Heat-Resistant Active Brazing of Silicon Nitride
Part 2: Metallurgical Characterization of the Braze Joint

Filler metals that equal the thermal stability of high-temperature ceramics are on the horizon

BY W. TILLMANN, E. LUGSCHEIDER, K. SCHLIMBACH, C. MANTER AND J. E. INDACOCHEA

ABSTRACT: Metallurgical characteristics of silicon nitride braze joints fabricated for service at elevated temperatures are discussed in Part 2. Filler metals containing palladium, platinum, copper, nickel, and silver were investigated. Most filler metals were arc melted, and then differential thermal analysis was performed to determine the liquidus and solidus temperatures. Wetting tests were employed as selection criteria.

The silicon nitride substrate was premetallized at a lower temperature with an AgCuInTi filler metal prior to brazing at elevated temperatures. The reaction layer developed during premetallizing remained stable at the higher brazing temperature, controlling the silicon nitride decomposition. Other braze joints were fabricated without premetallizing, using a Co-10Ti melt-spun foil, in order to avoid an extra processing step. Thermogravimetric results showed that the Co-10Ti filler metal oxidized quickly at first but passivated almost as fast. Overall it had good oxidation resistance.

Introduction

New types of lightweight ceramic materials with excellent strength at elevated temperatures and good thermal properties are in demand because conventional oxide ceramics are inadequate for many engineering applications. Among new engineering ceramics, silicon nitride and silicon carbide are two materials that have outstanding potential for high-temperature applications. The use of these high-performance ceramics strongly depends on the availability of appropriate joining techniques. Compared to metals, the restrictions imposed on ceramics are much higher concerning selection of a joining process that is able to meet thermal and mechanical stability demands. Ideally, the thermal stability of the braze joint should equal that of the ceramic substrate.

KEY WORDS

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Table 1—Filler Metal Compositions (w/o) of Selected High-Temperature Filler Metals

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_{lo} (°C)</th>
<th>T_{hi} (°C)</th>
<th>Composition (w/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgPdPt</td>
<td>1195</td>
<td>1250</td>
<td>53.0 Ag, 39.0 Pd, 5.0 Pt, 3.0 Ti</td>
</tr>
<tr>
<td>AgPdTi</td>
<td>Not Available*</td>
<td>56.0 Ag, 42.0 Pd, 2.0 Ti</td>
<td></td>
</tr>
<tr>
<td>AgPdPtTi</td>
<td>1195</td>
<td>1250</td>
<td>53.0 Ag, 39.0 Pd, 5.0 Pt, 3.0 Ti</td>
</tr>
<tr>
<td>PtCuTi</td>
<td>1208</td>
<td>1235</td>
<td>55.0 Pt, 43.0 Cu, 2.0 Ti</td>
</tr>
<tr>
<td>ZrCrCu</td>
<td>Not Available*</td>
<td>73.0 Zr, 12.0 Cr, 15.0 Cu</td>
<td></td>
</tr>
<tr>
<td>PdNiTi</td>
<td>1200</td>
<td>1225</td>
<td>70.0 Ni, 30.0 Hf</td>
</tr>
<tr>
<td>NiHf</td>
<td>1215</td>
<td>1320</td>
<td>90.0 Co, 10.0 Ti</td>
</tr>
</tbody>
</table>

*Samples partially melted during DTA or reacted with crucible.

Con nitride and forms a reaction layer at the filler metal/ceramic substrate interface. In our previous investigation (Ref. 3), formation of titanium nitride was found to be the rate-determining step in the growth of this zone, and the free silicon was later found to further interact with the metal to form titanium silicide. Other research (Ref. 4) reports the formation of metal silicide and free nitrogen as the rate-controlling step. For niobium, tantalum, aluminum, zirconium and other elements, the formation of the metal nitride is the rate-determining step because their nitrides are more stable than those of silicon nitride. It should be noted that the formation of the metal nitrides is not only a function of temperature but also depends on the partial pressure of nitrogen in the brazing atmosphere (Ref. 5).

