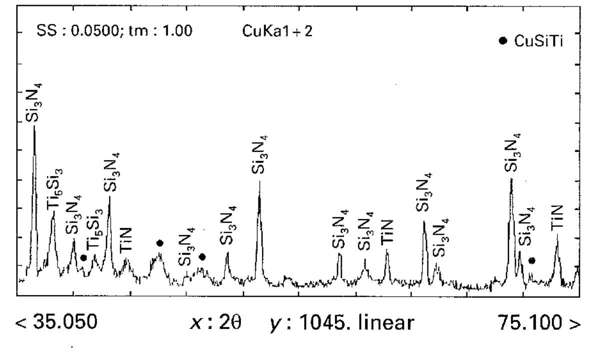

Figure 5 X-ray diffraction pattern of the reaction layer at the Si_3N_4/filler metal interface with Ticusil.

Si_3N_4 interface, has a thickness of approximately 5.0–6.0 μm. An EDX element profile across this interface was obtained by running a line analysis covering an extension of approximately 12 μm at about four or five different locations. These results were averaged and plotted as shown in Fig. 2. A similar procedure was followed for a UIC braze joint fabricated with the CB4 filler metal; its EDX element profile is plotted in Fig. 3. These results show, consistently, titanium segregation to the Si_3N_4 interface; also silicon was found to concentrate at the reaction layer, but at levels much less than titanium. The same results were obtained in the Si_3N_4/Si_3N_4 joints produced at the RWTH Aachen as shown in Fig. 4. These data are consistent with reports in the literature concerning the chemical reaction of titanium with Si_3N_4

$$Si_3N_4 + 4Ti \rightarrow 4TiN + 3Si \qquad (3)$$

X-ray diffraction of the reaction layer shows a spectrum of peaks consisting of Si_3N_4, TiN and Ti_5Si_3 as shown in Fig. 5. The excess silicon is expected to be rejected into the molten filler metal and thus react

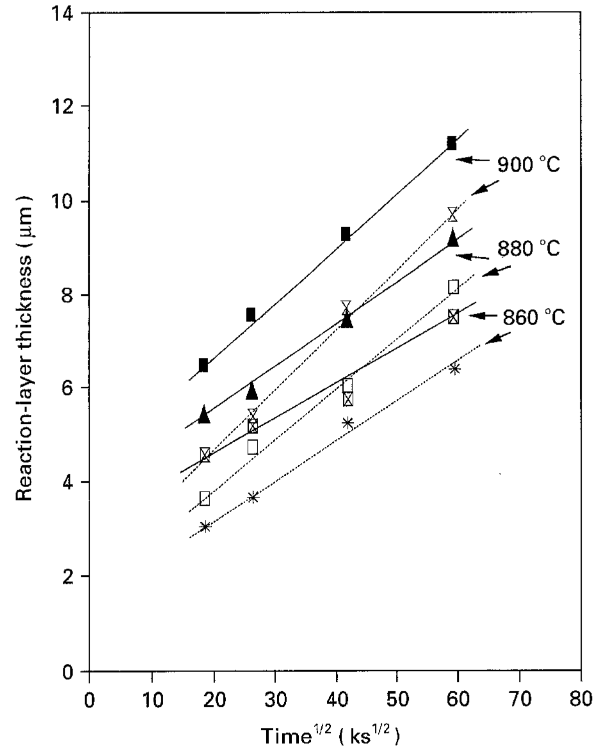

Figure 6 Reaction-layer thicknesses as a function of time for Si_3N_4/stainless steel braze joints. (-----) Ticusil, (—) CB4.

