

Brazing of Zirconia with AgCuTi and SnAgTi Active Filler Metals

T.H. CHUANG, M.S. YEH, and Y.H. CHAI

The self-brazing of partially stabilized zirconia using Ag₂₇Cu₃Ti and Sn₁₀Ag₄Ti active filler metals is investigated. It was shown that the contact angles of Ag₂₇Cu₃Ti and Sn₁₀Ag₄Ti on zirconia decreased with the increase of brazing temperature and remained constant at about 34 deg and 44 deg above 900 °C, respectively. The flexural strengths were 227 and 137 MPa for ZrO₂/Ag₂₇Cu₃Ti/ZrO₂ and ZrO₂/Sn₁₀Ag₄Ti/ZrO₂, respectively, after brazing at 900 °C for 10 minutes.

In these brazing systems, the titanium in the filler metals segregated at the interface and formed a TiO reaction layer responsible for the wetting and bonding when a ZrO₂ ceramic is brazed with Ag₂₇Cu₃Ti and Sn₁₀Ag₄Ti filler metals. Interfacial analyses by electron probe microanalysis (EPMA) showed that such TiO reaction layers of ZrO₂/Ag₂₇Cu₃Ti and ZrO₂/Sn₁₀Ag₄Ti possessed similar thicknesses at the same brazing condition, implying that the TiO interfacial reaction layers of both brazing systems were of the same nature and formation kinetics.

I. INTRODUCTION

BECAUSE of their special properties such as the ability to bear high temperatures, wear, and corrosion, fine ceramics have a significant potential for many structural and electrical applications. However, in many cases, the different ceramic parts must be connected by ceramic/ceramic joining technologies in order to fabricate complicated shapes or larger sizes. Additionally, other properties of ceramics (such as conductivity and toughness) are not comparable to those of metals. In such cases, ceramics may be joined to metals to obtain useful and stable components. As a result, the ceramic/ceramic and ceramic/metal joining technologies will be critical for the structural application of fine ceramics in the future. In general, ceramic/ceramic and ceramic/metal joining have, so far, been accomplished by using a metal inter-layer either by brazing or diffusion bonding.

Brazing is a convenient way to get a good joint. However, in either ceramic/ceramic or ceramic/metal joining, the poor wettability of conventional filler metals on ceramics is the critical problem in using the brazing method.^[1,2] To improve wettability, active elements such as titanium, zirconium, or hafnium are added to conventional filler metals, due to the chemical affinity of the active elements with the oxygen in oxide ceramics^[3] or the carbon and nitrogen in carbide^[4,5] and nitride ceramics,^[6,7] respectively.

In general, the active fillers can be divided into three groups, according to their melting points.

- (1) Low-melting-point active fillers:^[8] those with a melting point below 400 °C, a typical example being the addition of titanium to lead- or tin-based solders.
- (2) Medium-melting-point active fillers:^[3] those with a melting point between 700 °C and 1000 °C, a typical

example being the addition of titanium to silver- or silver-copper-based fillers.

- (3) High-melting-point active fillers:^[9,10] those with a melting point above 1000 °C, a typical example being the addition of titanium to platinum-, palladium-, or gold-based noble-metal fillers.

Among them, the most common active filler is the eutectic 72Ag-28Cu with an addition of about 3 wt pct titanium. It has been shown that good joints can be obtained with many oxide and nonoxide ceramics by using these kinds of active fillers.^[3-6] However, the interfacial thermal stress generated due to the difference in thermal-expansion coefficients of the ceramic and metal during the cooling process after brazing might deteriorate the joints. To solve this problem, low-melting-point active fillers have been developed. Although the brazing was also conducted at higher temperatures, the active fillers solidified at lower temperatures, which effectively alleviated the thermal stress between ceramic and metal.

Okamoto indicated in a review article that interfacial reactions are unavoidable in most metal-ceramic joining.^[11] The formation of interfacial phases affects the wetting process and the joining strength of the brazed ceramic components. However, Chung and Iseki demonstrated that the joining of ceramics could be accomplished by adsorption of the Ti element on the interface, regardless of whether an interfacial reaction layer was formed.^[12] For the brazing of Al₂O₃, SiC, and Si₃N₄ with AgCuTi active fillers, many research efforts have shown that the Ti in active fillers can react with Al₂O₃, SiC, and Si₃N₄ to form titanium oxides,^[13,14,15] titanium silicides,^[5] titanium carbides,^[5,16] and titanium nitrides,^[6] respectively. However, the brazing mechanism and the possibly related interfacial reactions between ZrO₂ and active fillers have been less often reported.

