

BRAZING OF METALS TO ZIRCONIA MECHANICALLY METALLIZED WITH TITANIUM

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Abstract. *Ceramics to metals joining has been widely made using direct brazing which is a quite versatile and well-known technique, but its fillers are rather costly materials than conventional filler alloys because they have an active metal in its composition. The mechanical metallization is a successfully technique at laboratory scale and specially applied to oxide ceramics, which was patented by Forschungszentrum Juelich in Germany. It consists basically on wearing out a conical-shape metallic tool against the ceramic surface to produce an active metal coating on it using established control parameters. This particular metallization is made at room temperature with low cost production and environmentally safe because it does not produce hazardous chemical residues. Indirect brazing process of zirconia to metals is achieved using active-metal-free filler alloys on previously metallized ceramic. These alloys dissolve part of this coating and its active metal reacts with the oxide ceramic to improve wetting on its surface at brazing temperature. Tetragonal zirconia polycrystals with yttria (TZP-Y) and partially stabilized zirconia with magnesia (PSZ-Mg) were mechanically metallized with Ti. Wetting conditions onto the ceramic surface were evaluated for two different filler alloys and thermal cycles and the better results selected for brazing tests. Metallic counterparts were brazed to zirconia in a high-vacuum furnace ($<3 \times 10^{-5}$ mbar) using commercial Ag-Cu and Au-Ni filler alloys. Helium gas leak detection test was made at the ceramic-metal interface; samples from reliable vacuum tight joints ($<10^{-8}$ mbar.l.s⁻¹) were examined by conventional microstructural analysis and linescan technique using energy dispersive X-ray analysis. Microhardness profiles were made across the joints interface where zirconia undergone a darkening effect during brazing. Interactions between the fillers and metallic members and with metallized ceramic surface have been examined. The best results were obtained for brazed joints with the eutectic Ag-Cu alloy when in its microstructure a reaction layer was revealed at the ceramic/metal interface. Metallurgically sound joints were produced due to superficial chemical interactions of Ti with the filler alloy and zirconia.*

Keywords: *mechanical metallization, brazing, ceramic-metal joining.*

1. INTRODUCTION

The progressive development of advanced ceramics could be associated to an increased demand for joining ceramics to themselves or to metals for producing hybrid components with reliable interfaces and improved engineering properties. Advanced ceramics include oxides, carbides, nitrides and a number of their composites. In fact, alumina and zirconia (ZrO₂) have been the most commonly investigated oxide ceramics for researchers aiming possibilities of industrial applications when joined with other materials (Liu *et al*, 2009). Moreover, zirconia exhibits higher strength and fracture toughness than alumina particularly at temperatures below $\approx 300^\circ\text{C}$ for K_{IC} values in the range 15-20 MPa.m^{1/2} (Hanson *et al*, 2000). These properties are beneficial in many technical applications from wire drawing dies, cutting and machining tools, gas turbines to oxygen sensors and solid oxide fuel cells, including those that require the ceramic to be bounded to a metallic member (Sciti *et al*, 2001; Smorygo, *et al* 2007).

Active metal brazing is the most common method for joining ceramics to metals in which is used filler alloy that contain a few percents of a reactive metal in its composition, such as V, Cr, Ta, Hf, Zr and specially Ti. These solutes promote lower contact angles and enhance the ceramic/metal wettability by reducing the oxide that constitutes the main ceramic phase (Muolo *et al*, 2004; Singh *et al*, 2007; Liu *et al*, 2009). Formation of a continuous interfacial reaction layer between the ceramic and fillers is an important factor for joint strength (Smorygo *et al*, 2007). Ceramic is joined to metallic member by chemical reactions at the joint during brazing temperature. However, higher costs of these fillers has driven forward alternative joining approaches such as previous metallization on the ceramic surface with an active metal for subsequent indirect brazing using active-metal free filler alloys (Nascimento *et al*, 2002).

Several techniques used for previous ceramic metallization, that are well-documented in the scientific literature, such as physical and chemical vapour deposition (PVD and CVD process, respectively), have nevertheless the handicap

of being more expensive and laborious than the here proposed mechanical metallization. By the other side the well-known Mo-Mn method is inappropriate for zirconia metallization because it does not have a glassy intergranular phase, which is a key factor for joining between the formed metallic film and ceramic substrate (Elsner and Petzow, 1990; Hanson *et al.*, 2000).

The mechanical metallization technique has been in continuous development, involving studies about oxide and non-oxide ceramics to produce reliable vacuum tight ceramic/metal joints with low cost production (Nascimento, 2001 and 2002). It has been observed that the typical microstructure at the interface is characterized by eutectic constituent close to a rich-Ti reaction layer and eventually by a precipitation zone between them (Nascimento *et al.*, 2002; Nascimento, 2007).