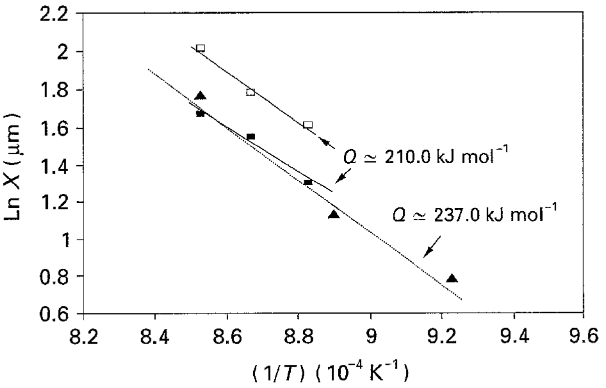

Figure 7 Arrhenius plots corresponding to the reaction layers of Si_3N_4 braze joints. (□) UIC-CB4, $t = 12$ min. (▲) UIC-Ticusil, $t = 12$ min. (■) RWTH-CB1, $t = 10$ min.

with titanium-forming titanium silicides at the interface. Those reactions are of crucial importance for improved wetting and adhesion of the braze matrix on the reaction layer, as the silicides obtain a metal-like atomic structure.

Measurements were conducted of the reaction-layer thickness in the Si_3N_4/stainless steel braze joints; as expected it grew with time and temperature. Earlier it was established that Si_3N_4 reacted with titanium from the filler metal forming TiN and Ti_3Si_5, components of the reaction layer. Because the reaction layer has a composition different from that of the filler metal or from the ceramic substrate, its nucleation and growth is treated as precipitation of a new phase. Its growth must involve atoms crossing the reaction layer, but also the depletion of titanium from the filler metal matrix. If the driving force for growth depends on titanium supersaturation of the matrix, then it would decrease as titanium is consumed. However, the reaction-layer growth must also depend on the diffusion of either nitrogen or silicon.

A diffusion-controlled growth is then considered for studying the reaction-layer kinetics

$$x = k D^{1/2} t \tag{4}$$

where x is the reaction-layer thickness, D is the diffusion coefficient, k is a constant and t is the processing time. A plot of x as a function of the square foot of time was produced for each processing temperature, D is constant at a fixed temperature

$$x = k' t^{1/2} \tag{5}$$

Fig. 6 shows a linear correlation between the reaction-layer thickness and the square root of the time for both filler metals. The activation energy of the reaction-layer growth is estimated by fixing the processing time and plotting the logarithm of the layer thickness as a function of $1/T$

$$x = k\,D_0 \exp\left(\frac{-Q}{RT}\right)^{1/2} t^{1/2} \tag{6}$$

$$x = kD_0^{1/2}\,t^{1/2}\left[\exp\left(-\frac{Q}{RT}\right)\right]^{1/2} \tag{7}$$

or

$$x = k''\left[\exp\left(-\frac{Q}{RT}\right)\right]^{1/2} \tag{8}$$

or

$$\ln x = \ln k'' - \frac{1}{2}\frac{Q}{RT} \tag{9}$$

Braze joints processed for 12 min were used to generate an Arrhenius plot. Fig. 7 shows the plots corresponding to the UIC-CB4 and UIC-Ticusil filler metals. The activation energies were estimated to be 210.0 kJ mol^{-1}. Data from the RWTH-CB1 braze joints (Si_3N_4/Si_3N_4) plotted in the same graph produced an activation energy of 237.0 kJ mol^{-1}. These activation energies are comparable to the activation energy of nitrogen in TiN (217.6 kJ mol^{-1}) [13].

As indicated earlier, for this reaction layer to grow, either nitrogen or silicon, and most probably both, must diffuse through the growing layer to meet the titanium segregated at the new interface, reaction layer/filler metal. Nitrogen is an interstitial atom, while silicon is a substitutional one; further the atomic radius of nitrogen is 0.071 nm compared to 0.117 nm for the silicon atom. In view of these circumstances, the growth of the reaction layer is most probably controlled by the fastest moving species, which in this case is nitrogen. The results from Fig. 6 seems to confirm this.

Other work performed at the RWTH on Si_3N_4/Si_3N_4 braze joints using a Cu–Ti5 filler metal produced an activation energy of about 318 kJ mol^{-1} [14]. This value is similar to that obtained by Nakao *et al.* [13] which corresponds to the activation energy for silicon diffusion in titanium nitride. This discrepancy in the activation energies could be explained by differences in the composition of the filler metals used and