Experimental Procedure

In developing high-temperature filler metals, several chemistries were considered, as seen in Table 1. Most of the compositions were arc melted in an argon atmosphere with the exception of Ni30Hf and Co10Tl, which were melted using a melt-spin technique. All filler metals were later rolled into foils about 100 µm thick. Differential thermal analysis (DTA) was performed on the filler metal samples to determine their liquidus and solidus temperatures and to characterize other thermal transition behavior. Wetting and spreading tests were carried out on the ceramic substrate at the brazing temperature. The brazing specimens produced for the microstructural characterization were squared, sintered silicon nitride samples, 10 x 10 x 2 mm. The brazed specimens were examined in the as-processed condition and some following heat treatment after brazing. Most of the vacuum brazes were processed at about 1250°C and at vacuum pressures of around 10^{-5} mbar. Standard metallographic procedures were followed during sample preparation.

Results and Discussion

Differential Thermal Analysis and Wetting Behavior

The immediate goal is to develop filler metals with liquidus temperatures of about 1100°C, or slightly higher, so they can meet high-temperature service demands (above 650°C). Initially, additions of Ti and Pd were made to an AgCu eutectic filler metal to raise the liquidus temperature, as well as to improve its oxidation resistance. Nonetheless, no significant change was observed in the eutectic temperature. From existing equilibrium binary-phase diagrams for Ag-Pd, Ag-Pt, Cu-Pd and Cu-Pt (Ref. 6), however, it was noted that the amount of Pt and Pd additions used in this work (about 18-20 wt-%) did not significantly increase the liquidus and solidus temperatures of the binary alloys. A filler metal of composition Ag29Cu19Pt3Ti had a melting temperature of about 780°C. Similar results were obtained when palladium was added to the eutectic alloy instead of platinum. Table 1 presents a list of the filler metals investigated. In some cases an exact critical temperature could not be measured because the filler metal reacted with the alumina crucible of the DTA instrument, those systems were dropped from the study. In the Pd- and Pt-based filler metals, Cu, Ag and/or Ti were added as liquidus temperature depressants. Some samples melted partially during the DTA study, which complicated the determination of the liquidus temperature. Consequently, only those alloys that had their liquidus temperature determined were selected for further work.

In earlier work, Tillmann (Ref. 6) noticed that silicon nitride decomposed during vacuum brazing at elevated temperatures. This was observed metallographically by the rough surface appearance of the substrate at the interface with the filler metal. Gas evolution, or bubbling, was observed at the ceramic/filler metal interface as the brazing temperature reached 1200-1250°C. The vacuum pressure (10^{-5}-10^{-6} mbar) and temperatures utilized for brazing at the high temperatures were found to correspond to conditions leading to the decomposition of the silicon nitride. Figure 1 is the phase stability diagram for Si3N4, which shows how silicon nitride will decompose into silicon and nitrogen gas within the temperature range of 1400°C-1600°C (1127°C-1327°C) at partial pressures of nitrogen between 10^{-4} and 10^{-7} mbar. Gas spectrographic analysis confirmed the presence of nitrogen.

![Fig. 1 — Silicon nitride stability as a function of nitrogen partial pressure and temperature.](image)

![Fig. 2 — Wetting angles of PdNi3Ti on silicon nitride as a function of temperature.](image)
Titanium nitride, on the other hand, is more stable than silicon nitride. In active brazing, a reaction layer consisting of titanium nitride (Ref. 3) is needed to ensure wetting of the ceramic by the molten filler metal, which ultimately provides the metallic bonding. Tillmann speculated that silicon nitride can be premetallized at a lower temperature (about 900°C), where a titanium nitride layer will develop. Such reaction layer should remain stable at a higher brazing temperature of 1200°C. This will ensure proper wetting and brazing and would also control the decomposition of the silicon nitride. The braze premetallizing in this work was performed using a Ag19.5Cu3Ti5In filler metal.

