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Review

Recent Advances on the Brazing of the Titanium Alloys to Oxide Ceramic Materials: A Comprehensive Review Study

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Abstract:
To fabricate components with exceptional properties, the joining of various titanium alloys with oxide ceramic materials (such as Al_2O_3, ZrO_2, and SiO_2) can significantly increase their application potential. This approach is particularly appealing for various applications that require materials with high-temperature resistance, wear resistance, and thermal stability, such as automotive and aerospace parts. However, there are various challenges, such as differences in their coefficients of thermal expansion (CTE) and Young's modulus in joining the titanium alloys to oxide ceramic materials. Among various joining techniques, the brazing method is a promising and cost-effective approach for joining titanium alloys to oxide ceramics. However, several technical challenges remain to be addressed for achieving successful dissimilar joints. This review aims to highlight these challenges and discuss the latest progress in developing brazed joints of titanium alloy to oxide ceramic materials, including Al_2O_3, ZrO_2, and SiO_2. In this review, for the first time, the parameters affecting the microstructure and mechanical properties of the Ti/oxide ceramic materials are reviewed and summarized.

Keywords: Titanium alloys, Oxide ceramics, Brazing, CTE, Mechanical properties.

1- Introduction

Joining metal to ceramic materials is important because these types of joints can combine the mechanical, physical, and thermal properties of both ceramic and metallic materials. Ceramic materials, though, have high hardness and mechanical strength values; they suffer from high brittleness. On the other hand, the metals and their alloys have generally lower mechanical strength values with higher ductility and formability. The joining of the alloys and ceramics can form structures with high mechanical strength and high ductility [1-10]. Up to now, various methods, including diffusion bonding [11-13], welding methods [14-18], brazing [19-23], etc., have been applied for bonding of the metals to alloys. Among joining methods, the brazing approach has many advantages, such as lower processing temperature, cost-effectiveness, and flexibility in materials compatibility, compared to the other methods.

Oxide ceramic materials such as Al_2O_3, ZrO_2, and SiO_2 are known as materials with high melting points, high mechanical strength and hardness values, high corrosion resistance, high electrical and thermal insulation, making them outstanding materials for many applications from electronics to aerospace [24-27]. However, the high brittleness of the oxide ceramics materials limits their processability and formability. In addition to the fundamental approaches for improving the intrinsic brittleness of the ceramics (such as coating methods, composite formation, etc.), joining with metals and alloys can improve the ductility of the ceramic materials [1, 4, 28, 29]. Titanium alloys, such as Ti-6Al-4V, owing to their low density, high ductility, and high specific strength values, can be introduced as the proper materials for joining with oxide ceramics [30-32].

In the brazing, the active elements of the brazing materials provide wettability and adhesion through chemical reactions with ceramic materials. One of the major challenges of joining metals to ceramic materials is their difference in the coefficient of thermal expansion (CTE). Therefore, researchers are focusing on the reduction of the CTE of the brazing filler materials by various methods, such as the addition of materials with low CTE [32].

The success of the brazing method for achieving reliable titanium alloys/ oxide ceramics joints with high mechanical strength, various factors, such as brazing process parameters (such as temperature, time, atmosphere, surface pre-treatment of metals, etc.), and filler materials are important. To the best of the author's knowledge, up to now, there is no review study regarding the brazing of the titanium alloys/ oxide ceramics joints by focusing on the filler materials. Therefore, this study, for the first time, aims to investigate the affecting parameters on the microstructure and mechanical properties of the titanium alloys/ oxide ceramics joints produced by brazing methods. In this work, the brazing of titanium and its alloys with three oxide ceramics of the Al_2O_3, ZrO_2, and SiO_2 is investigated and compared. In the following sections, based on the most common types of filler materials, the main affecting parameters on the microstructure and mechanical properties of the titanium alloys/oxide ceramic joints are reviewed and discussed.

2- Brazing of the Ti/Al_2O_3 joints

According to the literature, for brazing of the titanium alloys to Al_2O_3, various filler materials, including Ag-based filler, Cu-based filler, high entropy alloys (HEAs), and Ti-based filler materials, have been used. Fig. 1 schematically shows the main filler materials and provides their main affecting parameter and main properties. Table 1 also shows the main findings of the Ti alloys/Al_2O_3 joints using various filler materials that were reviewed in this study.