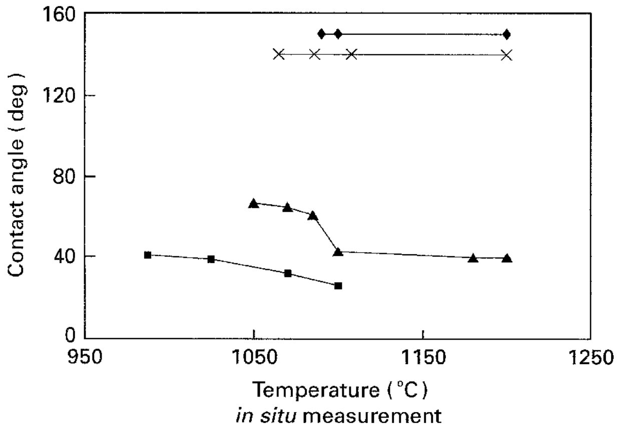

Figure 8 Contact angles of various copper-based filler metals on Si_3N_4 as a function of titanium and temperature. (×) Cu, (◆) Cu Ti1, (▲) CuTi5, (■) CuSiAlTi3.

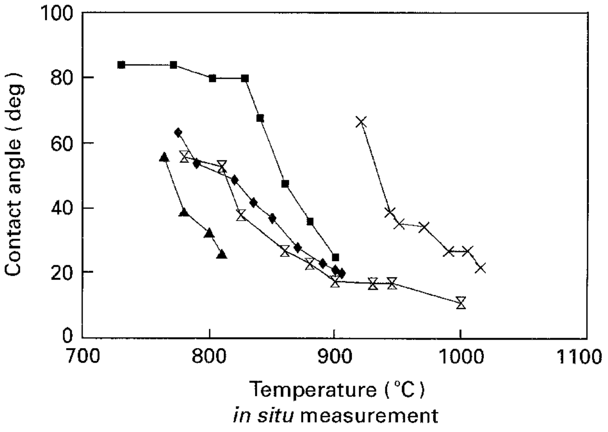

Figure 9 Contact angles of various Ag/Cu-based filler metals on Si_3N_4 as a function of titanium and temperature. (×) AgIn1Ti1, (◆) AgCu34, 5Ti1.5, (▲) AgCu 19.5 In 3 Ti3, (×) AgCu 26.5 Ti3, (■) AgCuGaTi1.2.

the processing parameters utilized. The braze joints that produced activation energies of 210.0 and 237.0 kJ mol^{-1} were fabricated with a filler metal base on the Ag–Cu eutectic. The braze joints that resulted in an activation energy of 318.0 kJ mol^{-1} were processed with a copper-based filler metal. It has been found that silver increases significantly the activity of titanium [7] which may influence the segregation of titanium to the Si_3N_4 interface. Wetting experiments performed at the RWTH offer results that further support the role of the activity of titanium on the contact angle and thus the reaction layer. These results also give evidence to the effect of silver on increasing the activity of titanium. Fig. 8 shows how the addition of 1 wt % Ti to the copper filler metal does not improve the contact angle; but increasing the titanium level, and hence the activity of titanium, to 5.0 wt % causes a significant reduction of the contact angle. Note that the lowest contact angle for the Cu–5Ti filler metal is about 43° at temperatures of 1100 °C and above. Fig. 9 shows how the inclusion of silver in the filler metal reduces the contact angles; for example, the Ag–34.5Cu-1.5Ti has contact angles of 20° at a temperature of 900 °C compared to 150° for the Cu–1.0Ti (Fig. 8) at a temperature of about 1100 °C. The other Ag/Cu-based filler metals containing 3.0 wt % titanium resulted in contact angles ranging from 17°–26° at temperatures between 860 and 900 °C. Note also that when the content of titanium was doubled from 1.5 wt % to 3.0 wt % in the Ag/Cu/Ti filler metals no change was detected in the contact angle, as observed in Fig. 9.

Another factor that must influence the reaction kinetics is the processing temperature. The Cu–5Ti braze joints were fabricated at 1100 °C, 200 °C higher than the Ag/Cu/Ti braze joints. This larger temperature increases the vacancy concentration, which in turn makes the silicon diffusion also significant in the growth kinetics. Hence, if both silicon and nitrogen diffusions affect the reaction-layer growth, then the slowest diffusing element would be expected to control the growth kinetics which, in the case of Cu–Ti braze joints, should be silicon.