In our study, in addition to the popular eutectic Ag₂₇Cu₃Ti active filler used to braze the zirconia/zirconia joint, the newly developed low-melting-point active filler Sn₁₀Ag₄Ti was also used to compare the results. Additionally, the interfacial reaction temperature (when a phase transformation takes place within the mix) of the active fillers with

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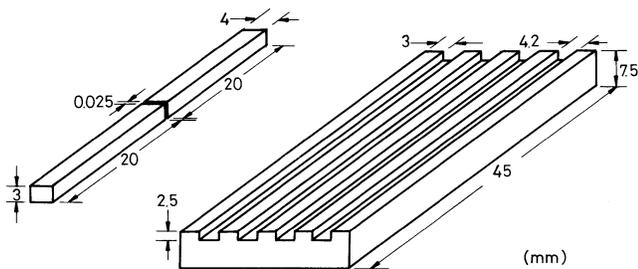


Fig. 1—Ceramic/filler metal/ceramic specimens and assembly brazing holder.

Table I. The Chemical Compositions, Liquidus and Solidus Temperatures, and Strength of the Active Filler Metals

Filler Metals	Compositions (Wt Pct)	Liquidus Temperature (°C)	Solidus Temperature (°C)	Strength (MPa)
Ag27Cu3Ti	70.5Ag-26.5Cu-3Ti	780	805	68
Sn10Ag4Ti	10Ag-86Sn-4Ti	221	300	57

zirconia ceramic was evaluated by differential thermal analysis (DTA), revealing comparable data to that of the critical wetting temperature measured by the contact-angle experiments. Furthermore, the interfacial bonding strengths of the zirconia/AgCuTi/zirconia and the zirconia/SnAgTi/zirconia joints were measured by a four-point bending test, and the brazing mechanism and the related possible interfacial reactions were discussed.

II. EXPERIMENTAL PROCEDURE

The interfacial reaction temperatures of active fillers and ceramics were evaluated by DTA. A DUPONT* 2000 ana-

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lyzer was used. In the DTA curve, the upward peak indicates an exothermic reaction and the downward peak indicates an endothermic reaction. To obtain a much-more-obvious peak, 25 mg ceramic powder was mixed with the active fillers to increase the reaction surface areas. The heating rate was 10 °C/min from room temperature to 1000 °C, in an argon atmosphere.

The zirconia ceramic Y-PSZ contains 5.02 wt pct Y_2O_3 and has a mean particle size of 0.026 μm (supplied by TOSOH Co. (US Div., N.J., USA), Japan). The powder was initially dry pressed at 10 kg/cm² to a green compact of 5 × 5.7 × 50 mm and then sintered at 1500 °C for 1.5 hours. The test bars for bonding were cut from the bulk plate to dimensions of 3 × 4 × 20 mm, and the bonding surfaces were ground and polished through diamond paste to an arithmetical average roughness (Ra) of 0.3 μm . The test bars were then placed into a fixture, as shown in Figure 1, and the active filler was inserted in between. Both filler metals of Ag27Cu3Ti and Sn10Ag4Ti were in the form of a foil with a 0.025-mm thickness (supplied by the Degussa Co., Hanau, Germany). The chemical compositions and melting ranges (liquidus and solidus) of both active fillers are also provided by the Degussa Co. (Table I). The brazing

Table II. Bonding Strengths of the Specimens Brazed with the Active Filler Metals in this Study

Group	Filler Metals	Brazing Condition	Bonding Strength (MPa)
A	Ag27Cu3Ti	900 °C, 10 min	227
B	Sn10Ag4Ti	900 °C, 10 min	137

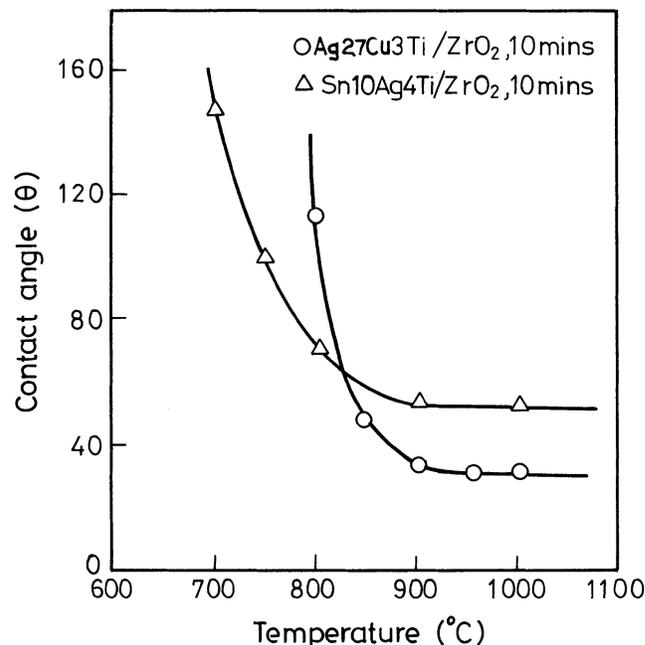


Fig. 2—The contact angle of Ag27Cu3Ti and Sn10Ag4Ti filler metals on ZrO₂ substrate as a function of temperature.

was conducted in a resistance furnace with a vacuum of approximately 10⁻⁴ torr, where the brazing temperature was 900 °C and the duration was 10 minutes. After brazing, the bonding strength of the joint was measured by the four-point bending test. The upper span is 30 mm, the lower span is 10 mm, and the crosshead speed is 0.1 mm/min. Five specimens were used for each brazing condition, and the average bonding strength is reported (Table II). In order to examine the bonding mechanism and the related interfacial reactions, polished cross sections of ceramic/filler/ceramic joints were examined using electron probe microanalysis (EPMA). The distributions of elements across the ceramic/filler metal interfaces were also analyzed by EPMA elemental mapping, particularly the distribution of active-element titanium. In addition, the wettability between the active fillers and the zirconia ceramics was evaluated by contact-angle (θ) measurements, using the sessile drop test at various temperatures for 10 minutes, which corresponded to the brazing duration in this study.

