



Wetting Behavior of Silver Braze Alloys onto Metallized Zirconia Inserts

Wetting experiments were conducted to find a strong metal-ceramic interface for drill bit inserts

BY J. C. PEREIRA, R. M. NASCIMENTO, A. E. MARTINELLI, W. ACCHAR, AND L. A. ROCHA

ABSTRACT

Drill bits with hard ceramic inserts are often used in oil well drilling operations. The cutting action and breakdown of the rock formation produces failures on the drill bits. Metal-ceramic interfaces showing good mechanical and thermal properties can minimize the most common failures on drill bits. Brazing is a well-established technique to join metal-ceramic materials. Wetting phenomena plays an essential role in the production of metal-ceramic interfaces when a liquid phase is present. Stabilized zirconia with yttria and magnesia can be an interesting material for ceramic inserts application on drill bits when oil well or the drilling fluid has acid characteristics. In this work, silver-based brazing alloys were melted onto zirconia substrates under a high vacuum. The effect of oxide stabilizers and the metallized surface on the wetting behavior were studied. Better results were found for the yttria stabilized zirconia system using AgCu with 3% Ti as the filler metal.

KEYWORDS

• Drill Bit • Brazing • Wetting • Contact Angle • Zirconia

Introduction

Metal-ceramic interfaces are present in several types of equipment and devices used in the oil well drilling industry. Oil well drill bits with hard ceramic inserts work under a combination of forces including cutting, scraping, chipping, crushing, and erosion from the impact of the drilling jet fluids. These forces during the breakdown of rock formations produce failures on drill bits, which are related to wear, total or partial rupture of the drill bit body or the ceramic inserts, thermal shock, and corrosion. Also,

improper fitting of the ceramic inserts on the bit body may cause its total detachment, and act as a source of damage (Ref. 1). Research to improve metal-ceramic interfaces with good mechanical and thermal properties can minimize some of the most common failures on oil well drill bits, optimizing their service life, and reducing drilling costs.

The joining between metal and ceramic materials is a complex process. Brazing is a widely used technique to join metal-metal, ceramic-ceramic, or metal-ceramic pairs. Most ceramics show nonwetting behavior, and in

these cases it is necessary to promote the wetting by premetallizing the solid surfaces before brazing or using an active braze alloy. Titanium (Ti) is the most commonly used active metal in braze alloys. It reacts to produce stable and wettable compounds, which can be associated to a multilayered system creating a chemical continuity between the metal and ceramic, and also minimizing the residual stress field occurring during the cooling in a dissimilar materials joining system (Refs. 2–4). Therefore, wetting phenomena play an important role in the production of metal-ceramic interfaces when a liquid phase is present. Wettability of a solid by a liquid is characterized in terms of their contact angle, θ , obtained from the balance of interfacial tension and defined from the Young-Dupré equation:

$$\cos \theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV} \quad (1)$$

Where σ_{SV} , σ_{SL} , and σ_{LV} are the interfacial tensions between solid-vapor, solid-liquid, and liquid-vapor phases, respectively. Any decrease in the liquid surface tension (σ_{LV}) caused by a chemical composition modification can increase the wettability only if the initial contact angle was already smaller than 90 deg (Ref. 5). High-temperature wetting is influenced by a large number of variables such as temperature, contact time, furnace atmosphere, roughness, crystal structure, composition, surface

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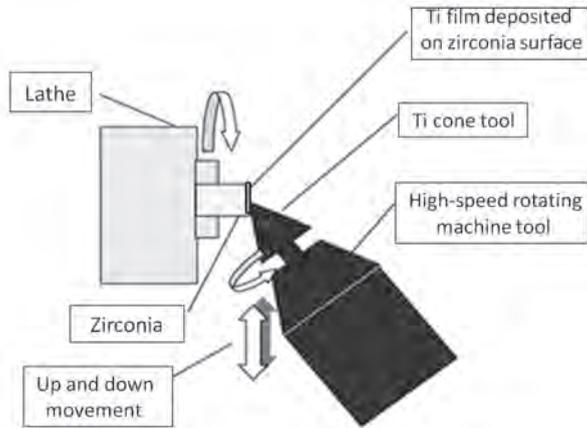


Fig. 1 — Mechanical metallization apparatus.

pretreatments, interfacial segregation, adsorption, and reactions (Ref. 6). In cases of reactive wetting, free energy change is induced because the nature of matter is changed through the chemical reaction at the solid-liquid interface. Young's equation does not describe the process. Even now there is no theory of general consensus to describe satisfactorily wetting and the kinetics of reactive wetting (Refs. 7–12). Spreading kinetics in a given system is strongly affected by the experimental conditions. The same system exhibits different kinetic patterns under different conditions. Hence, it is quite difficult to understand the underlying mechanism and suggest a suitable mathematical model to describe it. In complex reactive systems, chemical reactions, solute segregation, wetting, and spreading are interactively coupled (Ref. 13).

