Brazing Titanium-Vapor-Coated Zirconia

High-strength braze joints were obtained through the use of titanium vapor coatings to promote wetting on partially stabilized zirconia

BY M. L. SANTELLA AND J. J. PAK

ABSTRACT. Partially stabilized zirconia was vacuum furnace brazed to itself, to nodular cast iron, and to commercially pure titanium with a Ag-30Cu-10Sn wt-% filler metal. Wetting was obtained by coating the ZrO₂ surfaces with Ti prior to brazing by RF sputtering or electron beam evaporation. Braze joints made with Ti-sputter-coated ZrO2 contained high levels of porosity, but those made with Ti coatings deposited by evaporation, referred to as Ti-vapor-coated, contained little or no porosity. Brazing caused the ZrO2 within about 1 mm (0.04 in.) of the joint surtaces to turn black in color, and thermodynamic analvsis indicated that the discoloration was likely due to oxygen diffusion out of the ZrO₂ into the Ti vapor coating during brazing. Braze joint strength was determined by flexure testing in the four-point bend arrangement, and on a more limited basis, by shear testing. The latter method was used mainly as a screening test for ZrO2-Fe and ZrO2-Ti joints. Flexure testing of ZrO2-ZrO2 and ZrO2-Fe braze joints was done at 25°, 200°, 400°, and 575°C (77°, 392°, 752° and 1067°F) in air. For flexure testing, average strengths of joint specimens decreased with increasing test temperature. The lower average strengths of ZrO₂-Fe specimens compared to those from ZrO2-ZrO₂ joints was attributed to higher residual stresses in the ceramic-to-metal joints. At 25°C, fracture in the highest strength specimens was associated with considerable failure through the ZrO_2

M. L. SANTELLA is with Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, Tenn.

J. J. PAK is with Pohang Steel Co., Research Institute of Industrial Science and Technology, Pohang, Korea. beneath the Ti-vapor-coated surfaces. In contrast, debonding at ZrO_2/Ti -vaporcoating intertaces was prevalent in the lower strength specimens at 25°C, and the tendency for failure to occur by debonding increased with test temperature. The braze filler metal strength did not limit joint strength at temperatures of 400°C and below. Lapping of the ZrO_2 joint surfaces did not improve the strength of ZrO_2 -Fe joints. Joint strength at 575°C was limited by the strength of the braze filler metal layers.

Introduction

An essential consideration in the brazing of ceramic oxides is the need to promote wetting of the oxide surfaces by liquid braze filler metals. Many conventional brazing alloys, however, exhibit limited wetting on oxide surfaces so that producing strong oxide braze joints is difficult unless special techniques are used. Wetting of oxide surfaces by liquid metal alloys can be obtained by two general methods: 1) alloying braze filler

KEY WORDS

Brazing Ti-Vapor Coated Wetting Part-Stabilized ZrO₂ Shear Testing Microstructure Fracture Strength EB Evaporation RF Sputtering Vacuum Brazing metals with elements that activate wetting; and 2) applying coatings that promote wetting to the oxide surfaces prior to brazing.

The ability of Ti alloying additions to promote wetting of ceramics by liquid braze filler metals is well documented and effective (Refs. 1-8). This approach, often referred to as active metal brazing, has the advantage of being a relatively straightforward process, but it is not widely used because of the limited commercial availability of active braze filler metals. In contrast, the use of metallic coating to promote wetting of ceramics is a widely used, well-established practice that has several variations (Ref. 9). Metal coated ceramic surfaces can be brazed with standard commercial braze filler metals so that this approach offers considerable flexibility for selecting joining materials that are compatible with processing or joint property constraints. Although it is not used often as a pretreatment for brazing, a common method of metal coating ceramic surfaces is vapor coating. The success of vapor coatings as a means of promoting the wetting of oxide surfaces by liquid metals was demonstrated some time ago (Refs. 11, 12) but was not exploited for brazing of ceramics until more recently (Refs. 10, 13-17).

This paper describes the initial results of a study of the brazing of Ti-vaporcoated partially stabilized zirconia (ZrO₂). An anticipated application of this technology was brazing of ZrO₂ insulation pieces to various metallic components, primarily cast iron, in low-heat rejection diesel engines. The particular service requirements of the ZrO₂-Fe joints defined two important boundary conditions: 1) the brazing thermal cycle should not significantly alter the me-



Fig. 1 — SEM micrographs. A — ZrO₂ surface ; B — braze filler metal surface after fracture by shear testing at 25°C.

chanical properties of the cast iron, for instance, by overaging or inducing phase transformations of the microstructure; and 2) the braze joints should have reasonably good strength at the highest expected service temperature, about 400°C (752°F). These two constraints meant that it would be necessary to restrict the brazing temperature to between about 500° and 750°C (932° and 1382°F).

It was found that coating ZrO₂ with Ti prior to brazing at 735°C (1355°F) with a Ag-30Cu-10Sn wt-% filler metal was an effective way of producing highstrength joints. Braze joints made with Ti-sputter-coated ZrO2 contained relatively high levels of porosity. The porosity was eliminated by using electron beam evaporation rather than sputtering to produce the Ti coatings, and material coated by the former technique is referred to as Ti-vapor-coated ZrO₂. Flexure strength in the range of 200 to 571 MPa (29-82.8 ksi) was obtained for specimens of ZrO2-ZrO2 and ZrO2-Fe joints at temperatures up to 400°C. Joint strength generally was dependent on the adhesion of the Ti vapor coatings to the ZrO_2 surfaces after brazing, and it was not limited by the braze filler metal strength at temperatures of 400°C and below.