Filler alloy previously selected must also prevent grain growth and long-term thermomechanical degradation due to creep and oxidation, and have its coefficient of thermal expansion (CTE) closely matched with the brazed materials (Singh *et al.*, 2007). Not only about the filler, but it is also crucial avoiding CTE mismatch for individual components to be joined. For instance, partially stabilized zirconia and Ti-6Al-4V (ASTM Grade 5) have similar CTE values ($\approx 10 \times 10^{-6}/^{\circ}\text{C}$ and $9,7 \times 10^{-6}/^{\circ}\text{C}$ respectively). Copper member ($\approx 17 \times 10^{-6}/^{\circ}\text{C}$) can be joined to ceramic because it is able to undergo enough interfacial plastic flow to accommodate residual stresses produced at the joint interface (Nascimento, 2001). Other important consideration is that fillers must have *liquidus* temperature greater than work temperature of the joint, but lower than component's melting temperature. The eutectic Ag-Cu based filler is generally preferred for joining ceramic to metals because it is ductile and chemically inert, which reduces the oxidation and therefore minimizes residual stresses during cooling from brazing temperature (Sciti *et al.*, 2001; Singh *et al.*, 2008). In addition, zirconia stabilized with yttria or magnesia is wet and strongly bonded by Ag-Cu based filler even with small Ti percents in its composition (commercially 1.5-4.5 wt.% Ti) (Sciti *et al.*, 2001).

In the present study, the mechanical metallization with Ti on the ceramic surface was a previous stage for brazing zirconia to metals using two commercial active-metal-free filler alloys. Producing reliable vacuum tight brazing joints based on previous knowledge about wetting behavior for both analyzed zirconia ceramics and characterizing the resultant microstructure at the ceramic/metal interface were the main objectives in this study. And evaluating how the darkening effect in zirconia affects its hardness property at the brazed joint interface.

2. EXPERIMENTAL PROCEDURES

Ceramic materials rods $\varnothing 8.0$ mm were tetragonal zirconia polycrystals with yttria 5-10 wt.% (TZP-Y) and partially stabilized zirconia with magnesia 3-4.5 wt.% (PSZ-Mg) from Engecer Ltda./Brazil. Metallic counterparts were Cu-ETP (DIN EN 13601) and Ti-6Al-4V (ASTM Grade 5, annealed); conical-shape tools used for mechanical metallization process were produced from a rod of commercially pure Ti (ASTM Grade 2). Filler alloys were VH780 (Ag-28Cu) and VH950 (Au-18Ni). Table 1 shows properties of the materials used in this study, according to the manufacturers.

Zirconia samples (ZrO_2) were polished to 6 μm diamond and ultrasonically cleaned in acetone bath for 10 minutes before its metallization. Ti-6Al-4V alloy members were cleaned with ethanol to remove machining residues; copper members were first cleaned in a bath 5% HNO_3 to remove superficial oxides and later ultrasonically cleaned in ethanol.

Table 1. Properties of the materials used for joining ceramic to metals.

Component / Properties	TZP-Y	PSZ-Mg	Ti-6Al-4V	Cu-ETP
Purity / Composition (%wt.)	99.0-99.2% / 5.0-10.0 %wt. Y_2O_3 , ZrO_2 balance	99.0-99.2% / 3.0-4.5 %wt. MgO , ZrO_2 90.0-95.0%, others	ASTM Grade 5	99.9% Cu, 0.005-0.04%O DIN EN 13601
Apparent density at 20°C (g/cm^3)	5.5-6.1	5.1-5.6	4.43	8.93
Linear CTE ($10^{-6} \text{ }^{\circ}\text{C}^{-1}$)	10.4 (25-1000°C)	10.0-10.1 (25-1000°C)	9.7 (20-650°C)	17.7 (20-300°C)
E modulus (GPa)	206	204	113.8	130
Hardness (HRC)	83	76	36	—
Working temperature	1200°C	1000°C	—	—

Figure 1 shows a schematic illustration of the mechanical metallization process. Ceramic samples are attached to the lathe and turn on the counterclockwise under constant speed (800 rpm), while the conical-shape tool is attached to a reworking high speed that turn on the clockwise (27,000 rpm). During the contact between these two components, the metallic tool wears out and a titanium coating is deposited on the ceramic surface. Nascimento (2001) established the main control parameters for this metallization process. Oxidation behavior was not detected for metallization process under previously specified conditions (Nascimento, 2001; Nascimento *et al.*, 2002).

Wetting tests were made in a high-vacuum furnace at FZ-Juelich (PFEIFFER MOV262) with samples mechanically metallized with Ti, using two different wetting temperatures (soaking for 10 minutes) for each commercial filler alloy: 820°C and 880°C for VH780 (Ag-28Cu) filler; 980°C and 1050°C for VH950 (Au-18Ni) filler.

Working temperatures for VH780 and VH950 fillers are respectively 780-820°C and 970°C, according to the manufacturer. Contact angles were measured when samples were removed from the vacuum furnace in the end of wetting tests by software developed at UFRN (Brazil) using images analysis. Wetting conditions were also qualitatively analyzed by microstructural analysis techniques at the ceramic/filler interface; better results were selected for brazing tests. The standard thermal cycle used for both wetting and brazing tests is shown in Fig. 2: there are two levels for temperature homogenization (700°C and 750°C); third level is specific for wetting and subsequent brazing temperature.

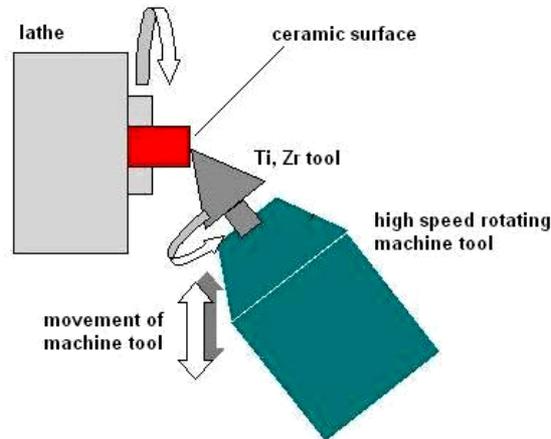


Figure 1. Schematic illustration of the mechanical metallization process (adapted from Nascimento, 2001).