III. RESULTS AND DISCUSSION

The wetting behavior of Ag27Cu3Ti and Sn10Ag4Ti filler metals on zirconia substrates is shown in Figure 2. For both filler metals, the contact angles decreased with increasing temperature. The Ag27Cu3Ti filler metal could not wet the

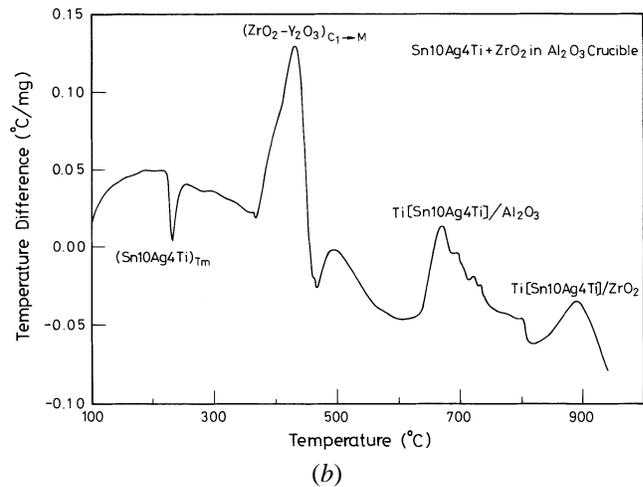
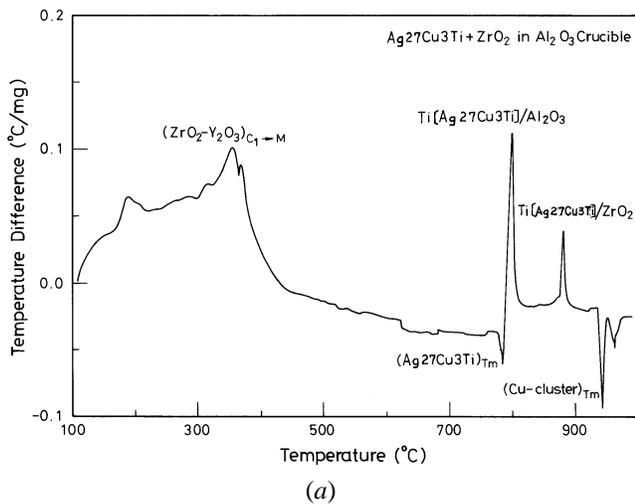


Fig. 3—DTA analyses for (a) Ag₂₇Cu₃Ti/ZrO₂ and (b) Sn₁₀Ag₄Ti/ZrO₂ systems.

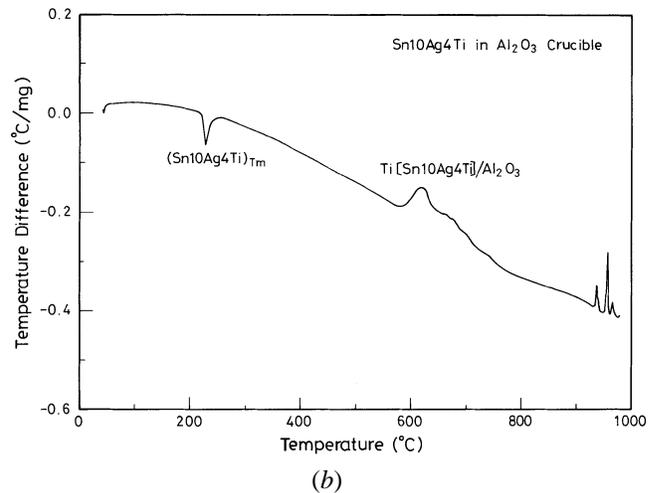
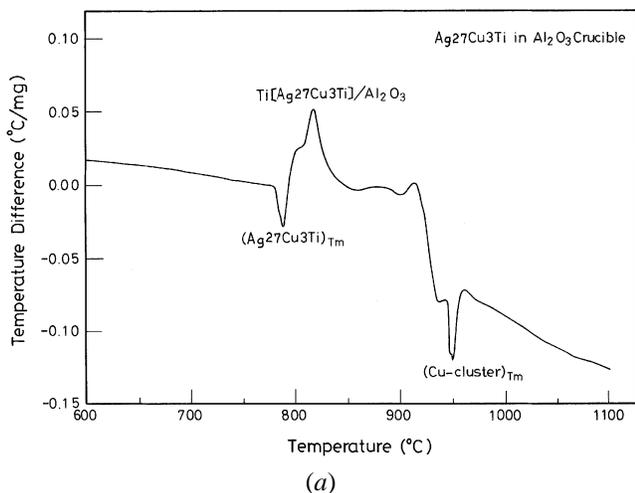