3.2. Reaction-layer kinetics in the SiC substrate

Analogous to the Si_3N_4 processing with an active filler metal, it is expected that titanium will react with the SiC to form the active metal carbide according to

$$Ti + SiC \rightarrow TiC + Si \qquad (10)$$

The free silicon is once again important for the secondary reaction product, namely the formation of titanium silicides. It is observed that the primary TiC layer in SiC does not function equivalently to the TiN layer in Si_3N_4; for instance, the reaction-layer thickness in the SiC substrate was measured to be less than 2 μm (Fig. 10a) when processed with AgCuTi3 filler metal for 180 min at 1000 °C. On the other hand, a reaction-layer thickness between 6.0 and 7.0 μm is obtained in the Si_3N_4 substrate at the processing temperature of 1000 °C and time of only 10 min using the same AgCuTi3 filler metal (Fig. 10b). Another feature that differentiates the reaction-layer characteristics between these two substrates is the contact angle measured. A contact angle of 18° was measured on the SiC at 1100 °C with a CuTi5 filler metal (Fig. 11), while a contact angle of 43° was obtained on the Si_3N_4 (Fig. 10b) with the same filler metal. No calculations of activation energies were conducted in the SiC braze joints. However, EDX measurements revealed that there, is a significant silicon-diffusion across the reaction layer leading to the formation of a thick interfacial silicide layer and to a silicon enrichment in the braze matrix.

3.3. Microstructural aspects of the reaction layer

In the case of the Si_3N_4 braze joints, samples were fabricated in the temperature range 840–900 °C to study the reaction kinetics at the ceramic filler metal interface. It was found that under these conditions a fairly stable reaction layer develops consisting of a very dense film-like layer of TiN next to the Si_3N_4 followed by a lesser dense layer consisting of TiN and

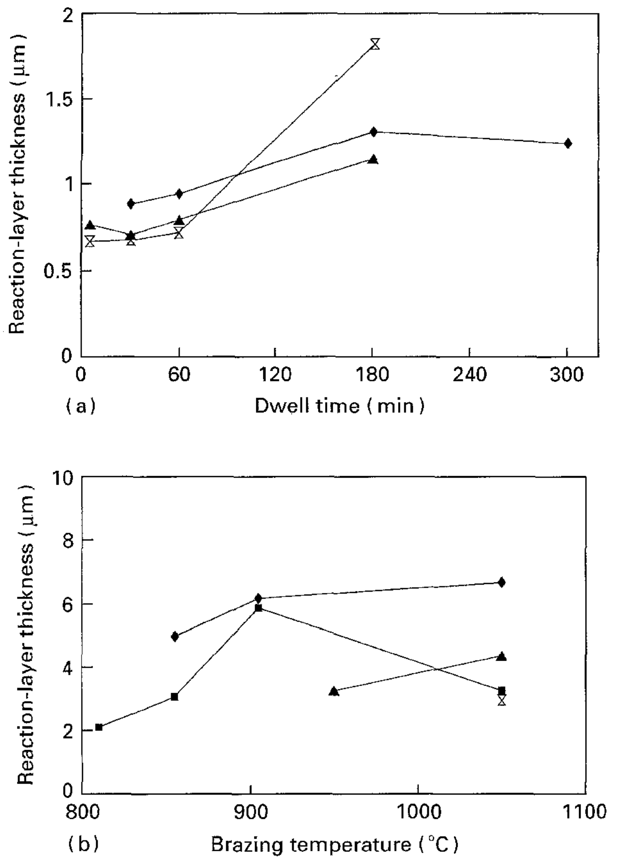

Figure 10 Reaction thicknesses in (a) SiC with AgCu filler as a function of time at a brazing temperature of 1000 °C, and (b) Si_3N_4 with AgCu filler metals as a function of temperature and fixed processing time of 10 min. (a) (⧖) AgCuTi3, (◆) AgCuHf3, (▲) AgCuZr3. (b) (■) AgCuInTi3, (◆) AgCuTi3, (▲) AgCuZr3, (⧖) AgCuHf3.