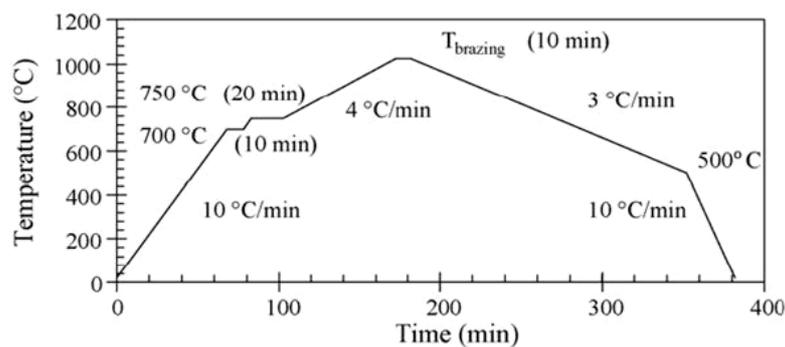


Figure 2. Standard thermal cycle used for wetting and brazing tests.

Each joint assembly was submitted to a normal load approximately 120 kPa on its top. Brazing ceramic to metals was made using a simple butt-joint configuration in a high-vacuum furnace (better than 3×10^{-5} mbar), which was also useful for He gas leak tests at room temperature (Inficon UL200 equipment) according to the scheme shown in Fig. 3.

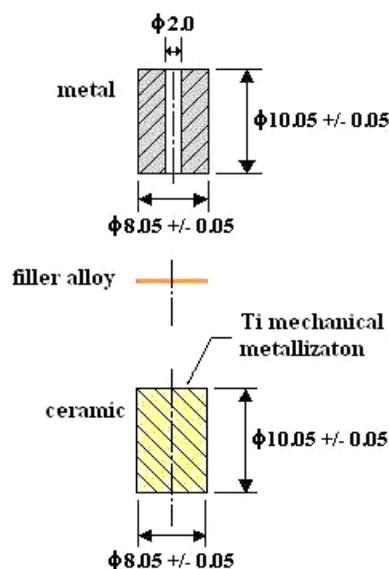


Figure 3. Brazing joints configuration also used for helium gas leak tests. Dimension in mm.

Samples were selected from tight ceramic/metal joints for microstructural analysis: mounted in epoxy and cut on a low-speed diamond wire, submitted to final polishing with 0,025 μm SiO_2 particles suspension. Cross-section at the joint interface was analyzed by optical and scanning electron microscopy (SEM) – Cambridge Stereoscan 360 equipped with the linescan technique by energy dispersive X-ray analysis (EDX), operating voltage of 20 kV. Microhardness measurements were made using a Vickers micro-indenter on a Shimadzu HMV-2 machine (load of 200 g for 10 s).

3. RESULTS AND DISCUSSION

3.1. Wetting tests and brazing conditions

Initially, zirconia samples were mechanically metallized with Ti and wetting behavior was investigated using two different filler alloys for two thermal cycles. Table 2 shows summarized results and selected wetting conditions for subsequent brazing process (see shaded areas). Results for both zirconia ceramics were better with the eutectic Ag-28Cu filler alloy than with Au-18Ni filler. There were partial wetting conditions using Au-18Ni filler alloy, but spreading on the metallized surface was not efficient for both zirconia ceramics. There was no adherence of melted Au-18Ni filler alloy on the substrate for tests at 1050°C. Although wetting results had not been so favorable for it, the former condition for this filler (see shaded area at 980°C in Table 3) was also investigated for subsequent brazing tests.

Table 2. Summarized results for wetting tests and selected conditions for brazing process.

Zirconia ($\varnothing 8.0$ mm)	Active metal	Filler alloy			
		VH780 (Ag-28Cu)		VH950 (Au-18Ni)	
		Wetting temperature, soaking 10 min			
		820°C	880°C	980°C	1050°C
TZP-Y, PSZ-Mg	Ti	OK	OK	partial wetting ⁽¹⁾	No adherence
		OK	OK	partial wetting ⁽¹⁾	

(1) Partial means wetting occurred (contact angle $<90^\circ$) but insufficient spreading on the ceramic surface.

Results were qualitatively evaluated and contact angles were measured when samples were removed from vacuum furnace: for wetting tests with Au-18Ni filler – the values were in the range 35° - 40° for tests at 980°C. For tests with Ag-28Cu filler there was visually total wetting on the metallized ceramic. For practical purposes contact angle values between 70° - 90° may be insufficient to provide satisfactory spreading on the ceramic surface (Akselsen, 1992; Nascimento, 2003).

3.2. Helium gas leak detection at the brazed joints

Brazed joints were submitted to a helium gas leak detector at room temperature. Table 4 shows summarized results for these tests, in which leak rates bellow 10^{-8} mbar. ℓ .s⁻¹ were considered totally satisfactory. Titanium was efficient as active metal for both mechanically metallized zirconia ceramics. Even though some wetting tests had been classified as partial (see area in Table 3 at 980°C), leak rates results were also satisfactory for $\text{ZrO}_2/\text{Au-18Ni}/\text{Cu}$ joints. Some samples from these reliable vacuum tight joints were examined by conventional microstructural techniques.