Fig. 4—DTA analyses for (a) Ag₂₇Cu₃Ti and (b) Sn₁₀Ag₄Ti with Al₂O₃ crucible.

zirconia substrate until the temperature reached approximately 800 °C. However, the contact angle of the Ag₂₇Cu₃Ti/ZrO₂ system decreased drastically to about 34 deg after 10 minutes at 900 °C and remained constant at higher temperatures. In the other case, the Sn₁₀Ag₄Ti filler metal began to wet the zirconia substrate after 10 minutes at approximately 770 °C. The contact angle remained constant at about 44 deg for temperatures higher than 800 °C. This result shows that, although the melting range of the Sn₁₀Ag₄Ti filler metal was between 221 °C and 300 °C, much-higher temperatures are required to wet the zirconia substrate. This result is consistent with the report of Lugscheider and Tillmann that brazing with low-melting filler metals is always conducted at elevated temperatures, owing to a decent thermodynamic activation.^[17]

The DTAs used to interpret the interfacial reactions of Ag₂₇Cu₃Ti/ZrO₂ and Sn₁₀Ag₄Ti/ZrO₂ are shown in Figures 3(a) and (b), respectively. Since the crucibles used for DTA were made of Al₂O₃, the interfacial reactions of both filler metals with the Al₂O₃ crucible should also be considered. For this purpose, Ag₂₇Cu₃Ti and Sn₁₀Ag₄Ti were directly placed into the Al₂O₃ crucibles and the DTAs conducted,

which are shown in Figures 4(a) and (b), respectively. An endothermic peak appeared between 780 °C and 805 °C (Figure 4(a)), corresponding to the melting range of the Ag₂₇Cu₃Ti filler metal. Since many Cu-rich clusters were included in the eutectic Ag₂₇Cu₃Ti filler metal, another endothermic peak at 940 °C to 960 °C should represent the complete dissolution of these Cu-rich clusters. The exothermic peak at about 800 °C in Figure 4(a) could, thus, be attributed to the interfacial reaction between Ti(Ag₂₇Cu₃Ti) and the Al₂O₃ crucible. Similarly, for the case of Sn₁₀Ag₄Ti in Figure 4(b), the endothermic peak at 220 °C to 250 °C and the exothermic peak at about 578 °C to 658 °C corresponded to the melting range (221 °C to 300 °C) and interfacial reaction temperature of the Ti(Sn₁₀Ag₄Ti)/Al₂O₃ crucible, respectively. In order to clarify the DTA results for such interfacial reactions of titanium in Ag₂₇Cu₃Ti and Sn₁₀Ag₄Ti active filler metals with an Al₂O₃ crucible, the titanium powder contained in the Al₂O₃ crucible was analyzed. Figure 5(a) shows that an exothermic peak from 613 °C to 800 °C existed, which is characterized by the interfacial reaction between pure titanium and the Al₂O₃ crucible. Further DTA in Figure 5(b), for the mixture of titanium powder

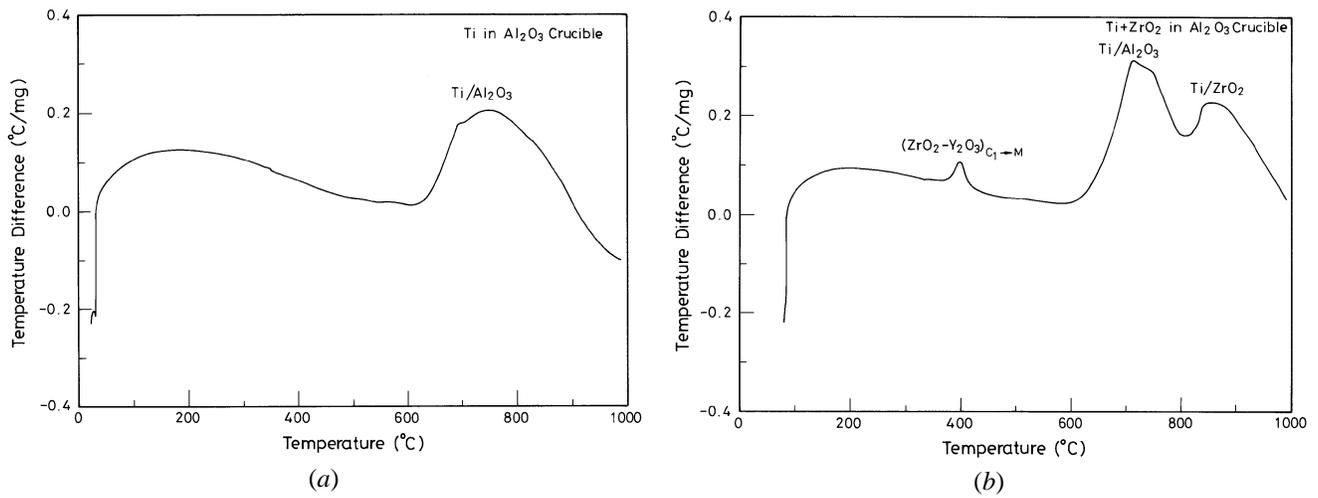


Fig. 5—DTA analyses for (a) Ti powder and (b) Ti + ZrO₂ powder with Al₂O₃ crucible.