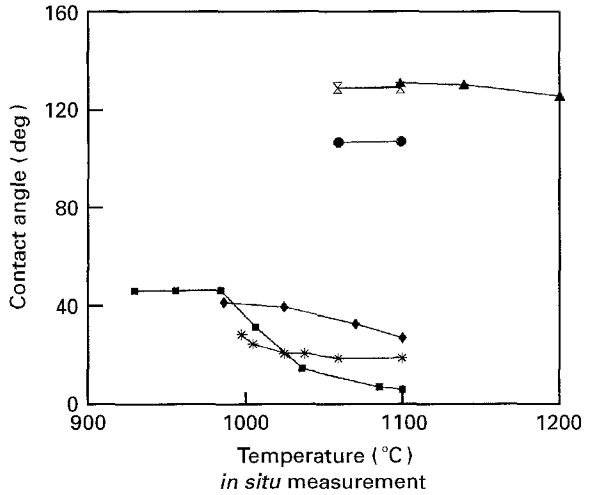

Figure 11 Contact angles of various copper-based filler metals on SiC as a function of titanium and temperature. (⧖) CuTi1, (●) CuTi2, (×) CuTi5, (■) CuTi10, (◆) CuSiAlTi3, (▲) Cu.

Ti_5Si_3, as shown in Fig. 1. However, the stability of the reaction layer and consequently the soundness of the braze joint is compromised if this is exposed to temperatures of 800 °C or higher, and more so if used in corrosive environments. In an attempt to expand the utilization of these braze joints to such elevated temperature work has begun at the RWTH-Materials Science Institute to find alternative filler metals.

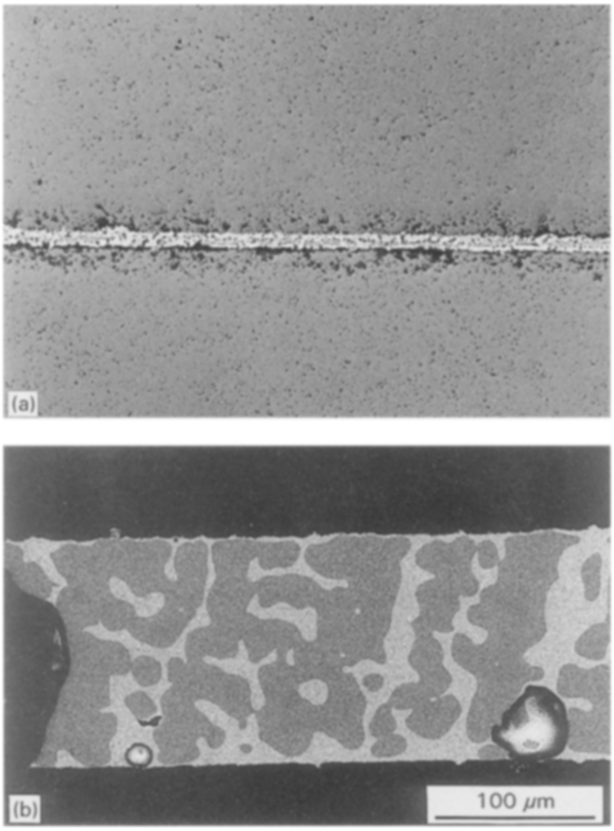

Figure 12 Micrographs of Si_3N_4–Si_3N_4 joints braze with PdNiTi3 at 1250 °C/10 min: (a) × 50 and (b) × 300.

Precious metals, such as palladium, platinum and gold, were used to raise the melting point of the filler metal and oxidation resistance.

A PdNiTi3 filler material was selected to braze Si_3N_4 to Si_3N_4. The joints were fabricated at 1250 °C under vacuum and for a processing time of 10 min. It was not possible to produce a sound joint. Some of these braze joints fell apart during processing as the furnace reached temperatures higher than 1100 °C. Fig. 12 shows some decomposition of the Si_3N_4 substrate next to the braze metal, as well as porosity present in the filler metal. In our discussion of the reaction-layer kinetics, it was noted that Si_3N_4 reacted with titanium temperatures of 840–900 °C; however, bubbling was detected in the last sample during processing as the temperature exceeded 1100 °C. In addition, the vacuum pressure became very unstable. Review of the thermal stability of Si_3N_4 at high temperatures as a function of nitrogen partial pressure, reveals that silicon nitride decomposes at about 1100 °C for partial pressures of nitrogen below 10^{-6} mbar (Fig. 13). This critical threshold can be reached during vacuum brazing because the total pressure is about 10^{-5} mbar at a temperature range of 1200–1300 °C. Mass spectroscopic measurements verified this nitrogen evolution, and consequently Si_3N_4 decomposition.