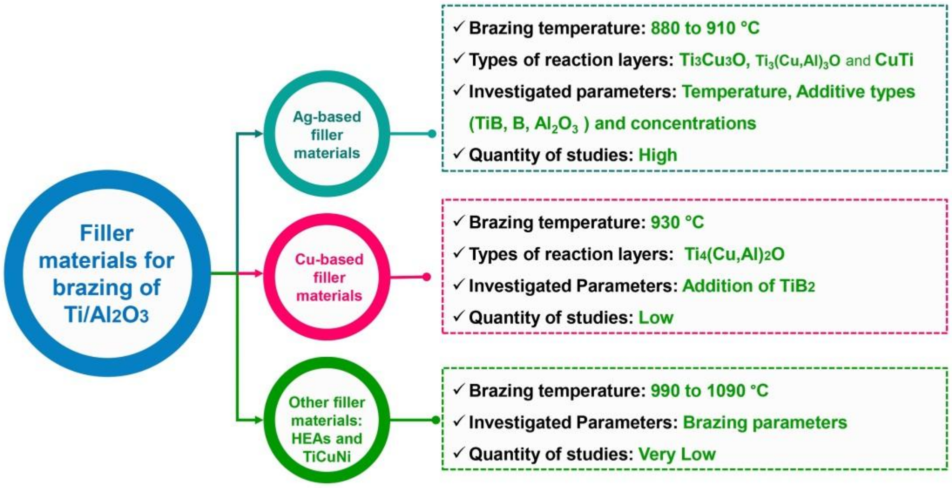

Fig. 1. The main filler materials for brazing of titanium alloys to Al_2O_3 and their details.

Table 1. The summarized information on the brazing process of Ti/Al_2O_3 joints

Joints	Filler materials	Brazing condition	Parameter	Shear strength	Reference

Al_2O_3/ Ti6Al4V	$(Ag_{72}Cu_{28})_{97}Ti_3$	910 °C for 10 min	Brazing temperature	33.3 MPa	[33]
Al_2O_3/ Ti_2AlNb	AgCu28/ Al_2O_3 composite filler	880 °C for 10 min	Concentration of Al_2O_3	110.49 MPa	[34]
Al_2O_3/ Ti_2AlNb	AgCu+ B composite filler	880 °C for 10 min	Concentration of B	111 MPa	[35]
Al_2O_3/ TiAl	Ag-Cu-Ti	880 °C for 10 min	Concentration of TiH_2	102 MPa	[36]
Al_2O_3/ Ti6Al4V	Cu-TiB_2 composite filler	930 °C for 10 min	Concentration of TiB_2	96.76 MPa	[37]
Al_2O_3/ Ti6Al4V	Ag–Cu–Ti + B	850 °C for 10 min	Brazing time, temperature, and titanium content	78 MPa	[38]
Al_2O_3/ Ti6Al4V	65.9Cu–24.4Ti–9.7TiB_2 composite filler	930 °C for 10 min	Brazing temperature	143.3 MPa	[39]
Al_2O_3/ Ti6Al4V	AlZnCuFeSi HEA	980 °C for 10 min	Concentration of Al_2O_3	84 MPa	[40]
Al_2O_3/ Ti6Al4V	TiCuNi	1050 °C for 60 s	-	168 MPa	[41]

In the following sections, the main affecting parameters on their mechanical properties are discussed.