Most wetting tests were conducted on premetallized ceramic substrates. These tests were qualitative in character and were performed at temperatures and times similar to those used in brazing. In most cases, foil specimens from the filler metals fabricated were utilized for the wetting tests. Premetallizing the silicon nitride, however, besides minimizing its decomposition at high temperatures, also improved its wetting. Figure 2 presents the wetting data of PdNi3Ti on silicon nitride as a function of temperature and shows the benefit of premetallizing. Note that in the case of the bare silicon nitride, a wetting angle of about 42 deg was measured near 1200°C, compared to an angle of 18 deg for the silicon nitride that was premetallized with AgCuInTi. As the temperature increased, instead of observing a decrease in the wetting angle for the bare ceramic substrate, the opposite occurred. The wetting angle at 1250°C increased to 63 deg. This corresponds to the temperature at which the silicon nitride was noted to have decomposed before. The premetallized substrate, on the other hand, did not display changes in wetting angle; it remained at 18 deg. This further supports the observation that the reaction layer formed during premetallizing remained present at the higher temperature and that the ceramic substrate did not decompose. As the temperature was increased, the wetting angle again changed in the samples that were not premetallized but remained unchanged at temperatures above 1270°C. It is evident that premetallizing the silicon nitride makes wetting a secondary issue.

**Metallurgical Evaluation**

**PdNiTi Filler Metal**

The (60Pd-40Ni)-3Ti braze samples were vacuum premetallized for 10 min-
utes at 900°C and then brazed at 1250°C for 10 minutes. Figure 3 depicts the condition of the braze joint after processing. No visible decomposition of the silicon nitride was observed at the ceramic substrate/filler metal interface. Energy Dispersive Spectroscopy (EDS) point analysis adjacent to this interface, within the premetallized reaction region, indicated that titanium nitride and titanium silicide were present. In addition, moderate levels of copper and nickel and a trace of indium were found. The copper and indium are consistent with the composition of the filler metal used for premetallization; the nickel comes from the PdNiTi braze filler metal. Away from the interface (or reaction layer), the levels of palladium and nickel in the same matrix (light phase of Fig. 3) increased, but the titanium and copper contents decreased. No silicon or indium was found at this spot. Figure 4 provides the semiquantitative results of the chemical analyses at these locations. The small black precipitates are titanium-copper intermetallics. These intermetallics evidently precipitated from the titanium present in the PdNiTi filler metal in the absence of nitrogen or silicon diffusing from the silicon nitride through the premetallized reaction region. The reaction layer resulting from premetallization apparently not only prevented decomposition of the ceramic substrate during brazing but also prevented or reduced the diffusion of elements between the filler metal and the silicon nitride. EDS analysis of the intermetallic particles indicated that they are either Ti₃Cu₄ or Ti₂Cu₃.

The fracture portions of the bend test specimens were examined, and it was found that the fracture occurred along the reaction layer at the interfaces between the ceramic substrate and the filler material. This was confirmed by chemical analysis on portions of the fracture that showed regions containing mainly titanium, silicon and nitrogen, as well as copper and nickel.

As a comparison, a nonpremetallized PdNiTi braze joint (20 minutes at 1250°C) was examined. The reaction layer was very thin, less than 0.5 μm, compared to approximately 2 to 3 μm in the case of the premetallized braze, and some porosity was found in places of the filler metal matrix near the silicon nitride. Because of the fine reaction layer, it was difficult to carry out relevant chemical analyses in the vicinity of the filler metal/ceramic interface. Figure 5A is a micrograph of the braze joint that shows an almost nonexistent reaction layer. X-ray mappings were produced to describe the dilute reaction layer and the movement of elements about the filler metal. Figures 5B-E correspond to the X-ray mappings of titanium, silicon, palladium and nickel, respectively. It was established that the titanium migrated toward the silicon nitride and a very thin reaction layer was evident. Silicon was found at the reaction layer, but it had also migrated deeper into the filler metal matrix. This contrasts with the premetallized sample, where silicon was confined to the reaction layer, and it was absent within the filler metal. This result gives further support for the role of premetallizing in controlling the decomposition of silicon nitride during brazing at elevated temperatures. It appears that silicon had segregated preferentially to regions richer in palladium. Palladium, concurrently, is present throughout the metal matrix, but its concentration is greater in those areas rich in silicon. X-
ray diffraction (XRD) analysis of the fracture surface of a braze bend sample showed PdSi and Pd$_2$Si. This is expected since palladium is known to be a strong silicide former. Nickel is found to have segregated only as a second phase, but this phase also contains palladium. Yet no compound or solid solution consisting of Pd and Ni was identified among the XRD peaks. Ni$_2$Si peaks were also recognized.