Diamond and the cermet WC-Co (tungsten carbide with a cobalt matrix) are the most-used materials for hard ceramic inserts on drill bits (Ref. 1). Stabilized zirconia has similar hardness and fracture toughness, $K1_C$, when compared with the WC-12Co cermet insert. Although its density is five times lower (Refs. 14, 15), zirconia is thermally and chemically more stable, and it is an interesting material to use as hard inserts for drill bits when the oil well or the drilling fluid has an acid character.

Wettability studies are necessary for the future production of metal-ceramic inserts in order to understand wetting mechanisms and select the best system. So, the temperature and time dependence of contact angle evo-

lution between silver-based braze alloy and zirconia substrates were evaluated. The influence of oxide stabilizers and the surface modification on the wetting behavior of zirconia substrates were also studied. Scanning electron microscopy/energy-dispersive spectrometer (SEM/EDS) technique and thermodynamic approach were used to characterize the interfaces and reaction products generated.

The aim of this work was to study the wetting behavior on mechanically metallized zirconia inserts and compare it with polished substrates using active and nonactive braze alloys. Mechanical metallization is a simple and fast method to metallize ceramics. Numerous advantages are associated with this process: conventional tools can be used, metallization occurs at room temperature, no chemicals are used, no hazardous residues are formed, a large choice of coating metals or alloys is available, easy automation of the process, adaptable for nonplanar surfaces, and applicable to large-scale production (Ref. 16). Mechanical metallization may be an excellent alternative route to conventional metallization (e.g., Mo-Mn process) and certainly to the use of active filler metals in brazing, resulting in significant cost

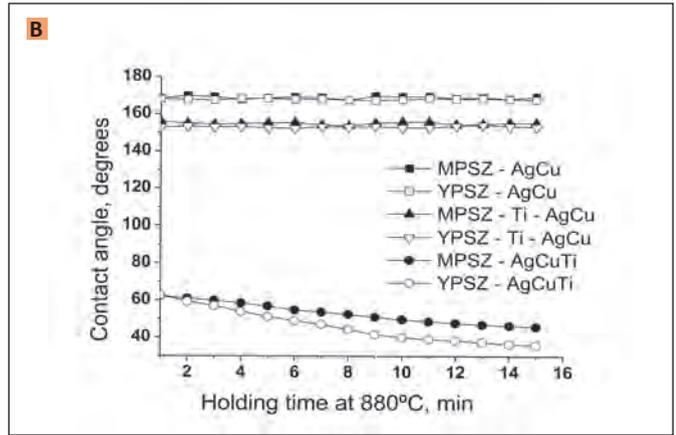
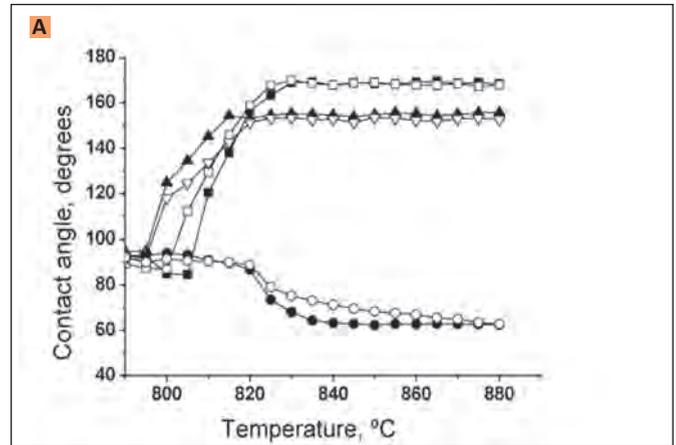


Fig. 2 — A — Contact angle as a function of temperature; B — holding time for six sessile drop experiments with AgCu-based braze alloys on metallized and polished zirconia substrates.

reduction for a wide range of applications (Ref. 17).

Experimental Procedure and Materials

Wetting experiments were performed using silver-based braze alloys onto yttria and magnesia partial stabilized zirconia substrates. The braze alloys tested were the eutectic 72Ag28-Cu at-% (Cusil – Wesgo Metals, Inc.) and the 70.5Ag26.5Cu3Ti at (CB4 – Umicore Precious Metals, Ltd.). Zirconia substrates were produced under an isostatic compression by Engocer-Brazil, using zirconia powder containing 6 wt-% of Y_2O_3 (YPSZ) and with 6 wt-% of MgO (MPSZ) as a sintering aid. The residual porosity was less than 5% and the grain size was in the range of 2–5 μm . YPSZ and MPSZ were cut into shape discs of 10 10 mm, and then divided in two groups: polished and surface Ti metallized.