Table 4. Summarized results of helium gas leak tests in the brazed ceramic/metal joints.

Brazing temperature at 820°C, soaking 10 min VH780 (Ag-28Cu)			
Zirconia (samples $\varnothing 8.0$ mm)	Active metal	ceramic/metal joints	Leak rates (mbar. ℓ .s ⁻¹)
TZP-Y, PSZ-Mg	Ti	TZP-Y/Ag-28Cu/Cu PSZ-Mg/Ag-28Cu/Cu	$< 10^{-8}$
		TZP-Y/Ag-28Cu/Ti-6Al-4V PSZ-Mg/Ag-28Cu/Ti-6Al-4V	$< 10^{-8}$
Brazing temperature at 980°C, soaking 10 min VH950 (Au-18Cu)			
TZP-Y, PSZ-Mg	Ti	TZP-Y/Au-18Ni/Cu PSZ-Mg/Au-18Ni/Cu	$< 10^{-8}$
		TZP-Y/Au-18Ni/Ti-6Al-4V PSZ-Mg/Au-18Ni/Ti-6Al-4V	No brazing or $> 10^{-4}$

Leak rate results for zirconia/Au-18Ni/Ti-6Al-4V joints were not satisfactory at all. Most of the joint assemblies were not brazed after they had been removed from the vacuum furnace and He gas leak detection was possible in just few of them. However, these brazed joints exhibited leak rates too much high ($>10^{-4}$ mbar. ℓ .s $^{-1}$). Possible explanations for this situation are: poor wetting behavior of the Au-18Ni filler on the mechanically metallized ceramic surface had already been previously verified; and an eventual excessive formation of intermetallic compounds in the microstructure at the ceramic/metal interface. Samples were also selected for microstructural analysis.

Schröder *et al* (2000) consider that the allowable maximum leak rate for most cases of technical application is in the range 10^{-6} – 10^{-8} mbar. ℓ .s $^{-1}$; for leak rate values bellow 10^{-8} mbar. ℓ .s $^{-1}$ it is possible to classify a component as vacuum tight, which means there would be approximately 3 ml of helium gas loss in 1 year (discontinuity diameter $\approx 0,4$ μ m). It is also believed that leak values around 10^{-3} mbar. ℓ .s $^{-1}$ means approximately 1 air bubble loss (≈ 1 mm 3) per second.

3.3. Microstructural analysis

Figure 4 shows a SEM image representative for wetting conditions using Ag-28Cu filler alloy at 820°C, in which was produced a continuous reaction layer at the filler/ceramic interface. This layer was not observed at 880°C and it was probably diluted in the microstructure of melted filler alloy. Formation of this layer at the interface is considered a key factor to the vacuum tightness and ceramic/metal joint strength (Nascimento *et al*, 2002; Smorygo *et al*, 2007). For wetting test using the Au-18Ni filler, there was formed a very thin reaction layer at the filler/ceramic interface at 980°C and there was not adherence of this filler on the metallized substrate at 1050°C. In addition, Fig. 4 also exhibits a continuous dark reaction sublayer that was formed closely to the metallized ceramic surface which is basically composed by Ti-O compounds (TiO, Ti $_2$ O $_3$, Ti $_3$ O $_5$... TiO $_2$). It is beneficial to improve wetting on the ceramic substrate by melted filler alloy from superficial reduction of zirconium oxide and precipitation of active metal oxides (Hanson *et al*, 2000; Sciti *et al*, 2001; Smorygo *et al*, 2007; Singh *et al*, 2008).

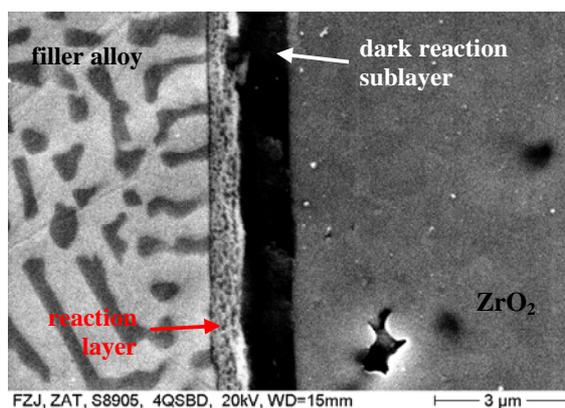


Figure 4. SEM image at Ag-28Cu/ZrO $_2$ interface, wetting test at 820°C. Reaction layer (see red arrow) and a dark sublayer closely to the ceramic surface.

Figure 5 represents ZrO $_2$ /Ag-28Cu/Cu joints; optical micrograph in Fig. 5a suggests formation of a sound brazed joint and melted filler alloy is well-diluted with the metallic member (Cu-ETP), which is really good to accommodate residual thermal stresses. SEM image in Fig. 5b shows a thin and partially discontinuous reaction layer between the ceramic and the filler, including an adjacent defect area. Reaction layers on mechanically metallized ceramic are usually discontinuous (Nascimento *et al*, 2002). The adjacent dark area represents a reaction sublayer closely to the metallized ceramic surface and it is basically composed by titanium oxides. Elemental qualitative analysis by linescan technique in the joint cross-section is also shown in Figure 5b. There was Ti diffusion from metallized area into the ceramic and it is also present in the reaction layer with Ag, Cu and traces of Y and Zr. Intermetallics inclusions were not found here.