**PtCuTi and PdCuPtTi Filler Metals**

Two other filler metals, PtCuTi and PdCuPtTi, were tested with some success. Partial wetting or nonuniform spreading was observed with PtCuTi filler metal. That is, there were few regions where a cavity or pore existed between the premetallized layer and the braze filler metal. A much better braze was attained with PdCuPtTi, wherein no discontinuities were observed between the premetallized reaction layer and the braze metal. In the PtCuTi brazes, a reaction layer about 2.0 μm thick was detected. EDS spot chemical analysis of the PtCuTi braze confirmed the presence of titanium-nitride and titanium-silicide in the original premetallized reaction layer at the interface with the ceramic substrate. This is consistent with our previous work (Ref. 3) and the results of the premetallized PdNiTi braze joint. Unlike the PdNiTi braze, no indium was found at this location, but copper and silver were present, as well as a small amount of platinum. Platinum, apparently, diffused in during braze fabrication. At the opposite end of the reaction layer and adjacent to the braze metal, the levels of copper and platinum increased while titanium decreased and silicon dropped altogether. Silicon was not found in the braze metal matrix either. The light gray phase is a palladium-rich phase. Based on observation of the copper-palladium phase diagram, and from the levels of palladium and copper measured, it appears that the light matrix conformed to the ordered β-Cu$_2$Pd phase. The dark gray matrix was rich in copper and, based on the EDS results, it corresponded to the Cu$_3$Pd-ordered phase. The black spots present in the microstructure were TiCu intermetallics.

**Fig. 8 -- Melt-spin Co-10Ti filler metal foil. Braze produced in vacuum at 1240°C for 10 minutes. The silicon nitride substrate was not premetallized.**

The PdCuPtTi filler metal contained the same amount of copper, about 43 wt-%, titanium was doubled to 4 wt-%, palladium was added at 2 wt-% and platinum was added at 2 wt-%, and palladium at 51 wt-%. The joints were fabricated at 1280°C for about 10 minutes using premetallized silicon nitride. Figure 7 shows the microstructure of the braze joint. Again, the ceramic substrate remained intact without any sign of damage due to the braze process. The premetallized reaction layer was about 2.0 μm. Chemical results from the EDS analysis showed an interface at the reaction layer/silicon nitride consisting of titanium-nitride and titanium-silicide. The light matrix of the filler metal was a palladium-rich phase. Based on observation of the copper-palladium phase diagram, and from the levels of palladium and copper measured, it appears that the light matrix conformed to the ordered β-Cu$_2$Pd phase. The dark gray matrix was rich in copper and, based on the EDS results, it corresponded to the Cu$_3$Pd-ordered phase. The black spots present in the microstructure were TiCu intermetallics.
and appeared to have segregated toward the reaction layer, but they stayed outside this region. This segregation might have been caused by a very limited decomposition of the silicon nitride at the beginning of the brazing operation, such that silicon and nitrogen managed to diffuse partially through the preexisting reaction layer. This, in turn, would drive the titanium to this location. Titanium segregated just outside the premetalized reaction layer cannot form titanium-silicide or titanium-nitride due to the lack of nitrogen and/or silicon atoms (as noted by the EDS results). Instead, titanium would combine with copper atoms to form titanium-copper intermetallics.

The metallurgical features of the PtCuTi, PdCuPTI and PdNiTi premetalized brazes are similar. The original reaction layer formed by braze premetalization seems to have controlled the decomposition of the silicon nitride during the brazing at high temperatures. It also seemed to limit any further diffusion of silicon or nitrogen across it. Silicides were not found in any of the filler metal matrices just outside the premetalized reaction layer. The presence of TiC intermetallics outside this reaction region is also evidence of the lack of nitrogen and silicon since titanium readily forms nitrides and silicides. Apparently, the excess titanium present in the filler metal, which does not have nitrogen or silicon to react with, will only combine with copper. The resemblance in microstructures of these two filler materials is a reflection of the similar characteristics of platinum and palladium and comparable amounts of copper and titanium.