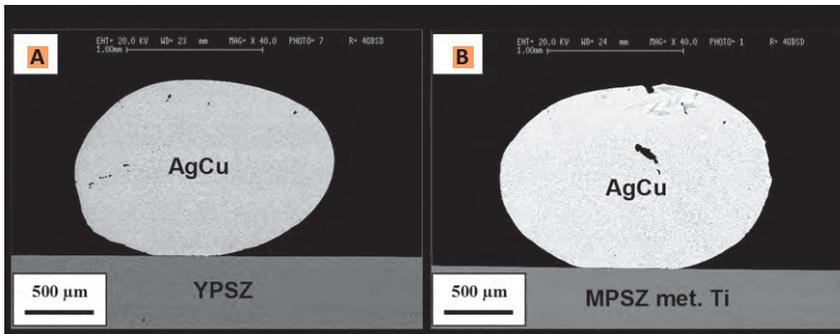


Fig. 3 — SEM view of sessile drop/substrate section. A — AgCu-YPSZ; B — AgCu-MPSZ surface mechanically metallized with Ti.

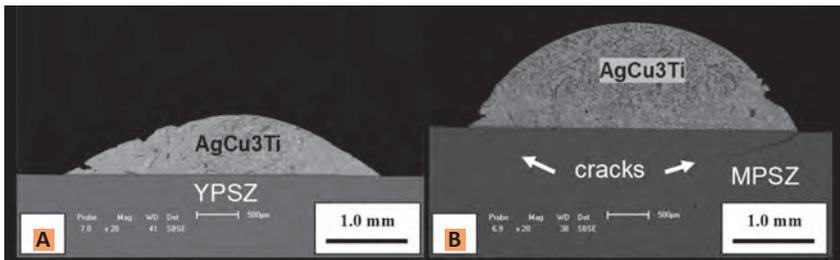


Fig. 4 — SEM views of sessile drop AgCu3Ti/substrate. A — YPSZ; B — MPSZ.

One set of samples was polished utilizing diamond paste to an average roughness, Ra, of about 0.20 μm . The other set was polished with a 15- μm diamond paste and then mechanically metallized with a CP Ti high-speed tool. The Ra measured was about 0.40 μm . It is well known that roughness has a strong influence on the wettability of surfaces (Ref. 5). Controlling Ra, the average slope of surface asperities, is an important consideration to obtain reproducible contact angle values. Special care must be exercised to characterize the surface of industrial polycrystalline ceramics in order to identify such local surface defects as scratches, porosity, or voids due to detached and pulled-out grains during substrate polishing, because they may pin the triple line and influence contact angle (Refs. 6, 13).

Planar ceramic surfaces can be mechanically metallized by frictioning a metal against them. Zirconia discs were fitted onto a lathe, which was rotating counterclockwise. A high-speed rotating cone tool made of Ti (99.9% purity) was placed against the zirconia. During this contact, the relative movement and the friction force promoted the wear of the Ti tool and deposited a metallic film on the planar hard ceramic surface. Studies on mechanical metallization of alumina with

Ti have shown that the quality of the metallic film deposited onto the ceramic is strongly affected by process parameters. These can be adjusted within wide ranges in order to optimize the quality of the films. Nascimento (Ref. 17) investigated some variables of the mechanical metallization process such as the speed of the lathe and the Ti cone tool, contact time, and load, and concluded that the best results in order to optimize the quality of the films (e.g., low distribution of voids) were found using a lathe speed of 800 rev/min, Ti cone speed of 27,000 rev/min, and time contact of 60 s. Adhesion of the Ti film onto the ceramic takes place by particle interlocking and physical bonding (Ref. 16).

Sessile drop technique was used for the wetting experiments, in which a cylindrical-shaped braze alloy, weighing about 0.2 g, was placed onto zirconia substrates. The system was heated at a rate of 5°/min up to 880°C and kept steady for 15 min. The temperature was then lowered down to room temperature at a rate of 3°C/min. All experiments were carried out inside a metallic furnace under a vacuum of 10^{-5} mbar. The furnace consisted of molybdenum heating elements located in a water-cooled stainless steel chamber, with silica glass windows fitted at each end of the stainless steel

tube to enable the illumination from the outside and to record the experiment. The wetting and spreading process was filmed by a CCD video camera and recorded with a speed of 25 frames/s. After the experiment, contact angles were measured with a SCA Dataphysics software directly from the magnified images of the molten braze alloy drop at 5°C intervals up to 900°C, and then every minute during 15 min at the isothermal holding time, with an accuracy of $\pm 4.5^\circ\text{C}$. Finally, the samples were cut, embedded in a resin, and polished for SEM-EDX analysis of a cross section of the interface zone, with the machine operating at 15 kV.