Materials and Experimental Details

The materials used for this work were: Nilsen Gr. MS partially stabilized ZrO₂; ASTM A476 Gr. 8003 nodular cast Fe; and ASTM B265 Gr. 1 commercially pure Ti. The filler metal used for brazing was a 50.8-µm-thick foil of Handy & Harmon Braze 604 (AWS designation: BVAg-18). The nominal composition of the BVAg-18 filler metal is Ag-30Cu-10Sn wt-%. The ZrO₂ surfaces used for brazing were prepared by diamond grinding to a 180- to 220-grit finish, and ultrasonically cleaned with acetone followed by ethyl alcohol and then air dried before being coated with Ti.

The ZrO_2 joint surfaces were coated with a 0.6-µm-thick layer of Ti either by RFsputtering, as described elsewhere (Ref. 10) or by vacuum evaporation. For evaporation coating, a Ti vapor was produced in the vacuum chamber by melting a pure Ti source with an electron beam melting system operating at 7 kV and 100 mA. Typically, the pressure inside the chamber at the time melting of the Ti began was 400 µPa and it dropped to 50 µPa during evaporation. The ZrO₂ was shielded from the Ti vapor until the pressure inside the chamber stabilized. A standard guartz oscillation technique was used to monitor coating thickness during evaporation, and thickness was verified by reference weighing tabs. A typical evaporation time to produce a 0.6-µm-thick layer using this procedure was 20 min. The ZrO₂ specimens were not preheated prior to coating.

The nodular cast Fe was also coated prior to brazing because carbon from the graphite nodules was believed to dissolve in the braze filler metal and restrict wetting (Ref. 10). To prevent this problem, all nodular cast Fe braze joint components were cleaned in a hot bath of commercial caustic solution and elec-



Fig. 2 — Microstructure of Ti-vapor-coated ZrO_2 brazed to Cu-plated nodular cast iron.



Fig. 3 — Microstructure at Ti-vapor-coated ZrO_2 surface after brazing with a Ag-30Cu-10Sn wt-% filler metal.

troplated with a 50-µm-thick layer of pure copper prior to brazing.

All brazing was done in vacuum. Joint assemblies were placed in an alumina tube, which was subsequently sealed and evacuated to a pressure of about 130 µPa. After evacuation, the tube was inserted into an air muffle furnace preset and equilibrated at the desired brazing temperature. A thermocouple positioned near each assembly was used to continuously monitor temperature during the brazing thermal cycle. The brazing temperature used was 735°C. The holding time at the brazing temperature was 10 min, after which the alumina tube was backfilled with argon to a pressure of about 20 kPa, and the tube was withdrawn from the furnace and cooled to room temperature.

The shear strength of joints between ZrO₂ and either nodular cast Fe or Ti was measured in air at 25°C (77°F) and 400°C using a device and technique described in detail by Hammond, et al. (Ref. 14). Relative to flexure testing, shear testing has only modest requirements for specimen preparation and so is a quick and inexpensive way to monitor the effects of materials and process variables on braze joint strength. The data obtained by shear testing were reproducible, but accurately determining shear strengths was problematic. Because of the difficulties of interpreting shear strength data and of performing the shear strength tests at elevated temperature, flexure testing was used for a more detailed determination of braze joint strengths.

Joint specimens for flexure tests were made using an approach outlined by Moorehead (Ref. 7). Individual coupons with dimensions of 25 X 14 X 3 mm (1 X 0.55 X 0.12 in.) were joined along the 25 X 3-mm edge. Typically, a piece of

filler metal foil was cut to match the interfacial area of the braze joint and was preplaced in the joint before heating to the brazing temperature. The test coupon assemblies were positioned with the braze interface in the horizontal plane. No load was applied to the assemblies during brazing, and no attempt was made to control the final thicknesses of the braze layers. Afterward the brazed specimens were surface ground on both faces, polished to a 1-µm diamond finish on one face, and cut into flexure test bars with dimensions of 28 X 2.5 X 2 mm (1.1 X 0.1 X 0.08 in.) and having a brazed joint in the center of each bar. Testing was done by four point bending at a loading rate of 22.7 kg/s (50 lb/s) with the polished side of the bar being the side loaded in tension. The flexure test fixture had an outer span of 19.05 mm (0.75 in.) and an inner span of 6.35 mm (0.25 in.). Flexure testing was done in air at temperatures of 25°, 200°, 400° and 575°C. The test bars were heated to the test temperature and equilibrated for 30 min prior to loading.

The microstructures of cross-sectioned and metallographically prepared joints, as well as those of fractured jointstrength test specimens, were examined optically and with a scanning electron microscope (SEM). Standardless, semiquantitative microchemical analyses were carried out in the SEM using an energy dispersive x-ray spectrometer (EDS) system.

