Heat-Resistant Active Brazing of Silicon Nitride
Part 1: Mechanical Evaluation of Braze Joints

A new class of palladium-based filler metals that wet to ceramics is tested for joint strength and oxidation resistance

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ABSTRACT. This paper assesses the mechanical properties of silicon nitride braze joints after fabrication and following exposure to elevated temperatures. These tests were conducted at room temperature and using four-point bending. The filler material used in the investigation is palladium-based, 58.2Pd-38.8Ni-3.0Ti. The silicon-nitride substrate was coated with a AgCulnTi filler metal prior to fabrication of the braze joint. Two different sample geometries were used in the fabrication of the braze joints. Weibull statistics was applied to the interpretation of the data, but the results contradict what is expected from monolithic fracture theories. Oxidation was found to be significant when the braze joints were exposed to 800°C in air, which reduced the joint strength. All specimens fractured at the reaction layer during the bending tests.

Introduction

The widespread application of mechanically and thermally stressed ceramic components in such devices as diesel engines, turbines, and heat exchangers, will depend on satisfying normal commercial criteria. Therefore, these ceramic components must perform in a more cost-effective manner than do present components, taking into consideration that any increase in cost must be accompanied by an even greater increase in performance of the system. If new uses are to be realized, it is also imperative that reliable joining techniques be available. Thus, if complex engineered shapes are to be made from ceramics, the least technically demanding and most economical means of joining assemblies must be chosen to easily fabricate components. Similarly, although ceramics possess uniquely desirable properties, their use normally depends on their incorporation into metallic structures. Oxidation means that it can be difficult to achieve chemical bonding between ceramics and metals and between ceramics when using a brazing filler metal. In fact, most of the established brazing alloys developed originally for joining metal components cannot be used to join ceramics to metals because they do not wet the ceramics, and they are not drawn into the joint by capillary action (Refs. 7, 8). In practice, successful brazing requires prior metallizing of the ceramic surfaces if typical filler metals are to be used. Recent developments, however, have led to a new class of brazing filler materials. These active filler metals that react chemically with the ceramics to form wettable products on their surfaces and, thus, do not need prior modification of the ceramic surface (Refs. 9–12).

Joints in important structural applications such as high-performance engines will experience great thermal and stress cycling. The materials' system must withstand cycling and provide a reliable, creep-resistant and oxidation-resistant joint. Commercially available active brazes tend to have an upper limit, concerning their application temperature, in the range of about 400°C (Refs. 13, 14). This is due primarily to the matrix composition of the brazing filler metal, which

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is generally silver based. Attempts are found in the literature to increase the service temperature of the filler metals by modifying the composition of the matrix system (Refs. 15-17). Some of the proposed solutions are driven by a very specific application and often require complicated brazing procedures, yet many cannot fulfill the oxidation requirements for temperatures higher than 800°C, since they are still based on silver.

This investigation is concerned with the development of high-temperature brazing filler metals with improved oxidation resistance and strength at elevated temperatures. The filler metals considered are based on precious metals, such as palladium, platinum and gold. Another requirement is that the filler metal should have a melting range above 1100°C. Results of the first of the filler metals studied, the palladium-based filler metal, are reported in this paper. The effect of joint geometry will also be assessed in terms of braze joint strength. In earlier studies (Refs. 18, 19), it was found that during vacuum brazing of Si₃N₄ joints above 1200°C, the silicon nitride substrate would decompose, resulting in poor braze joints at best. It was discovered then, that by precoating the ceramic substrate at 900°C prior to brazing, its decomposition would be controlled because of development of a titanium-nitride reaction layer, which apparently limited the diffusion of silicon or nitrogen into the braze metal (Ref. 20).

**Experimental Procedure**

A commercially available, pressureless sintered and hot-pressed Si₃N₄ substrate was used in this investigation. The braze specimens utilized to assess the effect of joint geometry on braze joint strength were 10- and 15-mm-diameter bars, 10 x 10 mm squares and rectangular cross-sections (3.5 x 4.5 mm). The corners in the square and rectangular samples are likely stress concentration spots. The silicon nitride surfaces were metallurgically polished to a finish of 1 µm and then ultrasonically cleaned in acetone prior to brazing.

