Brazing of Silicon Nitride with Reactive Filler Metals

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ABSTRACT

Silicon nitride braze joints were produced in a single step by reactive brazing at elevated temperatures without premetallizing. A filler metal of composition Co-10Ti was employed, with joining taking place during a 15-minute hold at 1300°C under a high vacuum. The reaction layer that developed was not uniform. In those locations where the reaction layer was thick, the silicon nitride remained stable. But regions that showed a thin reaction layer showed some degradation. Regardless of the reaction layer thickness, a gap was observed in places between the braze metal and the ceramic substrate. This was caused by the premature isothermal solidification of the braze metal as it got depleted of titanium. Titanium acts as a melting temperature depressant of the cobalt-rich alloy. Ni-13-Cr-7Hf was another high temperature filler metal developed that showed good wetting. During brazing with this filler metal at 1250-1275°C, hafnium did not diffuse readily towards the silicon nitride and thus prevented the substrate from decomposing. Ultimately these joints were fabricated after premetallizing the silicon nitride.

INTRODUCTION

As we approach the new millennium, the need to reduce the consumption of fossil fuels through better process efficiency has become increasingly evident. A new generation of advanced engineering ceramic materials continues to gain importance in the industry. These materials find widespread use in applications were components are expected to operate for long periods at elevated temperatures and in hostile environments. Silicon nitride (Si₃N₄) is one of the most important materials in this class. It possesses high strength and relatively superior oxidation resistance at elevated temperatures, excellent wear- and corrosion-resistance in aggressive media, has a low thermal-conductivity and expansion coefficient, and it is less dense than many other metals. These properties and its high melting point make Si₃N₄ a very suitable choice for high-temperature applications.

Due to their inherent brittleness, the fabrication of component shapes from monolithic ceramics, such as Si₃N₄, is difficult. This ongoing challenge has generated a continued interest in developing new joining technologies. Joining is also the only means of producing many of the ceramic/metal components of current interest to designers /1/. Among various joining techniques, brazing, due to its simple and economic character, has the largest potential to meet the requirements of joining ceramics for industrial applications /2/. Active-metal brazing /3/ using Ag-Cu-Ti alloys has attracted particular interest and is being used in the automobile industry to fabricate Si₃N₄/metal components /4/. Brazing with this specific filler metal can be carried out without any initial metallization of the ceramic surface. The components of the joint are fixed in a furnace (a slight load is applied) at temperatures ranging from 800 to 950°C in a vacuum or in an inert gas atmosphere. The maximum interfacial strength using this brazing filler metal exceeds 500 MPa, based on four-point bend test. Unfortunately, Ag- and Cu-based filler metals cannot be used at service temperatures above 500°C /5/. Therefore, to exploit the high temperature properties of Si₃N₄, it is necessary to employ filler metals having higher melting points.

There is a strong drive to develop filler metals with improved thermal stability to match the stability of ceramics at elevated temperatures. In general, these are refractory metal-based alloys having melting points greater than 1200°C. One such alloy is the Co-10Ti filler metal containing 10 wt.% titanium as the active
A second filler metal based on the conventional Ni-Cr alloy, which is used for brazing superalloys because of its superior strength and oxidation resistance at high temperatures, was also selected. However, Ni and Cr do not react with ceramics and are therefore not expected to wet the ceramic surface. To determine the applicability of the Ni-Cr alloy system, hafnium was added to the filler metal composition as the reactive metal. This paper presents the results of Si$_3$N$_4$/Si$_3$N$_4$ joints fabricated with these two experimental filler metals.

## EXPERIMENTAL WORK

The Co-10Ti filler metal foil was pressed between two Si$_3$N$_4$ specimens under an applied force of 7500 Pascals. Before commencing the heating cycle, the furnace chamber was evacuated to a pressure of approximately $10^{-4}$ torr. The entire assembly was then heated at a rate of 15°K/min. to the brazing temperature of 1300°C, held at this temperature for 15 minutes, and then furnace cooled to room temperature. A filler metal of composition 80Ni-13Cr-7Hf was used to produce the other set of brazes. Brazing was performed at 1250 to 1275°C in a vacuum following a similar heating procedure to that of the Co-10Ti brazes. The silicon nitride substrate in the later joints was initially premetallized at 900°C with AgCuInTi filler metal.