Results

Shear Testing of Ti-Sputtered ZrO₂ Braze Joints

Initial braze process development and joint strength evaluation were done using ZrO₂ specimens, which were sput-

Table 1— Shear Strength of Braze Joints Made with Sputter-Coated ZrO_2

Joint	Test Temperature, °C	Shear Strength, MPa	
ZrO₂-Fe	25	137 ± 8	
ZrO ₂ -Ti	25	140 ± 18	
ZrO ₂ -Ti	400	28 ± 6	

ter-coated with Ti prior to brazing. Shear test results for braze joints between Tisputter-coated ZrO2 and either nodular cast Fe or Ti are given in Table 1. Four specimens of each material combination were tested at 25°C. Both ZrO₂-Fe and ZrO2-Ti joints were evaluated because it was expected that the closer match in linear thermal expansion coefficient between ZrO_2 and Ti ($\alpha_1 ZrO_2$ = 10.2 μ m/m/°C, $\alpha_1^{Fe} = 13.1 \mu$ m/m/°C, α_1^{Ti} = 8.6 μ m/m/°C) would result in higher joint strength, although this behavior was not supported by the room-temperature shear tests. Also, three ZrO2-Ti joints were tested at 400°C, and, as Table 1 shows, their average shear strength was only about 20% of the room-temperature value.

All of the ZrO_2 -Fe and ZrO_2 -Ti joints fractured at the interface between the ZrO_2 and the braze filler metal, and these surfaces were examined in detail in an SEM. Figure 1A shows the typical appearance of a sputter-coated ZrO_2 surface after joint fracture at either test temperature. Small fragments of braze filler metal remained bonded to the ZrO_2 , but, overall, the surface appeared to be relatively undisturbed by brazing and shear testing. The appearance of the mating braze filler metal surface (Fig. 1B) showed that a considerable amount of porosity formed at the interface between



Fig. 4 — Free energy of ZrO_2 and titanium oxides (Ref. 21) and Ti-O solutions (Ref. 23).



Fig. 5 — Average strength of ZrO_2 - ZrO_2 , ZrO_2 -Fe, and ZrO_2 -Ti joint test specimens vs. test temperature.

Table 2 - Fracture Strength of Ti-Vapor-Coated ZrO2 Braze Joint Flexure Test Bars

Joint	Test Temperature, °C	Number of Test Specimens	Range of Strength, MPa	Average Strength, MPa
ZrO_2 - ZrO_2	25	14	269-571	421 ± 95
ZrO ₂ -ZrO ₂	200	7	239-459	355 ± 74
ZrO ₂ -ZrO ₂	400	12	199-370	297 ± 52
ZrO ₂ -ZrO ₂	575	9	48-149	101 ± 32
ZrO ₂ -Fe	25	31	25-399	274 ± 110
ZrO ₂ -Fe	200	4	58-363	246 ± 118
ZrO ₂ -Fe	400	22	109-364	213 ± 70
ZrO ₂ -Fe	575	7	16-101	51 ± 28

the ZrO_2 and the braze filler metal during brazing. This condition was observed over the entire area of contact for all of the braze filler metal interfaces regardless of whether the ZrO_2 was brazed to nodular cast iron or Ti. In some cases the contact area of the braze filler metal on the ZrO_2 was reduced by as much as 60%. This situation would be detrimental to joint strength and integrity at any temperature.

A considerable effort was directed toward eliminating the porosity in these joints by varying the sputter-coating conditions. These attempts were unsuccessful, and evaluation of an alternative coating process, electron beam evaporation, was undertaken. Joints made with ZrO₂ that were coated with Ti by the electron beam evaporation process rather than by sputtering were essentially porosity-free. The exact source of the porosity in the joints of sputtercoated ZrO2 was not established experimentally. However, published reports indicate that the inert gases used in the sputtering and ion etching processes can become entrapped in deposited coatings or etched surfaces (Refs. 18-20) and may be liberated by heating (Ref. 20). It was concluded that Ar evolution during brazing was the most likely source of porosity in the joints of Ti-sputter-coated ZrO₂, and all subsequent work was done

on ZrO₂ that was coated with Ti by electron beam evaporation.

Microstructure of Ti-Vapor-Coated ZrO₂ Braze Joints

A cross-sectional view of the microstructure of a ZrO2-Fe joint is shown in Fig. 2. The total thickness of the joint including the Cu coating was about 100 µm. The thickness of the Cu coating and the braze filler metal foil was the same (50 µm) before brazing, but after brazing, the thickness of the Cu coating was about 40 µm, indicating that it dissolved partially in the braze filler metal. The thicknesses of braze layers in the ZrO2-ZrO₂ joints were typically in the range of the original thickness of the filler metal foil. Both the ZrO2-Fe joints and ZrO₂- ZrO₂ joints were virtually porosity-free when examined metallographically.

At higher magnification (Fig. 3) two layers can be seen at the Ti-vapor-coated ZrO₂ surface after brazing. Microchemical analysis in the SEM indicated that the dark layer directly in contact with the ZrO₂ was the remnant of the original Ti vapor coating. The second layer, which formed between the Ti vapor coating and the braze filler metal, had an average composition of 22Ag-30Cu-25Sn-19Ti-4Zr wt-%. Figure 3 indicates



that the Ti vapor coating isolated the ZrO_2 from direct contact with the liquid filler metal, and that wetting was accompanied by reaction of the braze filler metal with the Ti coating to form a metallic or intermetallic reaction layer. The combined thickness of the two reaction layers was approximately the same as the thickness of the Ti vapor coating before brazing, nominally 0.6 µm.