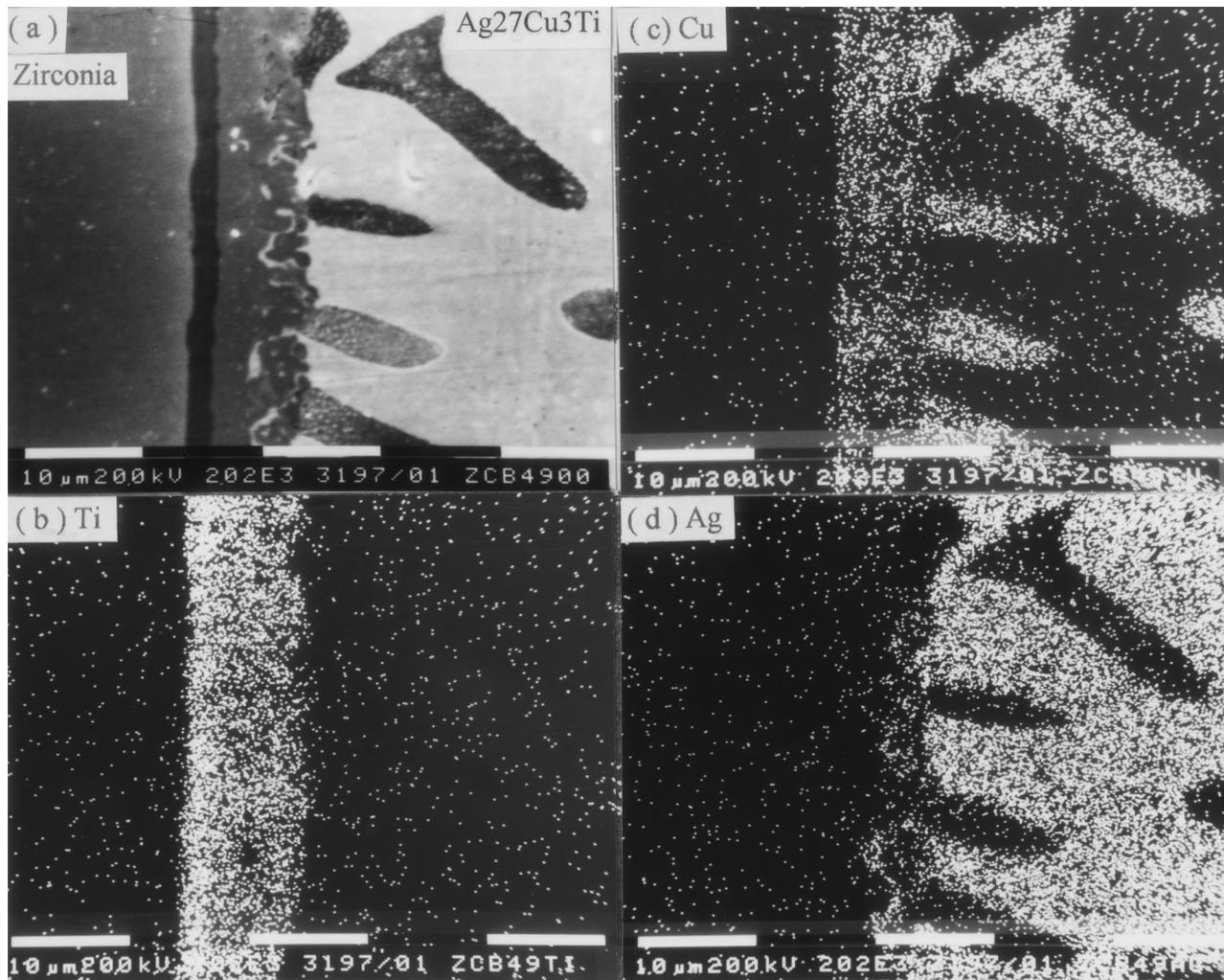


Fig. 6—Micrograph and EPMA analyses for ZrO₂/Ag₂₇Cu₃Ti/ZrO₂ system brazed at 900 °C for 10 min: (a) interfacial microstructure, (b) titanium mapping, (c) copper mapping, and (d) silver mapping.

and ZrO₂ powder contained in the Al₂O₃ crucible, showed an exothermic peak from 608 °C to 804 °C, which represented the interfacial reaction between pure titanium and the

Al₂O₃ crucible, as found in Figure 5(a). Since the ZrO₂ powder used in the present study was partially stabilized with 5.02 wt pct Y₂O₃, it possessed a polymorphic phase