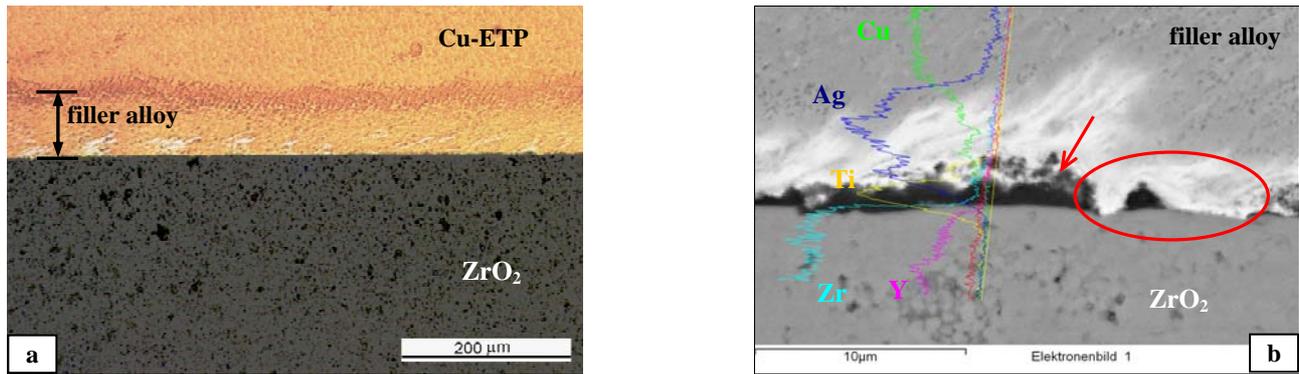


Figure 5. (a) Optical micrograph for TZP-Y/Ag-28Cu/Cu joint (brazing at 820°C); (b) SEM image + linescan technique. Reaction layer at the ceramic/filler interface (see red arrow) and defect area on the ceramic surface (see red circle).

Nascimento *et al* (2002, 2003) concluded that in defect areas on the ceramic surface after previous mechanical metallization with Ti, wetting took place because of melted filler alloy becomes active at brazing temperature. Although, the local availability of Ti had been lower in these areas it was produced a wavy reaction layer on the metallized ceramic surface with reduced thickness (about 2-4 μm) at the brazed ceramic/metal joint interface.

Figure 6 represents brazed ZrO₂/Ag-28Cu/Ti-6Al-4V joints at 820°C. SEM image in Fig. 6a suggests formation of a metallurgically sound joint showing a reaction layer at the ceramic/filler interface; there is also a diffusive zone in the metallic member and a reaction layer between the metal and filler alloy. Linescan technique result across the filler/diffusive zone interface revealed that there was diffusion of elemental Cu and Ag to the metallic member; and this reaction layer is really an intermetallic layer that contains mainly Ti and Cu, and lower contents of Ag, Al and V that indicate formation of a CuTi-rich zone. Formation of CuTi and CuTi₂ compounds in these regions is according to the Cu-Ti equilibrium phase diagram because copper has a strong tendency to produce intermetallics with titanium (Hanson *et al*, 2000; Smorygo *et al*, 2007). Figure 6b shows an elemental qualitative analysis by linescan technique across the ceramic/filler interface shown in Fig. 6a. There is a continuous reaction layer closely to a dark reaction sublayer (Ti-O compounds), which was formed from reduction of zirconium oxide. The interface is enriched in titanium and probably Ti content increased in the bulk of melted filler alloy as a result of its diffusion from the metallic member. The reaction layer contains elemental Ti from its diffusion from the coating on the ceramic surface and traces of Ag and Cu were also found here; intermetallics inclusions were not found.

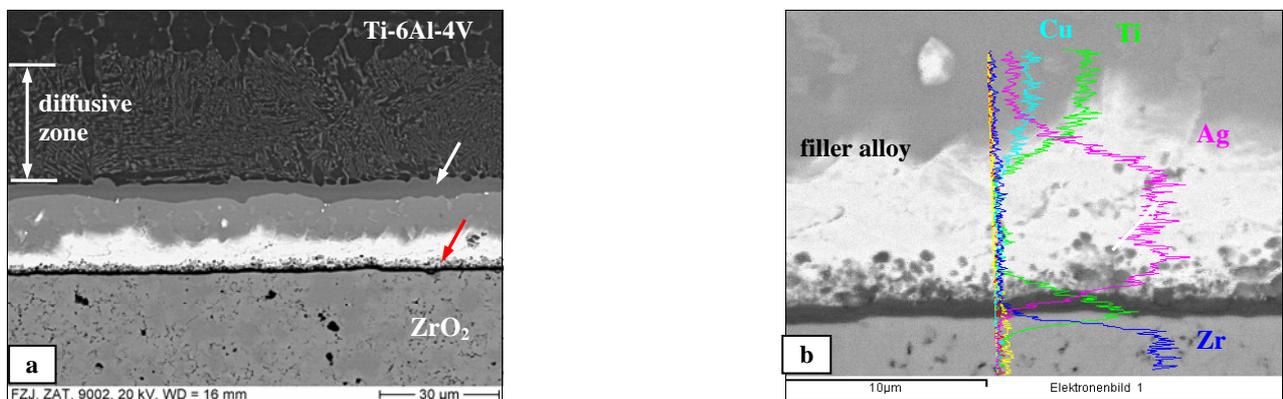


Figure 6. SEM images for ZrO₂/Ag-28Cu/Ti-6Al-4V joint (brazing at 820°C): (a) Reaction layer at the ceramic/filler interface (see red arrow), diffusive zone in the metallic member and an intermetallic layer at the filler/Ti-6Al-4V (see white arrow); (b) Linescan technique across dark reaction sublayer closely to the metallized ceramic surface.