The Si₃N₄ was initially coated with an AgCuInTi filler metal (72.5 wt-% Ag, 19.5 wt-% Cu, 5 wt-% In, 3 wt-% Ti) at 900°C for 10 minutes under a vacuum of 10⁻⁵ torr. The braze joint was produced using a PdNiTi filler metal (58 wt-% Pd, 39 wt-% Ni, 3 wt-% Ti) at 1250°C for 10 minutes in vacuum, 10⁻⁵ torr. The precoating and braze fabrication of the specimens were carried out in a fixture built out of stainless steel or vacuum-stable graphite, as shown in Fig. 1.

The braze joints were submitted to room temperature four-point bend tests; some of the joints were tested after processing and others after heat treatments of 24 h in air at 600°C, 800°C and 1000°C. In addition, some sets of braze joints were exposed to 800°C in air for 100 h and then bend tested. For the four-point bend test, a displacement rate of 0.4 mm/s was applied and using the experimental setup shown in Fig. 2. The data collected was plotted using Weibull statistics, an accepted procedure used in the evaluation of the strength of ceramic materials. In our study, the fracture probability was assessed according to the equation

\[ P_i = i - 0.5/m \]

where, \( i \) = individual specimen number, and \( m \) = total number of specimens tested.

Following the mechanical tests, some samples were selected for fractographic analysis. Our purpose was to establish the failure mode in terms of the fracture path. All samples were carefully handled after testing to avoid further damage of the fractured surfaces. These were examined via scanning electron microscopy, and chemical analyses of localized regions were carried out using energy dispersive x-ray analysis.

**Results and Discussion**

**Mechanical Evaluation**

In carrying out the analysis of the bending test results, it is important to state that none of the braze joint specimens fractured in the silicon-nitride substrate. The samples fractured at the reaction layer and the crack propagated interchangeably between the interfaces of the reaction layer/ceramic substrate and reaction layer/filler metal. This failure characteristic might suggest an adherence-related problem. Thus, these test results do not allow one to relate the adherence to material parameters in the region of failure (Ref. 21).

In the four point bend testing of the round bar braze joint samples, it was observed that increasing the substrate diameter from 10 to 15 mm did not affect the joint strength of the as-fabricated specimens. It remained constant at 117 MPa. This result contradicts what is commonly observed in monolithic ceramics, where the strength of these brittle solids shows a pronounced size effect in which the strength decreases with increasing size or volume of the specimen (Ref. 22). How-
ever, because of the location of the fracture in all the samples tested, fracture mechanics theories for monolithic ceramics, such as the Griffith theory, cannot arbitrarily be applied to explain the mechanical behavior of these braze joints. It must be recognized that the joint consists of the ceramic substrate, a reaction layer and ductile filler metal, each with distinct physical and mechanical properties. Yet, the brittle behavior of the fracture of all the test samples, and the variability of the results points to a treatment of the data following probabilistic aspects. A statistical theory of brittle fracture assumes that the specimen is divided into many volume elements, each containing a single crack with no interaction between the cracks in the different volume elements. The strength of the specimen is determined by the element with the longest crack, for this results in the lowest value of fracture stress. Therefore, the brittle-fracture strength is determined, not by an average value of the distribution of flaws, but by the single-most dangerous flaw. In the case of the round bar braze joint specimens, due to the fracture location, the critical link can be considered to be the reaction layer. Since both diameter specimens fail at the same bending strength, and the reaction layer characteristics in terms of thickness, microstructure and composition are the same, it suggests that the reaction layer could be considered as the most critical microstructural flaw. Apparently, there are no studies concerning the flaw distribution in this region and their connection with the failure probability of the braze joints. Further, the residual stresses present in these joints due to processing is another issue of significance in the strength of these braze joints and yet not included in any fracture probability. It has been demonstrated that the use of inter-layer metals reduce the residual stresses and increase the braze joint strength (Ref. 23).