2-1- Brazing of the Ti/Al_2O_3 joints with Ag-based filler materials

Ag-based filler materials are widely used for joining metal to ceramic materials owing to their several advantages, such as low melting range, excellent wettability, and fluidity, ensuring strong adhesion to both metals and ceramic materials [42-46]. However, to achieve stronger and more durable joints, the brazing parameters such as temperature and holding times should be optimized. For example, Wu et al. [33] studied the effects of different brazing temperatures (850-940 °C) for joining the Ti6Al4V/Al_2O_3 using $(Ag_{72}Cu_{28})_{97}Ti_3$ filler. Their results showed that at lower temperatures (850°C), limited diffusion and thinner reaction layers of Ti_3Cu_3O and CuTi phases were formed. When the brazing temperature increased to 910 °C, Ti_3Cu_3O and Ti_2O at the Al_2O_3 interface and CuTi and Ti_2Cu are formed via interdiffusion at the Ti6Al4V side. The shear strength values of 17.8, 23.6, 33.3, and 26.5 MPa were achieved for the brazed samples at 850 °C, 880 °C, 910 °C, and 940 °C, respectively. At lower temperatures than 910 °C, poor wetting and a thin reaction layer were observed, while at higher temperatures of 940 °C, excessive diffusion resulted in thicker, brittle layers.

In addition to the brazing parameters, the results of the previous studies have shown that the addition of some particles, such as TiB, B, Al_2O_3, etc., to the Ag-based filler materials can improve the mechanical properties of the Ti/Al_2O_3 joints by various mechanisms. For example, as mentioned earlier, the addition of particles can decrease the CTE mismatch between the Al_2O_3 and titanium alloys. The inclusion of the Al_2O_3 particles into the brazing filler materials can reduce the CTE mismatch. Moreover, these particles can act as a crack barrier, increasing the load-bearing capacity of the joints. In the study of Peng et al. [34], they investigated the effects of the addition of different contents of micron-sized Al_2O_3 particles (2, 4, 6, and 8 wt.%) in the $AgCu_{28}$ filler metal for the brazing Al_2O_3/Ti_2AlNb joints. The brazing process was performed at 880 °C for 10 min in the vacuum furnace. Fig. 2 presents the SEM images of the brazed samples with 0, 2, and 8 wt.% Al_2O_3 particles and the mechanical properties of the joints. As can be seen in Fig. 2a and 2b, the microstructure of the brazed samples consisted of four distinct zones. In Zone 1, at the Ti_2AlNb side, the $AlCu_2Ti$ intermetallic and Nb-rich solid formed an Ag-Cu eutectic matrix with dispersed Cu-Nb phases in Zone 2. In the brazing seam, zone 3, in the case without Al_2O_3 particles, the Ag-Cu eutectic + blocky $AlCu_2Ti$ was formed. However, by the presence of the Al_2O_3 particles, the Ag-Cu matrix + Al_2O_3 particles surrounded by $Ti_3(Cu,Al)_3O$ was observed. At the Al_2O_3 side, zone 4, by diffusion of the titanium from the Ti_2AlNb, the continuous $Ti_3(Cu,Al)_3O$ reaction layer was formed. As can be seen in Fig. 2c, the excessive Al_2O_3 particles caused to occurrence of the aggregation phenomenon in the brazing seam. As can be seen in Fig. 2d, the mechanical tests showed that there is an optimal concentration of Al_2O_3 particles for achieving the highest shear strength and hardness values. For example, the shear strength values of 110.49 MPa were obtained for the joints with 2 wt.% Al_2O_3, which was about 30% higher than that of joints without Al_2O_3 (85 MPa). However, the addition of the Al_2O_3 particles beyond 2 wt.% resulted in the reduction of the shear strength owing to due to excessive Ti_3Cu_3O and aggregation of the particles that increased brittleness. Their results showed that although the $Ti_3(Cu,Al)_3O$ was necessary for adhesion, its excessive formation (in the case of high concentrations of Al_2O_3 particles) had detrimental effects on the joints (Fig. 2e).