The other features shown in Fig. 3 are the Ag-rich and Cu-rich braze filler metal phases, which appear as light and dark regions, respectively, and the ZrO_2 . The dark features in the ZrO_2 are actually pores, which were not eliminated during sintering of the oxide. The microstructure at the brazed ZrO_2 surface was the same for joints of ZrO_2 - ZrO_2 and ZrO_2 -Fe.

Visual examination of the braze joints showed that the ZrO_2 within about 1 mm (0.04 in.) of the brazed surfaces became black in color as described by Hammond *et al.*, (Ref. 10). This discoloration indicated that either chemical reaction or mass transport between the ZrO_2 and the Ti vapor coating occurred during brazing. The most likely chemical reactions between these materials involve the reduction of ZrO_2 by Ti to form Ti oxides. However, standard free energy data (Ref. 21) indicate that these reactions should not occur at the brazing temperature of 735°C:

 $ZrO_2(s) + Ti(s) = TiO_2(s) + Zr(s)$

 ΔG° = +37.2 kcal/mole.

 $ZrO_2(s) + 6/5 Ti(s) = 2/5 Ti_3O_5(s) + Zr(s)$ $\Delta G^\circ = +21.8 \text{ kcal/mole.}$

 $ZrO_2(s) + 4/3 Ti(s) = 2/3 T_2O_3(s) + Zr(s)$ $\Delta G^\circ = +15.7 \text{ kcal/mole.}$

 $ZrO_2(s) + 2Ti(s) = 2TiO(s) + Zr(s)$

 $\Delta G^\circ = +11.8$ kcal/mole.

On the other hand, diffusion of oxygen from the ZrO2 into the Ti was considered likely because O is relatively mobile in ZrO2, and because it is interstitially soluble in α-Ti up to 34 at.-% (Ref. 22). Insight into this possibility was gained by examining the free energies of Ti-O solutions, and comparing them to the free energy of formation of ZrO₂ at 735°C. Figure 4 plots the variation of partial molar free energy of oxygen in Ti-O interstitial solutions (Ref. 23) against O concentration, and indicates both the limit of O solubility in Ti at 735°C and the free energies of formation of stoichiometric titanium oxides (Ref. 21). The dashed horizontal line indicates the free energy of formation of ZrO₂ at the same temperature (Ref. 21) As Fig. 4 shows, Ti-O solutions are more stable with respect to ZrO₂ than are Ti oxide phases. The high thermodynamic stability of Ti-O solutions coupled with the high gradient of O concentration across the ZrO₂/Ti interface and the good mobility of O indicate that the for-

Fig. 6 — Weibull distribution plot of ZrO₂-ZrO₂ braze joint fracture strength data from tests done at room temperature and 400°C.

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Fig. 7 — Weibull distribution plot of ZrO₂-Fe braze joint fracture strength data from tests done at: A — room temperature; B — 400°C.

mation of a Ti-O solution in a ZrO_2/Ti couple would be favored at the brazing temperature.

Flexure Testing of ZrO₂ Braze Joints

Specimens from both ZrO_2 - ZrO_2 and ZrO_2 -Fe joints were used for flexure testing, and a summary of the fracture strength (σ_f) data is given in Table 2. The average joint strength is plotted against test temperature in Fig. 5, and the strength data from tests at room temperature and 400°C are plotted using the Weibull distribution function in Fig. 6 for the ZrO_2 - ZrO_2 joint specimens, and in Fig. 7 for the ZrO_2 -Fe joint specimens. Linear regression analysis was used to determine the Weibull modulus numbers, m, and to fit straight lines through the data.

Table 2 shows that there was considerable scatter in the strength data for both types of joints, with the larger variations observed for the ZrO₂-Fe joints.

In both cases there was a tendency for scatter in the strength data to decrease with increasing temperature. The test temperatures of 200°, 400° and 575°C represent, respectively, 0.5, 0.75 and 0.95 of the solidus temperature (620°C; 1148°F) of the Ag-30Cu-10Sn wt-% braze filler metal. The highest strengths were obtained for the ZrO_2 - ZrO_2 joints. At room temperature, the strength of some ZrO_2 - ZrO_2 specimens approached that of the monolithic MS- ZrO_2 (\approx 600MPa; 87 ksi), but joint strengths were usually much lower, and decreased even further with increasing test temperature.

Figure 5 shows that the average strength of the ZrO_2 - ZrO_2 and ZrO_2 -Fe joints decreased moderately with increasing temperature up to 400°C, and then showed a more marked decrease at 575°C. Also, the strength of the two types of joints converged somewhat as the test temperature was increased.

The Weibull plots show graphically the distribution of joint strengths at room

temperature and 400°C. Not only did the joint specimens fracture at stress levels below the average fracture strength of monolithic ZrO_2 , but the scatter in the joint strength data was also much greater. Typical Weibull modulus values for this ZrO_2 are in the range of m = 20, which corresponds to a standard deviation in strength near 30 MPa (4.35 ksi).