The nitrogen evolution is apparently so intense that it disrupts the formation and stable growth of the diffusion-controlled reaction layer. It had been established earlier that the processing temperature and filler-metal chemistry affected the growth kinetics in

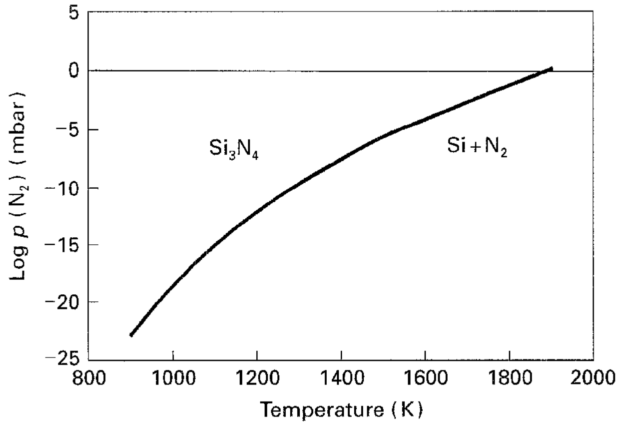

Figure 13 Silicon nitride stability as a function of temperature and nitrogen partial pressure. (—) $Si_3N_4 = 3$ Si(s, l) + N_2(g).

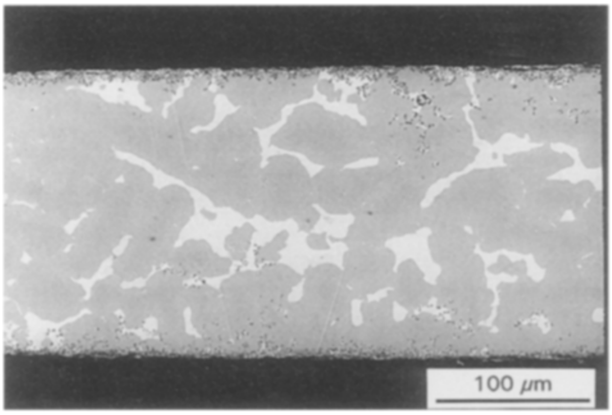

Figure 14 Si_3N_4–Si_3N_4 joint brazed with PdNiTi at 1250 °C/10 min, following pre-metallization with AgCuInTi at 900 °C/10 min.

the Si_3N_4 joints fabricated with AgCuTi3 and CuTi3. In both cases it was learned that development of the thin TiN reaction layer was fundamental to control the growth kinetics. In the PdNiTi3 braze joints it was thought that the lack of a stable TiN layer impeded the establishment of a controlled reaction-layer growth. An attempt was made to optimize processing of the braze joints at high temperatures by applying our findings from the reaction-layer kinetics study. The development of the TiN layer was thought to be a condition to produce the reaction layer and thus control the decomposition of the Si_3N_4, and most importantly to limit the nitrogen diffusion. To develop such a diffusion-resistant, or diffusion-limited layer, a premetallizing procedure was utilized. The Si_3N_4 parts were premetallized with AgCuInTi at 900 °C for 10 min prior to the high-temperature brazing at 1250 °C also for 10 min with PdNiTi filler metal. Fig. 14 is an optical micrograph of this braze joint cross-section. A sound joint was produced without voids or porosity. No nitrogen evolution was detected during processing. EDX examination of the reaction layer just shows titanium and silicon enrichment. The lighter phases in Fig. 14 are palladium-rich and PdCu solid solutions, whereas the dark areas are PdNi and CuNi solid solutions. Silver and indium were found to have alloyed the filler metal matrix.