Microstructural analysis at the brazed ZrO₂/Au-18Ni/Cu joints interface at 980°C revealed that Au-18Ni filler alloy was well-diluted closely to the metallic member (Cu-ETP); it was also formed a very thin partially discontinuous reaction layer and a dark reaction sublayer closely to the metallized ceramic surface as mentioned before. According to linescan technique results there was some diffusion of Ti and Zr into the bulk of melted filler alloy. Presence of elemental Au and Ni, including Ti were found in this reaction layer.

SEM images for brazed ZrO₂/Au-18Ni/Ti-6Al-4V joint at 980°C are shown in Fig. 7. Microstructure shows a diffusive zone in the metallic member and formation of intermetallic phases closely to the ceramic surface (Fig. 7a). EDX analysis by linescan technique detected traces of elemental Au and Ni from the filler alloy in this specified zone. It was noticed in this sample the presence of microcracking at the interface (see Fig. 7b). Excessive presence of intermetallics formed in the braze region, thus it may have caused so high residual stresses in the crystalline lattice and

subsequent cracking at the filler/ceramic interface – probably associated to the CTE mismatch for individual members to be joined. For instance, some intermetallic phases found here were composed by following groups: Ti-Au, Ti-Al-Ni-V and Ti-Al-Ni for regions A, B and C shown in Fig. 7b, respectively. Region D is a very thin reaction layer at the filler/ceramic interface that contains elemental Ti, Au and Ni, according to EDX analysis. The Au-Ti binary system is characterized by a series of well-established compounds, such as Ti_3Au , $TiAu_2$, $TiAu_4$ and α , β and γ -TiAu (Nascimento *et al*, 2007).

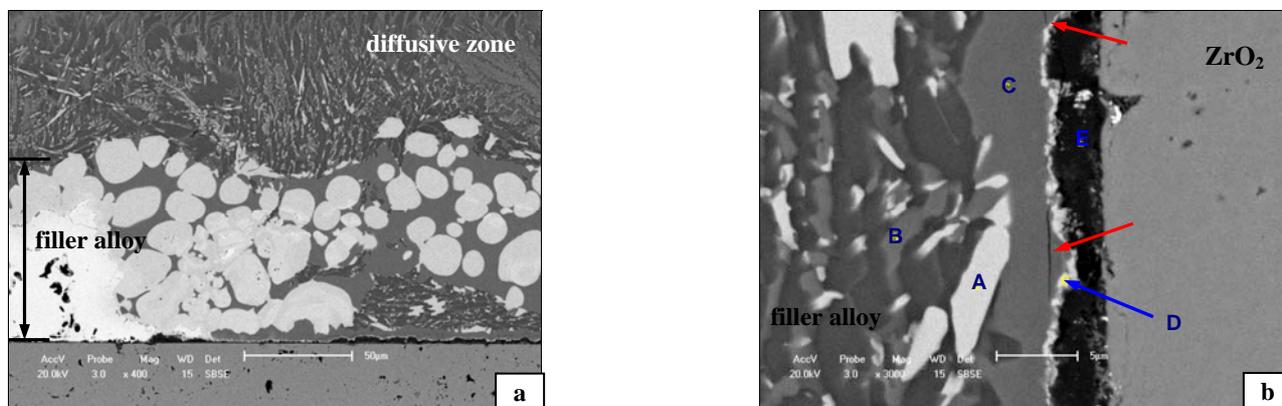


Figure 7. (a) SEM image for $ZrO_2/Au-18Ni/Ti-6Al-4V$ joint (brazing at $980^\circ C$); (b) Thin reaction layer at the interface (see blue arrow). Punctual EDX analysis in the intermetallic phases and presence of microcracking (see red arrow).

3.4. Darkening effect in zirconia ceramic

Figure 8 shows the influence of metallic counterparts and Ti coating from mechanical metallization in the darkening of zirconia ceramics verified closely to the brazed ceramic/metal interface. Dark area was more pronounced in PSZ-Mg than TZP-Y ceramic for the same brazing conditions (Ag-28Cu filler alloy for brazing tests at $820^\circ C$). It was noticed that at higher temperatures such darkening in zirconia was more extensive from the brazed joint interface, i.e. brazing tests at $880^\circ C$ using these metallic counterparts and the eutectic Ag-28Cu filler.



Figure 8. (a) $ZrO_2/Ag-28Cu/Cu$ joints; (b) $ZrO_2/Ag-28Cu/Ti-6Al-4V$ joints. Darkening effect in zirconia localized from the joint interface for brazing tests at $820^\circ C$ (TZP-Y in white and PSZ-Mg in orange color).