Upon completion of the brazing process, each sample was cross-sectioned with a diamond composite blade at low speed. The specimens were then cold mounted in resin and diamond polished to a surface roughness of 1 micron. No etching was necessary. Specimens were observed and photographed using an optical microscope and a scanning electron microscope (SEM). The compositions of the braze zone and the reaction layer were characterized using an energy dispersive spectroscopy (EDS) system capable of detecting lightweight elements like nitrogen. The spectroscopy results were confirmed by simulating the brazing process by means of the HSC thermodynamic computer program, which displayed the most probable reaction products based on their Gibbs free energies.

## RESULTS AND DISCUSSION

In the Si$_3$N$_4$/Co-10Ti/Si$_3$N$_4$ braze joints, a thick reaction layer developed almost immediately on both sides of the braze joints without degradation of the silicon nitride. Note that these samples were not premetallized.

Figure 1 exemplifies regions of the braze-joint with good bonding and adequate wetting. That is, there is a continuous interface between the filler metal and the ceramic substrate. Although there were several regions along the joint that exhibited continuous bonding, other spots showed porosity and what appeared to be lack of setting. Figure 2 illustrates a joint with a discontinuity between the ceramic substrate and the braze metal. This figure shows that the molten filler metal filed to spread over the silicon nitride. However, a reaction layer still
developed. In this same micrograph there are some signs of early solidification, that is, the braze metal froze at the brazing temperature and not during the cooling cycle.

A substantial amount of the reactive element, titanium, was added to the filler metal in order to contribute to the formation of a thick and dense reaction layer and, thus, control the decomposition of the silicon nitride. It was proposed /6/ that large amounts of reactive element would provide a greater driving force for the titanium flux towards the interface and enhance the formation of the reaction layer. The side of the braze-joint showing adherence presents a thick, uniform, and stable reaction layer. However, spots were also observed that lacked adherence. This occurred despite a thick reaction layer having developed at the silicon nitride/braze metal interface (as seen in Figure 3).

Few spots in the braze-joint had a thin reaction layer, and it appeared that there was some degradation of the silicon nitride at these locations. This is observed in the lower portion of the braze-joint of Figure 3.

The chemical analysis of the braze-joint via EDS shows the diffusion of titanium to the reaction layer with the cobalt remaining behind. At the same time, the nitrogen did not diffuse into the braze metal, it penetrated as far as the reaction layer. Silicon, on the other hand, did diffuse further, but it was also present at the reaction layer. The results of the EDS analysis are plotted in Figure 4. Based on the magnitude of the titanium, silicon, and nitrogen levels detected at the reaction layer, it appears that TiN and Ti$_x$Si$_y$ phases have been formed.

![Fig. 3: Si$_3$N$_4$ braze joint showing lack of wetting by filler metal. Thick and thin reaction layers are also observed. Rounded edges in solidified braze metal are evidence of early solidification. SEM micrograph (Magnification 400x).](image)

![Fig. 4: Elemental distribution across the silicon nitride joint brazed with Co-10Ti at 1300°C for 15 minutes.](image)
Previous investigations /1,7,8/ have proven that titanium reacts with silicon nitride to form a reaction layer comprised of titanium nitride and titanium silicides. Thermodynamic studies /9/ have suggested the following reactions should occur:

\[
\begin{align*}
\text{Si}_3\text{N}_4 + 4\text{Ti} &= 4\text{TiN} + 3\text{Si} \quad (1) \\
\text{Si}_3\text{N}_4 + 3\text{Ti} &= 3\text{TiSi} + 2\text{N}_2 \quad (2) \\
2\text{Si}_3\text{N}_4 + 3\text{Ti} &= 3\text{TiSi}_2 + 4\text{N}_2 \quad (3) \\
\text{Si}_3\text{N}_4 + 5\text{Ti} &= \text{Ti}_5\text{Si}_3 + 2\text{N}_2 \quad (4)
\end{align*}
\]

The reaction leading to the formation of titanium nitride, represented by Eq. 1, has the most negative Gibbs free energy compared to the other reactions (Eqs. 2 to 4). This leads to the conclusion that TiN will be the most dominant reaction product in the \(\text{Si}_3\text{N}_4\)-Ti reaction.