For the ZrO_2 -Fe joints tested at room temperature, some of the specimens had joint surfaces that were left in the asground condition, while others had joint surfaces that were lapped to a 1-µm-diamond finish before vapor coating with Ti. The Weibull plot of these data, shown in Fig. 7A, indicates that lapping of the joint surfaces did not improve joint strength. Another interesting feature of this data set was that the best linear regression fit was obtained with two lines rather than one. This implies there were two flaw populations responsible for the strength behavior of these joints.



Fig. 8 — SEM micrographs of ZrO_2 - ZrO_2 joint specimens tested at 25°C: A σ_f = 571 MPa; B — σ_f = 269 MPa.



Fractography of Braze Joint Flexure Test Bars

Optical examination of the broken test bars indicated that most of them fractured near one of the brazed surfaces regardless of materials and testing temperature. Subsequently, selected test bars were examined by SEM.

ZrO₂-ZrO₂ Joints

The fracture surface of one half of a high-strength ($\sigma_f = 571$ MPa; 82.8 ksi) ZrO₂-ZrO₂ joint tested at room temperature is shown in Fig. 8A. The fracture surface was relatively planar. However, closer examination showed that the fracture appearance of most of the surface was similar to that of monolithic ZrO₂. Further examination and microchemical analysis confirmed that failure in this specimen occurred in the ZrO₂ just below the ZrO₂/Ti vapor coating interface. The fracture appearance of a lower strength ($\sigma_f = 269 \text{ MPa}$; 39 ksi) specimen tested at room temperature is shown in Fig. 8B. In this case, some fracturing occurred in the ZrO2, but the relatively large smooth areas shown in Fig. 8B indicate that failure also was accompanied by a large amount of debonding between the ZrO₂ and the Ti vapor coating. No quantitative metallography was done on the fracture surfaces, but examination of several specimens suggested that fracture strength varied inversely with the amount of debonding at the ZrO₂/Ti interface.

The general fracture pattern of the ZrO₂-ZrO₂ joints tested at 200°C (392°F) was similar to that of joints tested at 25°C. For testing done at 400°C, fracture surfaces were typically smooth and contained only isolated fragments of metallic phases. Essentially no fracturing of ZrO2 was found for the 400°C tests, but failures were mainly associated with debonding at ZrO₂/Ti vapor coating interfaces. For the tests done at

575°C fracture occurred exclusively through the metallic braze filler metal phases.

ZrO₂-Fe Joints

The ZrO₂ half of a ZrO₂-Fe joint specimen tested at room temperature is shown in Fig. 9, and the appearance of this fracture surface is representative of specimens from the high range of joint strength referring to Fig. 7A. These specimens were characterized by relatively flat regions near the tensile faces of the flexure bars, and other areas where large fragments of ZrO2 were pulled out of the base metal. Detailed examination indicated that the fracture path in the flatter areas was through either the ZrO₂ or the intermetallic layer near the ZrO2/Ti interface. The fracture surfaces of ZrO2-Fe specimens with polished joint surfaces did not exhibit the large pulledout ZrO2 areas. Nevertheless, failure in these specimens was primarily through the ZrO₂ near ZrO₂/Ti interfaces. Failures of ZrO₂-Fe specimens in the low range of joint strength were the result of debonding at either the ZrO₂/Ti interfaces or the cast Fe/Cu interfaces, or of incomplete bonding during brazing.

The ZrO₂-Fe specimens tested at 200°C failed in much the same manner as those tested at room temperature. At 400°C, however, ductile failure through the Cu plating on the cast Fe was prevalent, and, at 575°C, ZrO2-Fe joint strength was limited by the strength of metallic phases in the braze layer.

Discussion

The flexure test results confirm that the use of a Ti vapor coating to enhance wetting can produce high-strength ZrO_2 - ZrO_2 and ZrO_2 -Fe braze joints. Because failure of the test bars generally was associated with debonding or fracture of the ZrO₂ near the joint surfaces,

it can be concluded that the strength of these joints was not limited by the strength of the 60Ag-30Cu-10Sn wt-% filler metal at temperatures below 400°C. The Vickers hardness of the filler metal after brazing was in the range of 900 MPa, which corresponds to a tensile strength near 300 MPa. (43.5 ksi). Many of the ZrO2-ZrO2 and ZrO2-Fe joint test specimens exceeded this strength level at room temperature and 200°C, as did a number of ZrO₂-ZrO₂ specimens at 400°C. Braze joint strength in excess of filler metal strength results from the development of a hydrostatic stress state in the relatively thin, ductile braze layers (Ref. 25).