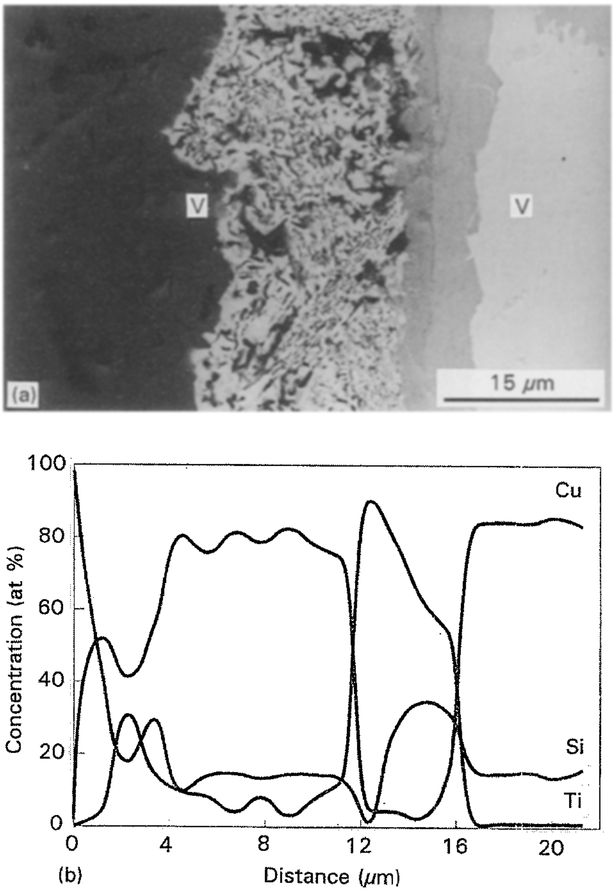

Figure 15 (a) Micrograph of the CuTi5–SiC interface fabricated at 1100 °C/60 min in vacuum, and (b) the corresponding element distribution.

During fabrication of the SiC braze joints the ceramic substrate interacted strongly with the CuTi5 filler metal. For example, the specimen produced at 1100 °C/60 min resulted in a decomposed area in the ceramic substrate adjacent to the reaction layer, consisting of SiC fragments embedded in a copper-matrix, as shown in Fig. 15. Apparently, the TiC reaction layer that developed could not prevent the copper diffusion into the ceramic substrate and thus avoid the decomposition of the SiC. The element distribution across the interface, observed in Fig. 15, shows that the second (light grey) layer has a high silicon concentration, providing evidence of a secondary reaction product, titanium silicide. Compared to Si_3N_4 joints fabricated with the same filler metal and equal processing temperature, the TiN reaction layer formed in the later braze joints proves to be a more efficient barrier for diffusion of elements. This is in view of the absence of a decomposed region in the Si_3N_4 substrate.

4. Conclusions

1. A reaction layer develops at the ceramic/filler metal interface during ceramic/metal brazing. The matrix composition of titanium-bearing filler metals is found to influence the ceramic wetting characteristics and reaction layer kinetics. It appears that silver affects the activity of titanium.

2. An activation energy similar to that of nitrogen diffusion in TiN was calculated for the reaction-layer kinetics of Si_3N_4 braze joints using AgCuTi filler metals. These joints were fabricated at 900 °C. The reaction layer consisted of a thin layer of TiN followed by a thicker layer containing TiN plus titanium silicides.

3. Fabrication of heat- and oxidation-resistant braze joints was not possible at 1250 °C with precious metal-based filler metals because of the decomposition of the Si_3N_4 substrate and lack of a stable reaction layer. Based on thermodynamic information, it was found that from the total pressure during brazing, Si_3N_4 will decompose into $Si + N_2$ at temperatures higher than 1100 °C.

4. The benefit of having a TiN reaction layer that limits the reaction kinetics was exploited by pre-metallizing the Si_3N_4 substrate before processing at 1250 °C. This additional step allows the formation of the TiN layer that prevented decomposition of the Si_3N_4 when processed with the PdNiTi3 filler metal. The braze joints produced were also mechanically sound.

5. The reaction layer formed in the SiC braze joints apparently consists of TiC and titanium silicides. It appears that TiC is not a good barrier for copper diffusion into the SiC substrate, which caused deterioration of the ceramic material. These brazes were fabricated with CuTi5 at 1100 °C/10 min.

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