Results and Discussion

Figure 2A and B present the evolution of the contact angle of the AgCu and AgCu3Ti braze alloys vs. temperature and holding time on MPSZ and YPSZ polished and Ti-metallized substrates.

High nonwetting contact angles were found for all AgCu systems. From the beginning, at the melting of AgCu alloy onto polished MPSZ and YPSZ, these systems showed higher contact angles and seemed to stabilize at 830°C close to $\theta = 170^\circ$. The SEM image (Fig. 3A) confirms the results mentioned above. It is clear that AgCu systems show almost a perfect drop shape, and so a nonwetting behavior. Also, it can be noted that there is no surface mechanical interlocking or chemical reaction between the dissimilar materials' surfaces. Ionivalent oxides, like ZrO_2 have high negative values of Gibbs formation energy, and gap energies of several eV, which make them thermodynamically stable and electrical isolators (Ref. 18), and in contact with nonreactive liquid metals (pure or alloys) they exhibit a nonwetting behavior, and contact angles that lie between 110 and 140 deg. Therefore, in nonreactive liquid metal/ionivalent oxide systems, wetting behavior results from physical van der Waals interactions (Refs. 19, 20). Another factor that may contribute to an increase of nonwetting condition is the formation of an oxide skin on the AgCu braze alloy surface. When thick oxide films are formed on a sessile drop, oxidation is evident, because, at melting,

the surface of the liquid is not smooth. The oxide skin layer reported previously may be related with Cu oxides, such as CuO and Cu₂O, instead of Ag oxides, e.g., Ag₂O, which is thermodynamically unstable at brazing cycle temperatures (Ref. 20). Thus, even a very thin skin on the sessile drop does not allow the establishment of a metal/oxide interface, and as a result contact angles are as high as 160 deg.

Stabilizer additives seem to have no influence on wetting behavior for systems with AgCu braze alloy onto zirconia polished and metallized substrates. YPSZ and MPSZ substrates were mechanically metallized with CP titanium in order to activate “in situ” AgCu braze alloy, and make it react with zirconia substrates to produce a reaction layer. Metallized substrates with Ti also produce high contact angles with melted AgCu braze alloy; however, the contact angle finds its equilibrium at $\theta_f = 155$ deg. Indeed, the results showed that the mechanical metallization process improved the AgCu wetting behavior on zirconia substrates; however, still in a nonwetting condition. It is clear that the wetting area AgCu alloy makes on metallized substrates is twice the value of polished ones.

Indeed, when the titanium is exposed to ambient air at room temperature, a passive oxide film is spontaneously formed on its surface. This passive film is amorphous, very thin (5–10 nm thick), and composed of three layers: the first layer adjacent to metallic titanium is TiO, the intermediary layer is Ti₂O₃, and the third layer, which is in contact with the environment, is TiO₂ (Ref. 21). Also, the high-speed friction between the Ti tool and the zirconia substrate produces hot spots during the contact. Some authors reported high flash temperatures (400° up to 600°C) for some severe sliding wear metal-ceramic systems (Ref. 22). Oxidation at high temperatures promotes the development of a crystalline oxide film. Increasing temperature induces the formation of a thicker oxide layer, which is accompanied with dissolution of oxygen beneath it (Ref. 23). These Ti oxide layers are stable at wetting temperatures, and so, act as barriers to atomic mobility between Ti film and the AgCu braze alloy. Deoxidation of initially oxidized film under high temperature

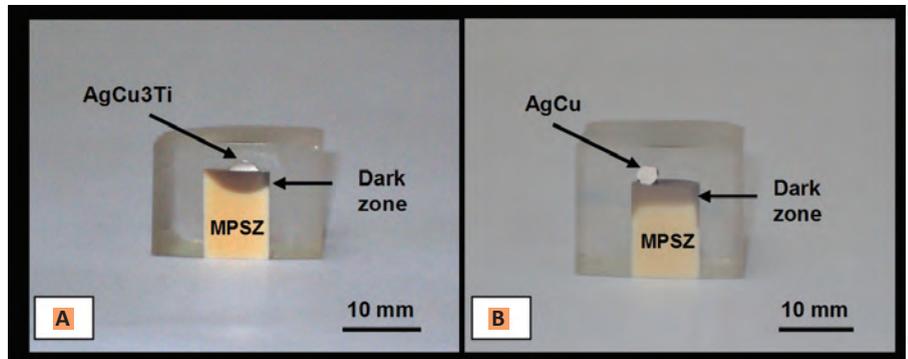


Fig. 5 — Darkening effect in MPSZ caused by the following: A — Ti reactive solute in the AgCu braze alloy; B — the metallic Ti film on MPSZ surface.

and vacuum or in reducing atmospheres would be necessary to disrupt and remove the oxide layer (Ref. 20). However, the classical sessile drop method and the furnace apparatus used turn the previous deoxidation process of the wetting experiment impossible to perform in this work.