Debonding, or loss of adhesion, at ZrO₂/Ti-vapor coating interfaces was clearly an important factor in determining ZrO2-ZrO2 joint strength. The SEM observations from ZrO2-ZrO2 joint specimens tested at 25°C indicated that the highest strengths were associated with partial or complete fracturing of the ZrO2 beneath the Ti-vapor-coated surfaces. The high-strength ZrO2-ZrO2 joint specimens failed almost entirely through the ZrO₂. In contrast, the trend for lower strength specimens was for failure to occur by debonding at the ZrO₂/Tivapor coating interfaces. The frequency of debonding at ZrO2 interfaces as a failure mode increased at 200°C, and debonding was the predominate failure mode at 400°C. Joint strength decreased progressively with temperature, and as was observed for room temperature testing, joint strength at a particular elevated temperature was roughly an inverse function of the debonded area on the ZrO₂ surfaces. Taken all together, these observations show that the ZrO₂-ZrO₂ joint strength had a strong dependence on the adhesion of the Ti vapor coating to the ZrO₂ surfaces.

Coating adhesion results from the atomic bonding forces between the substrate and deposited materials, and it can be strongly influenced by a variety of materials- and process-related factors (Refs. 24, 26, 27) For instance, chemical reactions and interdiffusion at the interface determine the local stress state and the modes of fracture nucleation and propagation. Important process considerations include substrate and deposition system cleanliness, method of substrate cleaning, deposition method and parameters, and substrate surface roughness.

Accounting for all of the factors that influence adhesion properties can be difficult, even in simple systems. Drawing firm conclusions about adhesion at the ZrO₂/Ti-vapor coating interfaces is beyond the scope of the present work because of complications such as chemical reaction between the Ti and the

braze filler metal, interdiffusion between the ZrO2 and the Ti, and the residual stresses superimposed on the ZrO₂/Ti interface by the braze filler metal. However, the frequent observation of debonding at ZrO₂/Ti-vapor-coating interfaces suggests that no strong chemical bonding between the ZrO₂ and the Ti was achieved. This view is consistent with the thermodynamic analysis presented earlier, which showed that chemical reaction between ZrO2 and Ti was unlikely to occur at the brazing temperature. Consequently, adhesion of the Ti vapor coating to the ZrO2 surfaces was likely due to weak chemical bonding (Refs. 24, 26). At a particular test temperature, joint strength and amount of debonding would be strongly influenced by localized variations in both ZrO₂ surface contamination and interdiffusion between the ZrO₂ and Ti.

The increase in extent of debonding with test temperature could be an indication that the interfacial energy between the ZrO₂ and the oxidized Ti coating was high. For instance, in material systems with high interfacial energies, annealing can activate diffusion processes, which work to minimize interfacial contact, and degrade adhesion (Ref. 26). Residual stresses due to thermal expansion mismatch strains are an important added complication in the fracture behavior of the joints. This effect also would have a temperature dependence because increasing the test temperature decreases the magnitude of thermal expansion coefficient mismatch.

The strengths of the ZrO₂-ZrO₂ joint specimens that fractured entirely through the ZrO2 were still lower than the average strength of monolithic ZrO₂. This fact along with the observation that failures in the ZrO2 always occurred near the brazed surfaces indicates that the cause of the reduced strength was associated directly with the brazed ZrO2 surfaces in cases where adhesion of the Ti vapor coating was not a limiting factor. Joint strength could have been limited by at least three other factors: surface damage due to machining, reaction between the ZrO₂ and the Ti, and residual stresses. Mizuhara and Malls (Ref. 29) have shown that preexisting surface damage can reduce joint strength, but no clear evidence of microcracking could be detected on the ground ZrO₂ surfaces used in the present work. The discoloration of the ZrO2 adjacent to the Ti vapor coating indicated that some compositional change occurred in these regions. However, in a separate set of experiments, it could not be established that the discoloration caused either a destabilization of the ZrO₂ microstructure or a deterioration of its mechanical properties. The presence of residual

stresses near the brazed ZrO_2 surfaces seems to be the most likely explanation for the lower strength of ZrO_2 - ZrO_2 joints compared to monolithic ZrO_2 . The difference in thermal expansion coefficients between the ZrO_2 and the braze filler metal ($\Delta \alpha_1 \approx 6-8 \ \mu m/m^{\circ}C$) will produce highly-localized tensile residual stresses in the ZrO_2 near brazed surfaces (Ref. 16) and could increase the probability of failure in these regions at stress levels below the fracture strength of monolithic ZrO_2 .

The overall strength and fracture characteristics of the ZrO2-Fe joint specimens were similar to those of the ZrO2-ZrO₂ joints at room temperature and 200°C. Important differences between the ZrO₂-Fe and ZrO₂-ZrO₂ joints were observed, however, as Fig. 7 shows, a bimodal distribution of ZrO₂-Fe joint strength was observed at room temperature. Failure in the lower strength range occurred primarily by metallic debonding, and may have been caused by improper materials handling or nonuniform heating. It is possible that similar processing-related flaws existed in both types of joints, but that their effect was accentuated by residual stresses in some of the ZrO₂-Fe joints to the point where they became dominant as failure initiation sites.

Failures of the high-strength ZrO₂-Fe joint specimens at room temperature and 200°C were associated with fracture of the ZrO₂ near the brazed surfaces and some debonding at the ZrO₂ interfaces at lower strengths. The difference in thermal expansion coefficients between the ZrO_2 and the cast iron ($\Delta \alpha_1$ ≈3 µm/m/°C) undoubtedly was responsible for the lower average room-temperature strength of the ZrO₂-Fe joints compared to the ZrO₂-ZrO₂ joints. The residual stresses produced in the ceramic-metal joints would be much larger than those produced by the braze filler metal layer of a ceramic-ceramic joint (Ref. 16). Furthermore, a tensile component of residual stress would exist normal to the brazed ZrO2 surface and it would reduce the level of applied stress necessary to cause failure (Ref. 16).