CoTi Filler Metal

Part of the investigation concentrated on producing braze joints without premetalizing the silicon nitride in order to avoid an additional step that would increase braze fabrication cost. Two filler metals were selected containing large amounts of reactive metals, Ni30Hf and Co10Ti. Substantial quantities of these two elements have been thought to contribute to the formation of a thin and dense reaction layer and, thus, control the decomposition of the silicon-nitride. It was believed that large amounts of reactive elements would provide a greater driving force toward the interface for the titanium and hafnium flux and enhance the formation of the reaction layer. The Ni30Hf brazes were quite brittle and did not stay together. The Co10Ti braze remained joined.

Figure 8 shows the condition of the braze. One side of the joint presents a thick, uniform and stable reaction layer, but the other side has a reaction layer that is not uniform and is fragmented in places. It appears that in a few spots the ceramic substrate broke loose. Those portions of the filler metal that remained attached to the substrate revealed a thick reaction layer. EDS analysis of the thick reaction layer indicated a region rich in titanium. The matrix microstructure consisted of two phases, α-CoSi and α-Co2Si. The presence of silicides in the microstructure is further evidence of the titanium nitride decomposition effect due to brazing, yet the ceramic substrate/filler metal interface did not appear significantly damaged.

Oxidation Behavior of Filler Metals

Oxidation tests were conducted in air at 600°, 800° and 1000°C for 24 h and at 800°C for 100 h for the PdNiTi filler metal. Part 1 of this paper (Ref. 8) reported that a reduction in bending strength occurred as a result of the braze joints being exposed to air at elevated temperatures. The samples that experienced the most significant drops in strength were those exposed to 800° and 1000°C. These results correlated with the filler metal degradation observed during microstructure analysis. It was observed in the PdNiTi samples that oxidation was not limited just to the filler metal but also compromised the reaction layer and the substrate. PtCuTi brazes were submitted to oxidation testing but were not mechanically tested at the moment. Instead, a qualitative assessment based on metallographic analysis was carried out. These last samples were exposed to 800°C for 100 h in air. Figure 9 compares the condition of the PdNiTi and PtCuTi brazes following oxidation. The PtCuTi braze joint was found to remain microstructurally unchanged and in a better state than the PdNiTi brazes. The filler metal pertaining to the PtCuTi joint remained intact and there was no sign of decomposition of the reaction layer nor of the silicon-nitride. The oxidation behavior of the melt-spun CoTi foil was assessed using thermogravimetric measurements at 1000°C along with the PdNiTi foil. The results are presented in Fig. 10. At short exposure times of less than an hour, the CoTi foil oxidized very rapidly, and, by the time an hour had passed, its weight change was four times greater than that found in the PdNiTi filler metal. However, for exposure times over one hour, the CoTi filler metal looked as if it had passivated and no further change in weight was perceived. The PdNiTi filler followed a parabolic-time law. It initially behaved better than the melt-spun filler, but, after about 7 h of exposure, it surpassed it and continued to oxidize. At 21.5 h, the PdNiTi filler oxidized more than 1.5 times the CoTi filler metal. This behavior remained unchanged for the remaining test length.

Conclusions

1) Silicon nitride decomposes when brazed in 10⁻¹ torr of vacuum at 1250°C. By premetalizing the ceramic substrate at 900°C under the same vacuum conditions, with a AgCu40 filler metal, the decomposition is avoided. It also enhances wettability at elevated temperatures.

2) The palladium and platinum filler metals showed significantly similar microstructural features. The PtCuTi filler metal exhibited better oxidation resistance than did PdNiTi.

3) The melt-spun CoTi filler metal, after an early sudden increase in oxidation, passivated and remained unchanged after about two hours. It ultimately showed better oxidation resistance than the PdNiTi filler metal.

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