Figure 4 shows the results of the bending tests done on the rectangular samples. The bending strengths were higher in these samples (131 MPa) than the round specimens (117 MPa). This is also surprising, since if the tests were conducted in monolithic ceramics of exactly the same geometries, the rectangular samples would have lower bend strengths. Because of the geometries involved, the rectangular samples would have a higher volume of material under high stresses than the round bar samples, consequently the probability of encountering critical-sized flaws is also higher. The results presented in Fig. 5 for the square cross-section samples are consistent with this thinking. However, like in the round bar braze joints, the specimens failed in the joint, at the reaction layer. Further, the presence of a microstructure inhomogeneity and existence of residual stresses from brazing complicates the analysis. The Weibull moduli obtained are all inconsistent with what is commonly observed in homogeneous monolithic ceramics. This gives further evidence that the fracture probability function cannot be applied in the case of brazed-ceramic joints when the failure occurs in the joint. Further studies are needed to consider the flaw distribution in the reaction layer, the effect of residual stresses and the heterogeneous microstructure and their role in the fracture probability and strength of a brazed-ceramic joint.

Oxidation Tests

Exposure of the braze samples to 1000°C for 24 h in air caused a significant reduction of the bending strength of the 1-mm-diameter samples from 117 to 66 MPa — Fig. 5. The 15-mm round bar samples also experienced some drop in bending strength (117 to 109 MPa), but not near the magnitude of the smaller-diameter samples. This difference in strength is due most likely to the difference in the amount of unaffected material remaining at the braze metal-ceramic
substrate between the 10-mm and the 15-mm-diameter samples. The oxidation conditions were the same in all cases, thus the oxidation penetration depth would be expected to be similar. It was difficult to carry out measurements in terms of oxidation penetration on the fractured samples. Special coupons were fabricated along with bend samples for the metallurgical aspect of the work. Although a more extensive metallurgical discussion of the braze joints is presented in a future paper, Fig. 6 provides a cross-sectional view of the joint, which shows minor degradation of the ceramic substrate and slight oxidation of the braze metal after a 24-h exposure in air at 600°C — Fig. 6A. The degradation of the silicon nitride and oxidation of the filler metal was more extensive in the specimen exposed at 1000°C for 24 h — Fig. 6B. Figure 7 shows the bending strengths as a function of oxidation conditions. The 10-mm round joints show a drop in bending strength to about 105 MPa, as they were exposed to 600°C for 24 h, but it dropped further as they were exposed to 800°C and 1000°C for 24 h where the bending strength is 66 MPa. Note that exposures of the 10-mm-diameter sample to 1000°C/24 h or 800°C/100 h did not produce further decreases in strength. Apparently the additional damage caused by increasing the temperature by 200°C (from 800°C to 1000°C) at 24 h or by extending the time at temperature by 76 h at 800°C is not significant to further diminish the mechanical properties. The 15-mm-diameter braze joints did not show a decrease in bending strength. The Weibull modulus was examined during the oxidation testing — Fig. 8. In every test the larger-diameter braze samples consistently had higher Weibull modulus values, which is also consistent with the results of the bending tests of the as-fabricated braze joints.

Fractography

Examination of the fracture surfaces of all samples submitted to four-point bend tests, disclose no differences in either fracture location or fracture morphology. Figure 9 exemplifies the fracture surface encountered in all the braze joints that were tested in bending. Failure took place at the reaction layer with a fracture path migrating through the reaction layer interchangeably between the filler metal and ceramic substrate with the reaction layer. Lumps of silicon nitride were seen attached to the filler metal, as well as craters can be observed in the parts of silicon nitride exposed to the fracture (Fig. 9A); the dark grey structure is the silicon-
nitride and the white structure is the filler metal. A higher magnification of this area is presented in Fig. 9B. A microchemical analysis was performed in spots at both sides of the fracture structures and the results are consistent with the metallographic analyses.

Conclusions

1) Weibull statistics, when applied to ceramic braze joints, yield results that contradict those expected of monolithic ceramics.
2) The lack of information on the flaw distribution of the reaction layer, the heterogeneous structure of a ceramic braze joint and the residual stresses from fabrication are considerations that most likely affect the fracture probability.
3) The reaction layer, an important component in the wetting and bonding of ceramics with filler metals, also becomes the weakest link. All samples fractured at this location.
4) The bending tests on the 10-mm-diameter samples clearly show that when these braze joints are exposed for 24 h in air between 600°C and 1000°C the strength decreases. Minor degradation of the silicon nitride was seen at 600°C, but became much more significant at 1000°C. Oxidation of the 15-mm-diameter specimens was not notable.

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