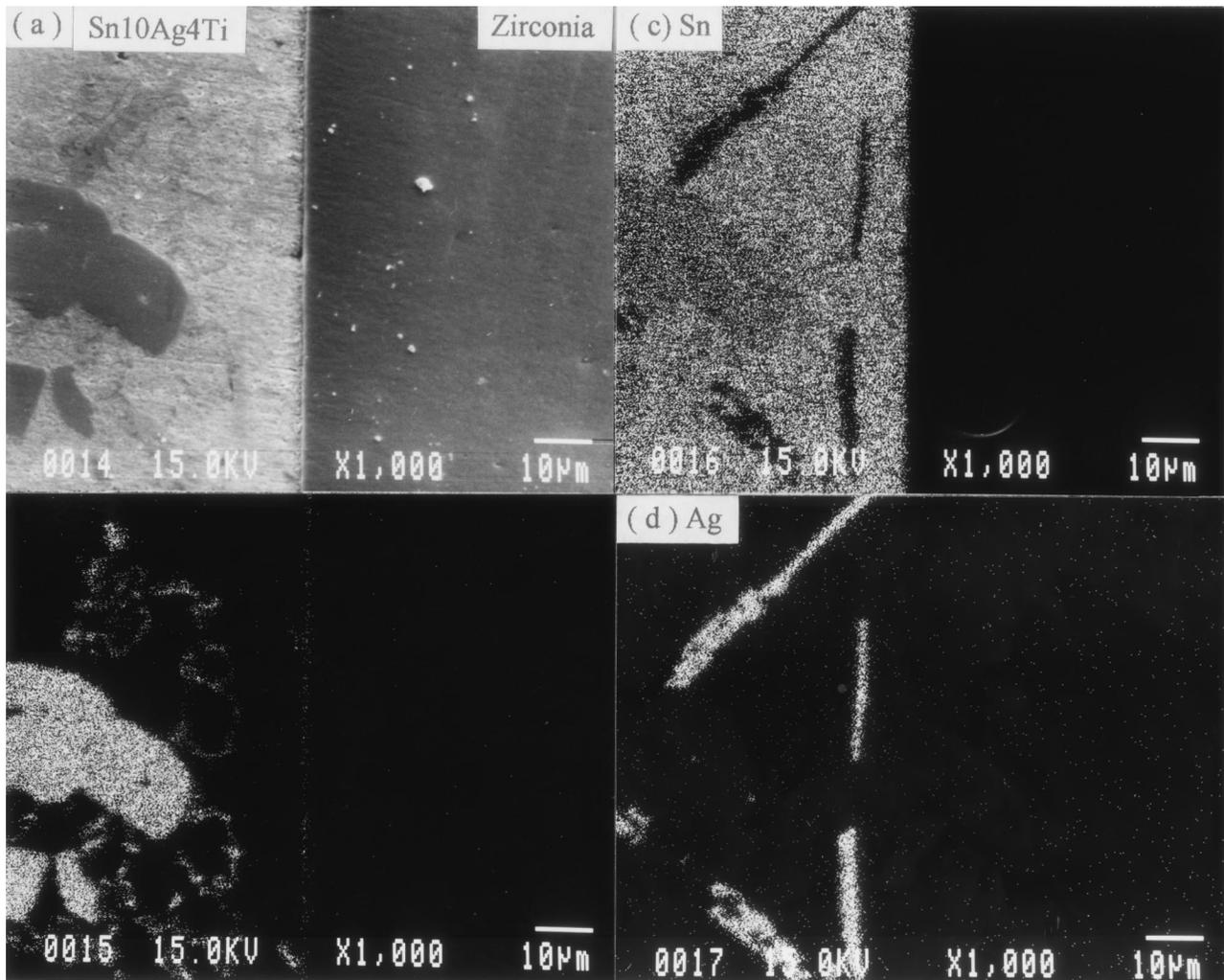


Fig. 7—Micrograph and EPMA analyses for $ZrO_2/Sn10Ag4Ti/ZrO_2$ system brazed at 700 °C for 10 min: (a) interfacial microstructure, (b) titanium mapping, (c) tin mapping, and (d) silver mapping.

transition from a cubic structure (CaF₂ type) to a monoclinic structure (C1 → M) at about 400 °C, according to the report of Srivastava *et al.*^[18] The exothermic peak at approximately 371 °C to 410 °C should be attributed to such a C1 → M phase transition in $ZrO_2 - Y_2O_3$ ceramic powders. The interfacial reaction between pure titanium and ZrO_2 could, thus, be evidenced by the other exothermic peak appearing at about 804 °C to 900 °C.