As mentioned previously, rough surfaces have a significant influence on the wetting behavior of fluids. Mechanically metallized surfaces have twice the value of roughness ($R_a = 0.40 \mu\text{m}$) than when compared with the polished ones ($R_a = 0.2 \mu\text{m}$). However, it can be noted that in nonwetting systems, metallized substrates show a better wetting condition when compared with the polished substrates. So, in these systems, the roughness effect on wetting behavior of metallic liquids as the main effects may be masked or overcome by the magnitude of interfacial interactions between metal AgCu droplet (or by the oxide skin) and the passive oxide barrier on the Ti film.

To summarize, for nonreactive and nonwetting liquid metal on an oxide system, wetting seems to result from physical van der Waals interactions, which lead to high contact angle values, and improved wetting can be achieved either by adsorption at metal/oxide interface of oxygen supplied by a gas with a controlled partial pressure of oxygen, P_{O_2} , or by introducing a reactive alloying element, like Ti, modifying in situ the interface (Ref. 24).

AgCu with 3% Ti (AgCu3Ti) solute wets zirconia substrates starting from the lower temperatures of the thermal cycle. Contact angle for AgCu3Ti onto YPSZ decreases in a slower manner

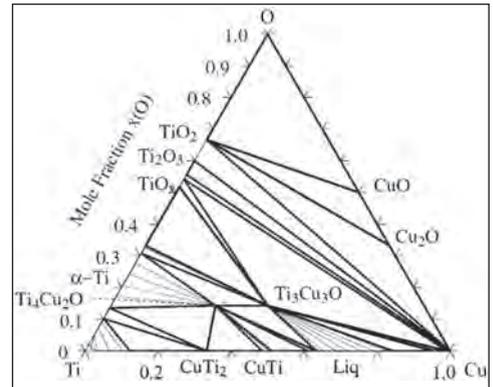
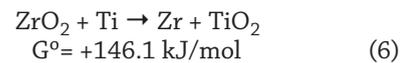
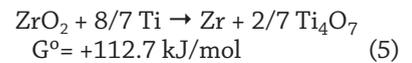
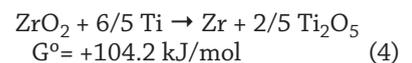
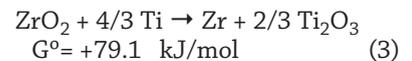
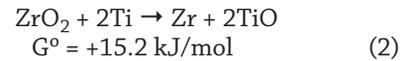


Fig. 6 — Ternary Ti-Cu-O phase diagram at 880°C.

when compared with M-PSZ, and both systems reach a very similar value at 880°C. For the holding time, contact angle continues to decrease and after 10 min reaches a steady value $\theta_f = 40$ deg and $\theta_f = 55$ deg onto YPSZ and MPSZ substrates, respectively. That can be shown on Fig. 4A and B, which corroborate the results exposed earlier in Fig. 2. Contrary results were found by Li et al. using Ti50Al metal alloy onto zirconia substrates with different concentrations of oxide stabilizers, for higher temperatures 1770 K (Ref. 25). These authors found a better wetting for MPSZ than for YPSZ substrates. At high temperatures MgO is prone to decompose due to its high vapor pressure. In vacuum, when MgO contacts with alloy melt, it partially decomposes into element Mg and active O. The element Mg enters the furnace chamber in the form of gas, which provides a favorable condition for metal elements from Ti50Al alloy melt to combine with active O. However, for lower temperatures, the effect of MgO decomposition is not the predominant

the surface zone of oxygen; a pattern of temper colors (blackening) develops in the zirconia ceramic. This pattern begins to be observed at the zirconia /titanium interface and, as the reaction progresses, the blackened region expands. The formation of any of the titanium oxides by a simple reduction of zirconia is not energetically favorable at 880°C, and the possible reactions are according to Santella's (Ref. 27) work as follows:



However, XRD analysis of the dark zone performed by Santella did not reveal the presence of elemental zirconium, but the presence of ZrO (Ref. 27). Zirconia is sensitive to stoichiometric changes (Refs. 18, 31). When zirconia is in contact with active metals, the main role played is the metal to oxygen interaction, and as a result zirconia loses the oxygen and becomes non-stoichiometric. According to Durov et al., such material contains F-centers (anion vacancies, held electrons), which are responsible for the darkening effect of the oxide. Dark zone spreading is due to diffusion of F-centers from the ceramic-metal interface toward the ceramic bulk in a way contrary to oxygen movement (Ref. 30). At the interface, this process may be described as follows:

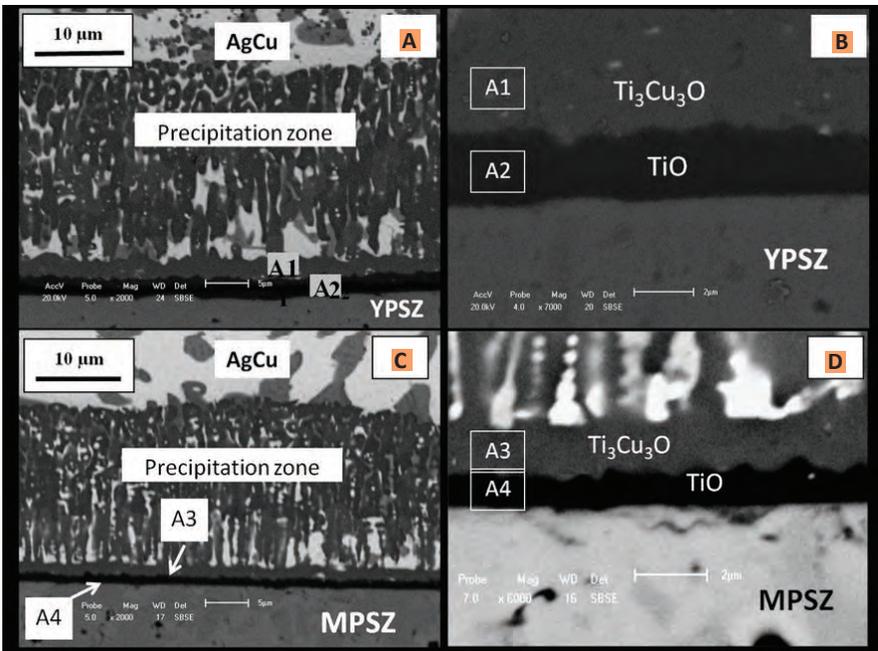
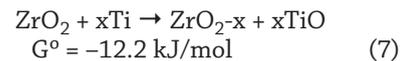


Fig. 7 — Interface microstructure. A, B — AgCu3Ti-YPSZ; C, D — AgCu3Ti-MPSZ.

key factor, but the oxygen ratio. In contact with a reactive solute, Y₂O₃ decomposition provides more active O to the system to react with Ti, and so, shows a slightly decreased contact angle when compared with the system with MPSZ.

AgCu₃Ti reveals a better wettability on YPSZ, suggesting that oxide stabilizers may influence the wetting and spreading, and explain the difference in contact angle values. In general, all systems containing the braze alloy AgCu₃Ti exhibit a good wetting behavior, and there is a chemical reaction layer between the braze alloy and the ceramic substrate. For the AgCu₃Ti/MPSZ, cracks were observed at the interface through the inner ceramic, unlike for YPSZ substrates. The coefficient of thermal expansion (CTE) of MPSZ (5–6.5 · 10⁻⁶/K) is three times lower than that of AgCu braze alloy (Ag: 19.7 · 10⁻⁶/K and Cu: 17.0 · 10⁻⁶/K, respectively) when compared with YPSZ (9 · 10⁻⁶/K) (Refs. 14, 26).

During cooling from the wetting temperature, this high mismatch on CTE produces an internal stress that may lead to failure. The type of failure observed is used to qualitatively characterize the mechanical strength of the MPSZ-brazing alloy bond. In this study, cohesive failure was observed, which takes place in the zirconia substrate, and leads to the conclusion that the interface is stronger than the zirconia itself. A darkening effect was observed on zirconia substrates in the region of the interface (Fig. 5A and B), as also reported by several authors (Refs. 26–30). This effect was also observed on metallized zirconia substrates (nonreaction systems).

So, this effect happens in zirconia when in contact either with an active melt (e.g., AgCu₃Ti) or with a solid active film (metallized Ti) on its surface. The addition of Ti to silver-copper eutectic alloy promotes wetting, and during this process the active element titanium reacts with zirconia, depleting

Table 1 — Results of Microprobe Analysis for the Reaction Layer Zones of the AgCuTi/YPSZ and MPSZ Systems and Thickness

Layer	Chemical Composition (t-%)							Thickness (µm)
	Ag	Cu	Ti	Zr	Y	Mg	O	
A1	5	39	43	1	—	—	12	2.5–3
A2	1	5	47	3	1	—	43	2
A3	7	38	41	1	—	—	13	1.5–2
A4	3	7	42	8	—	3	37	1

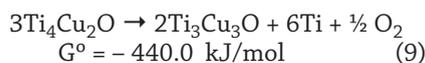
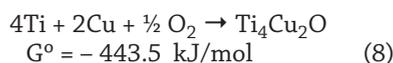
This process is thermodynamically favorable to occur at 880°C, and the dark zone spreading is subordinated to parabola law as investigated by Durov and coworkers (Ref. 30).