The data in Fig. 7A also clearly show that there is no advantage to lapping the joint surfaces compared to using them in an as-ground condition. No surface microcracking was observed on metallographically prepared specimens of ZrO₂ or by dye penetrant examination. Nevertheless, some concern remained about the possible effects of surface damage owing to the findings of Mizuhara and Malley (Ref. 29) and some of the ZrO₂-Fe tests coupons were made with lapped ZrO₂ joint surfaces. Lapping removed 50 to 100 µm of material from the ZrO₂ surfaces and should have removed any machining damage that may have been present (Ref. 30). The only explanation that can be offered for this behavior is that the superior toughness of the MS-ZrO₂ compared to other ceramics (*e.g.*, Al_2O_3 or Si₃N₄) was responsible for its relative insensitivity to surface damage induced by grinding.

The strengths of both the ZrO₂-ZrO₂ and the ZrO₂-Fe joints converge to relatively low values for testing at 575°C, and in all cases, failures were associated with fracture through the metallic phases. This is not surprising as the solidus temperature of the braze filler metal is near 620°C. The test data presented indicate that the practical limit for obtaining reasonably strong joints with Ag-30Cu-10Sn wt-% filler metal is in the area of 400°C.

Summary and Conclusions

Zirconia surfaces were coated with Ti by RF sputtering and electron beam evaporation. The Ti-coated ZrO_2 was easily vacuum brazed to itself and to Cuplated nodular cast Fe with a Ag-30Cu-10Sn wt-% filler metal. Braze joints made with Ti-sputter-coated ZrO_2 contained high levels of porosity. In contrast, joints made with ZrO_2 which was Ti coated with the electron beam evaporation process were free of porosity.

The Ti coatings reacted with the ZrO_2 during the brazing operation as evidenced by a darkening of the ceramic beneath the coated surfaces. Thermodynamic analysis predicted that the most likely reaction between the ZrO_2 and Ti was oxygen diffusion from the ZrO_2 into the Ti coating.

Flexure bars for four-point bend testing were made from both ZrO₂-ZrO₂ and ZrO₂-Fe joints and tested at 25°, 200°, 400° and 575°C. The highest strengths were recorded for room-temperature tests: 571 MPa for ZrO₂-ZrO₂, and 399 MPa for ZrO₂-Fe. In both cases, failures in the high-strength joint specimens were associated with fracture of the ZrO₂ beneath the Ti-vapor-coated surfaces. At 25°C, lower joint strength correlated with increased metallic debonding at ZrO2 vapor coating interfaces. Residual stresses due differential thermal expansion undoubtedly contributed to the lower strength of the ZrO₂-Fe joints compared to the ZrO₂-ZrO₂ joints. Lapping the joints surfaces did not improve the strength characteristics of the ZrO2-Fe joints. The distribution of ZrO₂-Fe joint strength at room temperature was bimodal. Debonding and incomplete fusion defects were the causes of failure in the lower strength distribution, and they were likely the result of process-related problems.

The strength of the joints decreased

at elevated temperatures. For the ZrO₂-ZrO₂ joints the decrease in strength was accompanied by an increase in the amount of metallic debonding at the ZrO₂ vapor coating interfaces. At 400°C, no fracture of the ZrO2 was observed, and failure occurred predominantly by debonding. Failure in the ZrO₂-Fe joints was accompanied by an increase of ZrO₂/Ti interface debonding at 200°C, and was dominated by ductile failure in the Cu plating at 400°C. For temperatures of 400°C and below, joint strength was not limited by the strength of the Ag-30Cu-10Sn wt-% braze filler metal. At 575°C, joint failure in both types of joints occurred through the braze filler metal layer.

This study confirmed that vapor coating with Ti is an effective way of promoting the brazing of ZrO_2 . Analysis of braze joint test specimens indicated that adhesion of the Ti vapor coating to the brazed ZrO_2 surfaces was generally very good. The data further suggested that obtaining good coating adherence is a prerequisite to obtaining high-strength braze joints, and that improvements in adhesion would improve joint strength at all test temperatures.

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References

1. Allen, B. C., and Kingery, W. D. 1959. Surface tension and contact angles in some liquid metal-solid ceramic systems at elevated temperatures. *Trans. AIME* 215, pp. 30–36.

2. Armstrong, W. M., Chaklader, A. C. D., and Clarke, J. F. 1962. Interface reactions between metals and ceramics: I, sapphire-nickel alloys. *J. Am. Ceram. Soc.* 45, pp. 115–118.

3. Ritter, J. E., Jr., and Burton, M. S. 1967. Adherence and wettability of nickel, nickeltitanium alloys, and nickel-chromium alloys to sapphire, *Trans. AlME* 239, pp. 21–26. 4. Naidich, Y. V., Zhuravlev, V. S., Chup-

4. Naidich, Y. V., Zhuravlev, V. S., Chuprina, V. G., and Strashinskaya, L. V. 1973. Adhesion, wetting, and formation of intermediate phases in systems composed of a titanium containing melt and an oxide. *Sov. Powder Metall. Metal Ceram.* 12, pp. 895–899.