Researchers have already reported this typical darkening effect in zirconia at the ceramic/metal joints interface using active brazing – filler alloys containing Ti as active metal. This phenomenon is attributed to the formation of a non-stoichiometric zirconia (ZrO_{2-x} , where $0 < x \leq 0.02$), caused by an active metal with high affinity for oxygen (Hanson *et al*, 2000; Muolo *et al*, 2004; Smorygo *et al*, 2007). In other words, there is a partial scavenging of oxygen from the ceramic by titanium, leading to O-deficient area that appears dark (Singh *et al*, 2007).

The darkening effect of zirconia ceramic from the brazed joint interface can be also influenced by some factors, such as: dwell time at brazing temperature; the substrate to which zirconia is being joined; and the percentage of active metal in the filler composition. There was not damage or significant effect for mechanical strength because of this discoloration region at the joint interface (Hanson *et al*, 2000; Smorygo *et al*, 2007).

3.4.1. Microhardness measurements

Vickers microhardness profiles across the investigated ceramic/metal interfaces are shown in Figure 9. The measurements were made under a 200 g load and loading time of 10 s; indentation were performed on zirconia about 50 μm far from the interface. Figures 9a and 9b show that hardness is only slightly higher inside of the thin braze region than the average hardness of the metallic member. Probably contents of Ag from the filler contributed for this higher hardness values in the eutectic composition region. Microstructural analysis showed that melted Ag-28Cu filler alloy is

well-diluted at the interface with Cu-ETP. However, hardness is notoriously lower within braze region using Ti-6Al-4V as metallic member (see Fig. 9c). Hardness rises rapidly upon entering in ceramic region, which leads to a sharp discontinuity in the microhardness profile at the ceramic/filler interface. Microhardness measurements from closely to braze region into the depth of zirconia revealed that besides of its typical darkening effect (see previous Fig. 8) there was no negative influence of this mechanical property in the ceramic material.

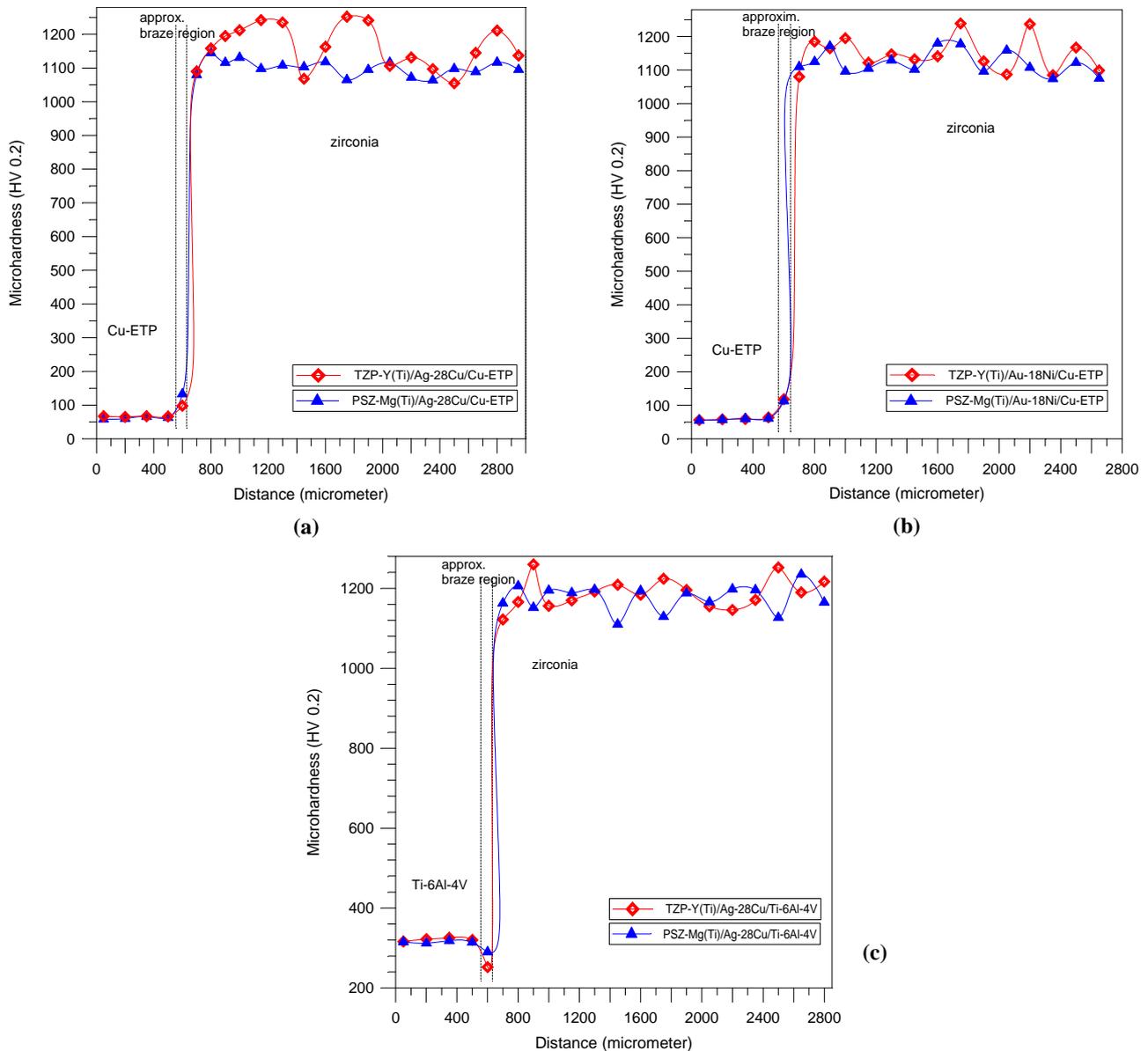


Figure 9. Microhardness profiles across the ceramic/metal interface, (Ti) means titanium mechanical metallization: (a) $ZrO_2/Ag-28Cu/Cu-ETP$; (b) $ZrO_2/Au-18Ni/Cu-ETP$; (c) $ZrO_2/Ag-28Cu/Ti-6Al-4V$.