The extensive oxygen vacancy presence in stabilized zirconia due to the introduction of aliovalent cations (MgO or Y₂O₃), and the stabilization of the cubic phase to lower temperatures will also allow the zirconia phase to withstand high degrees of nonstoichiometry.

Also, it was observed that the darkening area was more pronounced on the YPSZ substrates due to higher presence of aliovalent impurities and F-centers than for MPSZ ones.

For the chemical analysis of the Ag-CuTi/zirconia systems, reaction products can be understood by the thermodynamics of the Ti-Cu-O system (Fig. 6), and, similar to studies with the joining of zirconia or alumina using AgCu filler metals with Ti, as a reactive element (Refs. 26, 30, 32, 33). The formation of M₆X-type compounds, like Ti₄Cu₂O or Ti₃Cu₃O and Ti oxides, at the interface are characteristic of these systems (Refs. 34, 35).

Using previous studies from Arroyave (Ref. 34) and Kelkar et al. (Ref. 35), and the free energy of formation M₆X-type compounds, Ti₄Cu₂O and Ti₃Cu₃O, at 880°C are given by



The high negative values suggest that these reactions are susceptible to occur, and the reaction products are thermodynamically stable even at 880°C.

Singh et al. calculated ΔG values of oxides as a function of temperature. These calculations suggest that the primary oxides of Ti have the largest negative ΔG values, and are therefore thermodynamically stable from room temperature up to 1300°C (Ref. 26). Although the formation of Ti₄O₇, Ti₃O₅, Ti₂O₃, and TiO₂ are thermodynamically more stable than TiO in a oxygen-rich atmosphere, under high-vacuum conditions, the formation of TiO is expected (Ref. 36).

The chemical reaction between the

brazo alloy and the zirconia results in two clear reaction layers at the interface, as can be seen from Fig. 7A–D. Table 1 presents the chemical composition of these layers and its thickness. SEM analysis of the microstructure of the AgCu3Ti zirconia substrates (Fig. 7A and C) showed that it is composed of a eutectic AgCu matrix containing particles with a composition close to Ti₂Cu intermetallic presented in the Cu-Ti phase diagram. Strong Cu-Ti interactions decrease the Ti activity at the metal-ceramic interface, and can also modify the type of Ti compound formed at the interface, as also reported by Valette et al. (Ref. 37). It can be seen there is a precipitation zone of small and dendritic precipitates, which have a chemical composition in the Cu-Ti system.

For the AgCu3Ti/YPSZ pair, the first layer (A1), with light gray color, is adjacent to the braze alloy, and has a thickness of about 2.5 to 3 μm . This layer is rich in Cu, Ti, and O. According to Kelkar et al. (Ref. 38), it can be attributed to Ti₃Cu₃O, M₆X-type compound as commented on previously. These results also match those from Muolo et al. (Ref. 39) working on similar systems using zirconia and AgCu-based braze alloy with 5 at-% Ti, and with Voytovych and co-workers (Ref. 32) who found the same results on AgCu-Ti (2.9 at-%) onto alumina. Indeed, EDX analysis of layer A1 gives a Ti-Cu ratio close to unity, consisting of Ti₃Cu₃O compound. The second layer (A2), bordering the substrate, is about 2 μm thick and Ti-rich and O-rich. The ratio O/Ti = 0.91, corresponding to TiO_{0.91} as a reaction product, and so fairly attributed to TiO compound. The AgCu3Ti-MPSZ system shows similar results as the one on YPSZ discussed previously. The layer A3, facing the braze alloy, is also a Ti-Cu-O-rich phase, in a proportion that suggests the formation of Ti₃Cu₃O. The layer A4 is a thin layer with 1- μm -thick Ti- and O-rich elements in a ratio of O/Ti = 0.88, and so correlated with the TiO oxide.

However, it is important to point out that the interaction volume generated by elastic and inelastic scattered electron beam inside the substrate material was calculated using Monte-Carlo simulation and led to region volume of 3 μm^3 and an estimated depth

of analysis in a range of 1.5 μm . This indicates the reaction layer analysis could receive chemical information from the adjacent zones, overcoming the presence of a small amount of Ag, Cu, Zr, and Y or Mg, depending on the zirconia substrate.