5. Standing, R., and Nicholas, M. 1978. The wetting of alumina and vitreous carbon by copper-tin titanium alloys. *J. Mater. Sci.* 13, pp. 1509–1514.

6. Nicholas, M. G., Valentine, T. M., and Waite, M. J. 1980. The wetting of alumina by copper alloyed with titanium and other elements. *J. Mater. Sci.* 15, pp. 2197–2206.

7. Moorhead, A. J. 1987. Direct brazing of alumina ceramics. Adv. Ceram. Mater. 2, pp. 159–166.

8. Nicholas, M. G. 1986. Active metal brazing. Br. Ceram. Trans. J. 85, pp. 144–146.

9. Pattee, H. E. 1972. Joining ceramics to metals and other materials. *Welding Research Council Bulletin 178*, WRC, New York, N.Y.

10. Hammond, J. P., David, S. A., and Santella, M. L. 1988. Brazing ceramic oxides to metals at low temperatures. *Welding Journal* 67(3): 227-s to 232-s.

11. Weiss, S., and Adams, C. M., Jr. 1967. The promotion of wetting and brazing. *Welding Journal* 46(2): 49-s to 57-s.

12. Brush, E. F., Jr, and Adams, C. M., Jr. 1968. Vapor-coated surfaces for brazing ceramics. *Welding Journal* 47(3): 106-s to 114s.

13. Hammond, J. P., David, S. A., and Woodhouse, J. J. 1986. U.S. Patent 4,621,761.

14. Hammond, J. P., David, S. A., and Woodhouse, J. J. 1985. Indirect brazing of structural ceramics for uncooled diesels. pp. 523–529, Proceedings of the 22nd Automotive Technology Contractors' Coordination Meeting, Society of Automotive Engineers, Warrendale, Pa.

15. Santella, M. L., Hammond, J. P., David, S. A., and Simpson, W. A. 1986. Zirconia to cast iron brazing for uncooled diesel engines. pp. 235–241. Proceedings of the 23rd Automotive Technology Contractors' Coordination Meeting, Society of Automotive Engineers, Warrendale, Pa.

16. Santella, M. L. 1988. Brazing of titanium-vapor-coated silicon nitride, *Adv. Ceram. Mater.* 3, pp. 457–462. 17. Santella, M. L., and Manley, L. C. 1989. Strength and microstructure of titanium-vapor-coated silicon nitride braze joints. Accepted for publication in Proceedings of the 3rd International Symposium, Ceramic Materials and Components for Engines, American Ceramic Society, 1989.

18. Winters, H. F., and Kay, E. 1967. Gas incorporation into sputtered films. *J. Appl. Phys.* 38, 3928–3934.

19. Markworth, A. J. 1972. J. Appl. Phys. 43, pp. 2047.

20. Lee, W. W. Y., and Oblas, D. 1975. Argon entrapment in metal films by dc triode sputtering. J. Appl. Phys. 46, pp. 1728–1732.

21. Chase, M. W., Curnutt, J. L., Prophet, H., and McDonald, R. A. JANAF thermochemical tables supplement. *J. Phys. Chem.* Ref. Data 4, pp. 137–147.

22. Massalski, T. B. 1986. *Binary Alloy Phase Diagrams*. Vol. 2, ASM International, Materials Park, Ohio.

23. Mah, A. D., Kelley, K. K., Gellert, N. L., King, E. G., and O'Brien, C. J. 1957. Thermodynamic properties of titanium-oxygen solutions and compounds. *Bur. Mines Rep. Invest. 5316*.

24. Mattox, D. M. 1973. Thin film metallization of oxides in microelectronics. *Thin Solid Films* 18, pp. 173–186.

25. Dalgleish, B. J., Lu, M. C., and Evans, A. G. 1988. The strength of ceramics bonded with metals. 1988. Acta Metallurgica 36(8):2029–2035.

26. Mattox, D. M. 1982. Adhesion and surface preparation. pp. 63–82. *Deposition Technologies for Films and Coatings*, R. F. Bunshah, ed., Noyes Publications, Park Ridge, N.J.

27. Hondros, E. D. 1986. Bonding of metal/ceramic interfaces. pp. 121–136, *Science of Hard Materials*, E. A. Almond, C. A. Brookes, and R. Warren, eds., Adam Hilger Ltd., Bristol.

28. Baglin, J. E. E., and Clark, G. J. 1985. Ion beam bonding of thin films. Nuclear Instruments and Methods in Physics Research B7/8, pp. 881–885.

29. Mizuhara, H., and Mally, K. 1985. Ceramic-to-metal joining with active brazing filler metal. *Welding Journal* 64(10):27–32.

30. Rice, R. W., and Mecholsky, J. J. 1979. The nature of strength controlling machining flaws in ceramics. pp. 351–377, *The Science* of *Ceramic Machining and Surface Finishing* II, B. J. Hockey and R. W. Rice, eds., National Bureau of Standards Special Publication 562, U.S. Government Printing Office, Washington, D.C.