Figure 5 displays the results obtained from the HSC thermodynamic computer program, showing the probable reaction products that form during this brazing process. It can be seen that TiN is the most stable reaction product and has the higher drive to form compared to the \(\text{Co}_2\text{Si}_3\) phases. Thus the spectroscopy results clearly support the data obtained from previous investigations and are in conformity with the thermodynamic data.

The segregation of titanium towards the silicon nitride causes the depletion of this element from the filler metal. The change of the Co-Ti composition appears to have an effect on its liquidus temperature. Referring to the Co-Ti equilibrium phase diagram (Figure 6), a small change in the amount of titanium on the cobalt-rich end of the phase diagram causes significant changes in the liquidus and solidus temperatures. This is because both solidus and liquidus curves have steep slopes at this end.

Figure 4 shows that the titanium levels in the braze-metal across the major portion of the joint were in the range of 5 atomic percent. The phase diagram shows that this composition would be mostly solid at the brazing temperature of 1300°C used in this work. As the amount of solid phase increases, the fluidity decreases and the spreading diminishes. The rounded braze metal edges and gaps between the braze metal and reaction layer are an indication of an early solidification (Fig. 3).

Nevertheless, these results show that it is possible to circumvent the two-step brazing process. Degradation of the silicon nitride was contained, except in spots where the reaction layer was too thin. However, the level of titanium in the filler metal needs to be optimized to prevent the limited fluidity of the molten braze metal and its early isothermal solidification.

The second filler metal used in our investigation was the 80Ni-13Cr-7Hf alloy system. As indicated previously, hafnium was selected as the reactive element. One of the first findings during brazing with this system was that the silicon nitride degraded rather readily,
Fig. 6: Equilibrium phase diagram of the cobalt-titanium system /10/.

despite the high levels of the reactive metal. Previous research /11/ has shown that excessive amounts of hafnium resulted in brittle intermetallic phases that prevented fabrication of a braze joint. This was caused by the hafnium reacting with nickel, nitrogen, or silicon. An alternative used to prevent breakdown of the silicon nitride and yet produce a sound braze joint was to premetallize the ceramic substrate and also reduce the levels of hafnium in the NiCrHf brazing metal.

Figure 7 shows a silicon nitride braze joint, processed at 1250°C for 5 minutes. The premetallized reaction layer is well defined and it remained intact during final brazing. There was, however, diffusion of elements in and out of this region. Silver and copper diffused into the braze metal. Copper went into solid solution with nickel, but silver precipitated out as a pure phase.

Figure 8 shows the microstructure encountered in the NiCrHf braze joint. The light phases in the microstructure are silver-rich; the matrix of the filler
metal (gray region of micrograph) was analyzed to be 76Ni-12Cr-11Cu (wt.%).

The small dark dots seen in some places had a composition of 50Ti-38Ni-6Cr-6Hf. The hafnium moved towards the silicon nitride despite the presence of an existent reaction layer. On the other hand, titanium diffused into the braze metal and combined with nickel, hafnium, and chromium, and precipitated as small particles within the Ni-Cr-Cu matrix. Figure 9 gives a more detailed description of the precipitates and other micro-structural features at the reaction layer.

Fig. 9: Reaction layer of the silicon nitride joint brazed with Ni-13Cr-7Hf filler metal at 1250°C for 5 minutes in a vacuum.

CONCLUSIONS

1. Silicon nitride braze joints were produced by the direct brazing method employing Co-10%Ti as filler metal. A thick titanium-rich reaction layer developed that prevented degradation of the ceramic substrate during brazing. Limited silicon nitride degradation, during brazing, was observed at those places where the reaction layer was thin.

2. EDS results showed that cobalt remained in the braze metal and titanium segregated toward the reaction layer. The titanium depletion of the filler metal caused the braze metal to solidify during brazing. This early solidification produced gaps between the braze metal and the silicon nitride.

3. Brazing with Ni-13Cr-7Hf was only possible with the silicon nitride premetallized. Hafnium from the braze metal moved towards the existing reaction layer, while copper dissolved in the matrix. Silver moved from the existing reaction layer towards the braze metal, but it did not dissolve in the Ni-Cu-Cr matrix. It was present as islands of pure silver.

REFERENCES