In referring to the results shown in Figures 4 and 5, the DTA peaks in Figures 3(a) and (b) for $Ag27Cu3Ti/ZrO_2$ and $Sn10Ag4Ti/ZrO_2$ can be identified. In Figure 3(a), two endothermic peaks appeared at 775 °C to 790 °C and at 930 °C to 963 °C, representing the melting range of the $Ag27Cu3Ti$ filler metal and the complete dissolution of the Cu-rich cluster, respectively. The exothermic peak at 790 °C to 810 °C was attributed to the interfacial reaction of the titanium element in the $Ag27Cu3Ti$ filler metal with the Al_2O_3 crucible. The second exothermic peak at about 310 °C to 400 °C represented the (C1 → M) polymorphic phase transition in the $ZrO_2 - Y_2O_3$ ceramic. Additionally, the exothermic peak for the interfacial reaction of the titanium element in $Ag27Cu3Ti$ filler metal with ZrO_2 powder appeared at about 870 °C to 895 °C.

Similarly, in Figure 3(b), the endothermic peak at 219 °C

to 250 °C correspond to the melting range of $Sn10Ag4Ti$ (221 °C to 300 °C), as given in Table I. The exothermic peak at about 627 °C to 750 °C represented the interfacial reaction of $Ti(Sn10Ag4Ti)$ with the Al_2O_3 crucible. The second exothermic peak at approximately 366 °C to 455 °C was attributed to the polymorphic (C1 → M) transformation. The interfacial reaction of the titanium element in the $Sn10Ag4Ti$ filler metal with ZrO_2 powder occurred at the third exothermic peak, at about 860 °C to 910 °C.

The interfacial microstructure and elemental distributions of the $ZrO_2/Ag27Cu3Ti/ZrO_2$ joint, after brazing at 900 °C for 10 minutes, are shown in Figure 6. It is obvious that double reaction layers, with a total thickness of about 12 µm, are formed at the interface. The elemental mapping showed that almost all titanium atoms segregated to the double reaction layers. However, the outer layer (near the ZrO_2 side), with a thickness of about 2 µm, possessed more titanium than the inner layer (near the filler-metal side). On the other hand, some copper atoms and silver atoms also segregated to the inner layer, but were absent from the outer layer (Figure 6(c)). Quantitative analyses by EPMA showed that the inner layer consisted of a Ti_2Cu compound with a small amount of $TiAg$ strips. Since oxygen was mainly found in the outer layer, it can be deduced that the outer layer was