Figure 10 shows optical micrographs with microhardness indentation at the ceramic/metal interface for TZP/Ag-28Cu/Cu-ETP and TZP-Y/Ag-28Cu/Ti-6Al-4V joints for brazing tests at 820°C. Microstructure is completely diluted at the Ag-28Cu/Cu-ETP interface (see Fig. 10a), while the braze region is well-defined for the couple Ag-28Cu/Ti-6Al-4V in Fig. 10b. Microhardness measurement in the braze region was slightly lower than in the metallic member, probably because of interdiffusion of elemental Ag and Cu from the filler alloy to the metal (see Fig. 10b).

In addition, residual thermal stresses due to the mismatch among the coefficients of thermal expansion (CTE) of individual components should be also considered. The CTE of Ti-6Al-4V ($9.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) is comparable to the zirconia CTE ($10.0-10.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), but the CTE of Cu-ETP ($17.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and the CTE of the filler alloys are rather high – CTE of Ag-28Cu (20-400°C) and Au-18Ni (20-550°C) are $17.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $14.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively. According to these data, tensile strains can develop at the ceramic/metal interface due to differential contraction during cooling from the brazing temperature. However, it is believed that residual stresses can be accommodate by plastic flow from the large ductility of these filler alloys (Sciti *et al*, 2001; Smorygo *et al*, 2007; Singh *et al*, 2008).

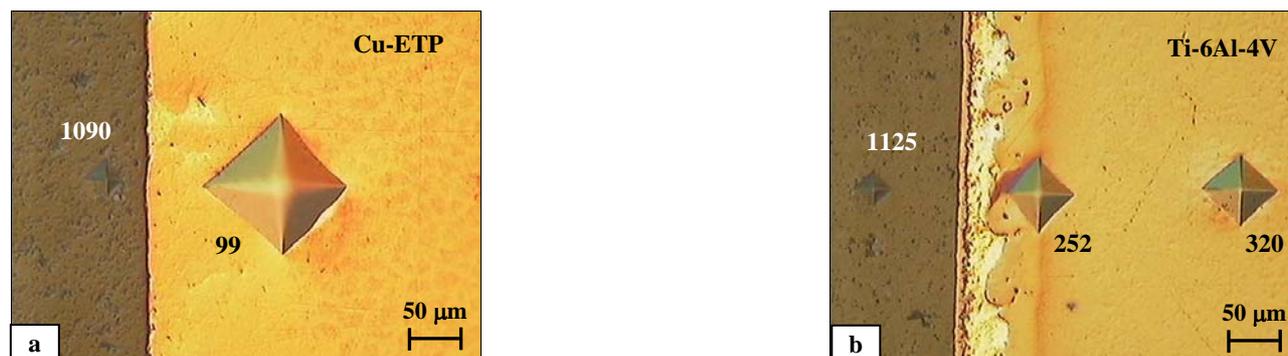


Figure 10. Microhardness indentation ($HV_{0.2}$) at the ceramic/metal interface for brazing at 820°C: (a) TYP-Y(Ti)/Ag-28Cu/Cu; (b) TYP-Y(Ti)/Ag-28Cu/Ti-6Al-4V. (Ti) means metallization with titanium. Magnification 500X.

4. CONCLUSIONS

Zirconia ceramics were mechanically metallized with titanium and ceramic/metal brazing joints were successfully produced using active-metal-free filler alloys for both Ti-6Al-4V and Cu-ETP as metallic counterparts. Results based on helium gas leak detection were satisfactory with leak rates below 10^{-8} mbar.l.s⁻¹, which characterize reliable vacuum tight components. Microstructural analysis at the metallurgically sound joints interface revealed formation of a thin reaction layer associated to a dark sublayer (Ti-O compounds) closely to the ceramic/filler interface, whose appearance depends on the specific filler alloy and metallic member to be joined. There was chemical interdiffusion between individual components of the joint assemblies, which probably led to compositional changes across the joint interface. Excessive presence of intermetallic phases was noticed at the ZrO₂/Au-18Ni/Ti-6Al-4V joints interface, which may have caused high residual stresses in the crystalline lattice associated to the CET mismatch of individual members and subsequent microcracking at the ceramic/filler interface. The darkening effect in zirconia from the ceramic/metal joint interface was directly influenced by Ti coating on the ceramic surface, brazing thermal cycles and the metallic counterparts. Visually, it was little more pronounced in PSZ-Mg ceramic than for TYP-Y ceramic. Microhardness measurements were taken across the joint interface along the darkening region in inner surface of zirconia and there was no measurable negative effect in this mechanical property.

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