To sum up, the reactions' process can be described as follows: at the early stages of the zirconia/braze alloy interactions, oxygen will diffuse out of the zirconia lattice. Due to the strong Ti-O interaction, Ti will segregate to the zirconia/braze alloy interface (Ref. 38). Since in all these wetting experiments the braze alloy interlayer was a thin foil of about 50 μm , it is expected that this titanium segregation will cause the titanium content in the brazing alloy to decrease as the interfacial reaction progresses. Since most of the titanium will be present in the reaction layers at the zirconia/braze alloy interface, a diffusion path in this case will begin with the highest activity of titanium in the reaction layer immediately adjacent to the zirconia surface. Using the Arroyave (Ref. 34) calculations for these wetting conditions, the phase with the highest driving force (2.73) for precipitation was TiO, and it is therefore expected that this phase will be found adjacent to the zirconia surface. The titanium activity decreases monotonically toward the reaction product with the lowest Ti activity, and lowest driving force (1.49) Ti₃Cu₃O will precipitate adjacent to the braze alloy.

The reaction layer of AgCu3Ti/YPSZ systems is almost twice as thick as the ones from AgCu3Ti/MPSZ pairs. Both systems showed the same reaction products formed at the interface. This means that the nature of the reaction products is not influenced by the type of oxide stabilizers in PSZ, but the kinetics of wetting and the rate of reaction layer growth are.

Wettability depends on the bonding characteristic of the new phase formed at the interface. When a reactive solute Ti is provided to the AgCu/zirconia system, liquid Ti can react to dissolve several at-% O (up to 34 at-%) (Ref. 20) and form semimetal character oxides, such as TiO and Ti₃Cu₃O. The excellent wetting behavior observed for this system can be explained by the double in situ modification of the interface, i.e., the adsorption of oxygen at the liquid side and

the formation of a semimetallic oxide at the solid side. At the interface between a metal and a metal-like compound, bonding would be at least partially metallic, leading to high adhesion energy and better wetting than in metal-ionovalent compound systems (Ref. 20). Indeed, the formation of Ti_3Cu_3O and TiO compounds at the interface play the major role in wetting of $AgCu_3Ti$ /zirconia systems. Naidich found good wettability of Cu droplet onto $TiO_{0.86}$, due to its metallic character ($\rho = 3 \cdot 10^{-4} \Omega m$) (Ref. 40). But also the excellent wetting can be explained by the formation of Ti_3Cu_3O , which is known to have a metallic character, as shown by its electrical resistivity ($\rho = 5 \cdot 10^{-6} \Omega m$), similar to those of Ti alloys ($\rho = 1.5 \cdot 10^{-6} \Omega m$) (Ref. 32), and much lower than that of zirconia ($>10_{12} \Omega m$ (Ref. 14)).

The system $AgCu_3Ti$ -YPSZ showed better wetting and spreading behavior, and no cracks of any origin were observed. On the other hand, the counter pair $AgCu_3Ti$ -metal should not present any wetting, spreading, and adhesion problems, since it's well known that liquid metals wet metallic substrates whatever the intensity of interfacial interaction unless the metallic surfaces are oxidized (Ref. 20). So, based on these assumptions, this system seems to be suitable for the production of strong and reliable metal-ceramic joints with an insert fitting on steel cone drill bits for oil drilling operations when using acid fluids.

Conclusions

Contact angle and microstructure at the interface of partial PSZ with yttria or magnesia, polished and mechanically metallized with Ti substrates using $AgCu$ -based brazing alloys, with or without active elements, were studied in order to produce metal/ceramic joints to use on drill bits.

1) $AgCu$ eutectic alloy does not wet zirconia substrates, as also reported by other authors. Contact angles are higher than 90 deg, and so present a nonwetting condition. Contact angles for polished YPSZ and MPSZ zirconia have close values, about $\theta_f = 170$ deg, and are about a magnitude of 20 deg higher than for the mechanically metallized zirconia systems.

2) Indeed, the metallization process

of zirconia substrates increases the wetting behavior; however, it is still in a nonwetting condition, $\theta_{eq} > 90$ deg. Oxidized Ti film on zirconia substrates acts as a barrier to wetting.

3) Roughness seems to have no influence on wetting for the inert systems. Indeed, systems with metallized substrates have higher Ra values and show lower contact angles when compared with systems with polished zirconia. The magnitude of interfacial interactions may overcome the effect of roughness on the contact angle.

4) Good wettability and spreading was found with $AgCu_3Ti$ in all substrates. The presence of reactive solute Ti improves wettability and spreading on zirconia substrates by the formation of wettable compounds at the interface. $AgCu_3Ti$ reacts with zirconia substrates to form $TiOx$ and M_6X -type compounds, which are responsible for the excellent wetting behavior. It can be concluded that in these systems, zirconia stabilizer oxides do not have influence on the nature of reaction products formed at the interface; however, they do have influence on the kinetics of the reaction layer growth, and so on the wetting behavior.

5) Presence of cohesive cracks in the $AgCu_3Ti$ -MPSZ system may be due to the mismatch of CTE between ceramic substrate and the braze alloy.

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