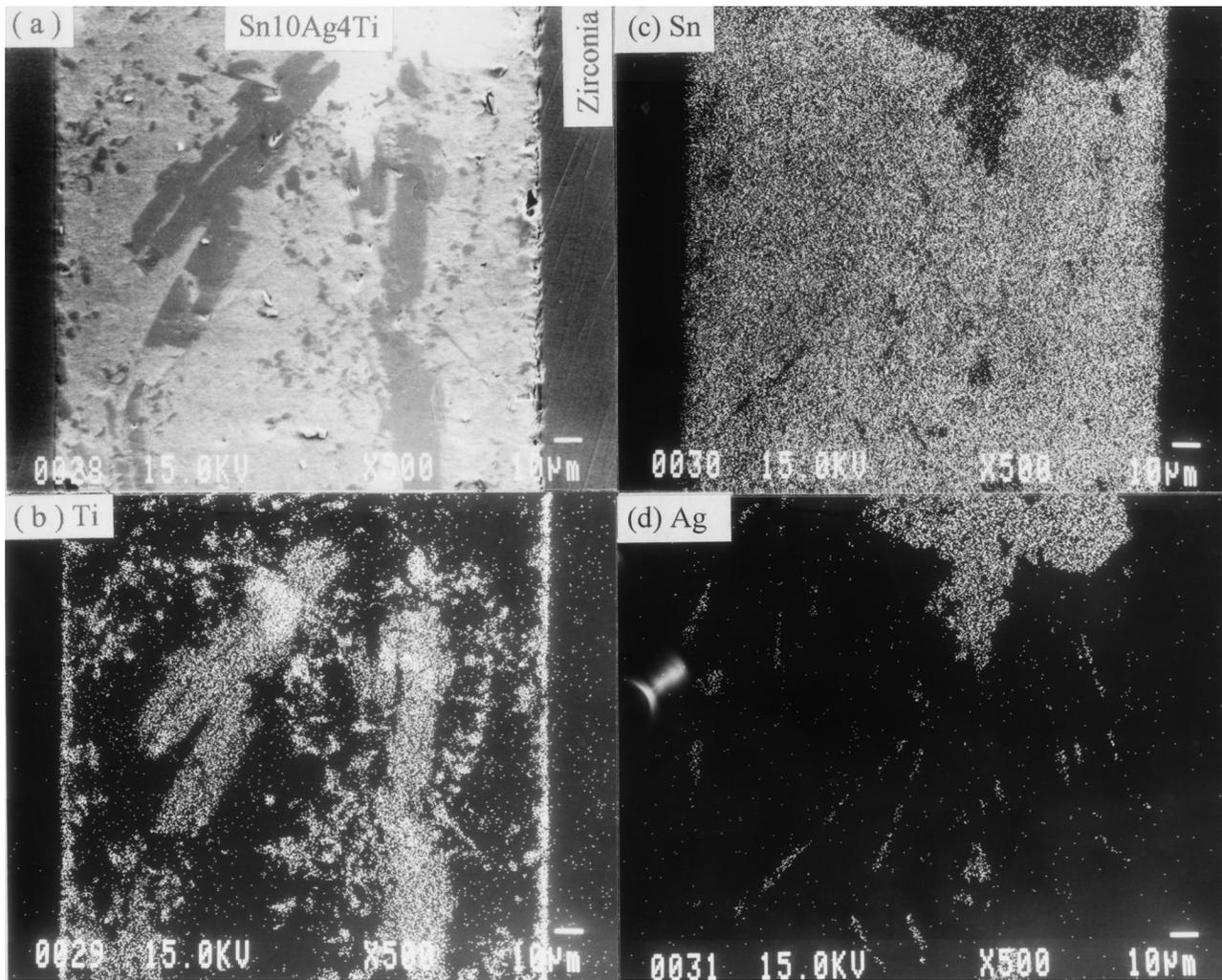


Fig. 8—Micrograph and EPMA analyses for $ZrO_2/Sn10Ag4Ti/ZrO_2$ system brazed at $900^\circ C$ for 10 min: (a) interfacial microstructure, (b) titanium mapping, (c) tin mapping, and (d) silver mapping.

composed of TiO . We suggest that the formation of such a TiO outer layer inhibited the further diffusion of titanium into ZrO_2 and caused the reaction of titanium with copper to form a Ti_2Cu inner layer. This conclusion is consistent with the DTA result in Figure 3(a), which showed an exothermic peak for the interfacial reaction of $Ti(Ag27Cu3Ti)/ZrO_2$ at about $870^\circ C$ to $895^\circ C$. A four-point bending test showed that the bonding strength was 227 MPa for $ZrO_2/Ag27Cu3Ti/ZrO_2$ brazed at $900^\circ C$ for 10 minutes.

Figure 7 shows the micrograph and EPMA elemental mapping for the $ZrO_2/Sn10Ag4Ti/ZrO_2$ system brazed at $700^\circ C$ for 10 minutes. It was found that the titanium clustered in the interior of the $Sn10Ag4Ti$ filler metal after brazing (Figure 7(b)) and reacted with tin to form the (Ti,Sn) compounds (Figure 7(c)), rather than segregating at the filler-metal/ceramic interface. In addition, some Ag strips with Sn depletion were also observed in the interior of the $Sn10Ag4Ti$ filler metal, attributed to the low solubility of silver in tin (Figure 7(d)). In this case, the bonding strength was very minimal. On increasing the brazing temperature to $900^\circ C$, Ti-rich clusters and Ag strips in the interior of the $Sn10Ag4Ti$ filler metal dissolved, and the accumulation of titanium at the $Sn10Ag4Ti/ZrO_2$ interface was obvious, as shown in

Figure 8. The bonding strength increased to 137 MPa. The attainment of a sound joint for $ZrO_2/Sn10Ag4Ti/ZrO_2$ with the increase of the brazing temperature to $900^\circ C$ was consistent with the satisfactory wettability of $Sn10Ag4Ti$ on a ZrO_2 substrate at about $900^\circ C$, and both results were correlated to the segregation and reaction of titanium at the $Sn10Ag4Ti/ZrO_2$ interface. Comparing Figure 8(b) to Figure 6(b), it is interesting to note that the thickness of such a TiO reaction layer at $ZrO_2/Sn10Ag4Ti$ was similar to that of the TiO outer layer at $ZrO_2/Ag27Cu3Ti$ interface. This observation implies that the nature and formation kinetics of both TiO interfacial reaction layers were the same, regardless of whether the source of titanium was from $Ag27Cu3Ti$ or $Sn10Ag4Ti$.

IV. CONCLUSIONS

The contact angles of $Ag27Cu3Ti$ and $Sn10Ag4Ti$ on zirconia decreased with the increase of brazing temperature and remained at approximately 34° and 44° above $900^\circ C$, respectively. For the brazing of zirconia with zirconia using $Ag27Cu3Ti$ and $Sn10Ag4Ti$ active filler metals at $900^\circ C$ for ten minutes, the respective bonding strengths were 227 and 137 MPa.

During the brazing process, titanium in both filler metals segregated at the ceramic/filler metal interface. The TiO reaction layers in both brazing systems possessed similar thicknesses of about 2 μm , which implies that the nature and formation kinetics of both TiO interfacial reaction layers were the same regardless of whether the source of titanium was from Ag₂₇Cu₃Ti or Sn₁₀Ag₄Ti.

It was also noted that an exothermic peak appeared at about 870 °C to 895 °C in the DTA of Ag₂₇Cu₃Ti mixed with ZrO₂ powder, representing the interfacial reaction of Ti(Ag₂₇Cu₃Ti)/ZrO₂. Similarly, an exothermic peak appearing at 810 °C to 910 °C was observed in the DTA curve of Sn₁₀Ag₄Ti mixed with ZrO₂ powder, which was attributed to the interfacial reaction of Ti(Sn₁₀Ag₄Ti)/ZrO₂.

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