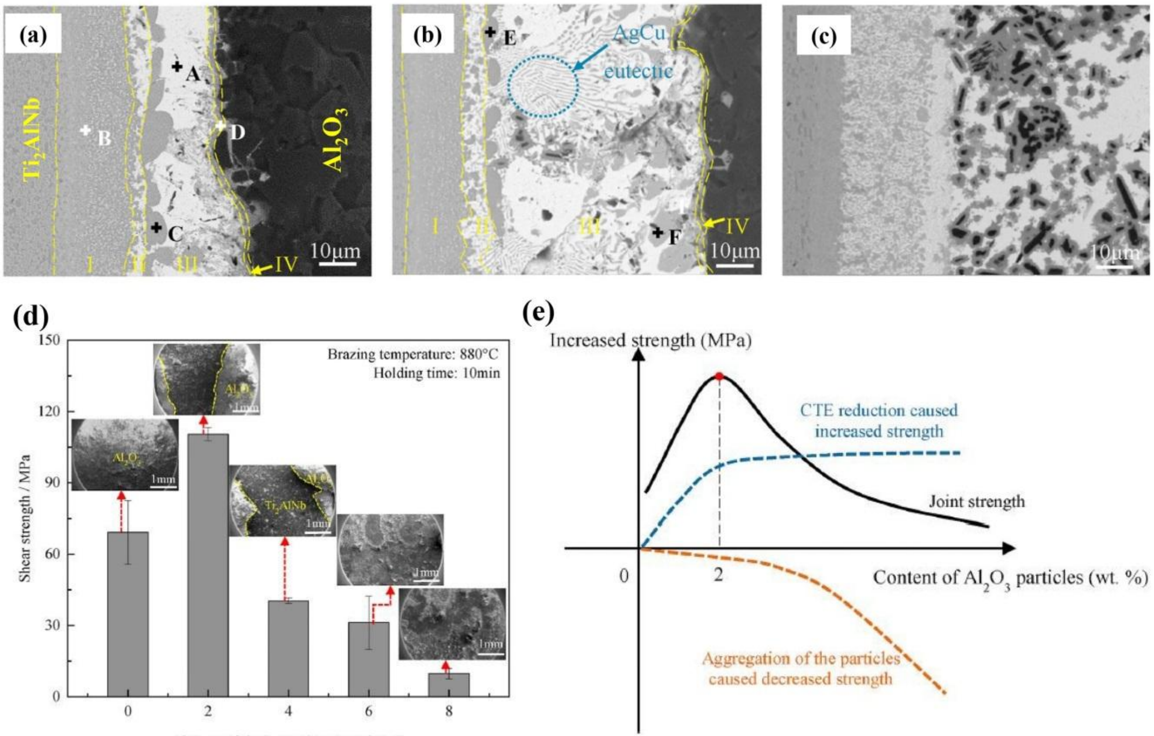

Fig. 2. The SEM images of the Al_2O_3/Ti_2AlNb joints brazed with $AgCu_{28}$ with (a) 0 wt.% Al_2O_3, (b) 2 wt.% Al_2O_3, (c) 8 wt.% Al_2O_3, (d) shear strength of samples, and (e) change of the properties of joints as a function of Al_2O_3 contents, reproduced from [34].

Some studies have shown that the addition of some elements, such as boron (B), can reduce the brittleness of the Ti/Al_2O_3 joints by the formation of the TiB whiskers and reduction of the Ti-Cu intermetallic. For example, Qiu et al. [35] studied the effects of the addition of different contents of B (0 to 1.5 wt.%) in the eutectic Ag-Cu filler for brazing of the Ti6Al4V/Al_2O_3 joints. In their work, the Ag-Cu filler and B powders were milled to form Ag-Cu+ B composite filler. The brazing process was conducted at temperatures of 840-920 °C for 10 min under a vacuum environment. Fig.

3 shows the microstructure and mechanical properties of the Ti6Al4V/Al_2O_3 joints brazed with Ag-Cu filler with different contents of B powders. As can be seen in Fig. 3a to 3d, the SEM analysis proves the formation of the TiB whiskers with a diameter range of 0.1 to 0.3 µm and Ti_2Cu_3 particles in the brazing seam. By the diffusion of the titanium from the Ti6Al4V side to the Al_2O_3 side, the Ti_3Cu_3O layer with a thickness of 1.5 µm was formed, improving the adhesion. The investigation of the brazing temperature revealed that the optimal brazing temperature was 880 °C, which resulted in a shear strength value of 85 MPa (Fig. 3e). The effectiveness of the addition of B in improving the shear strength of the samples was dependent on their concentrations. The addition of the 0.5 wt.% B resulted in increasing the shear strength to 111 MPa while further increment of the B concentration to 1.5 wt. % reduced it to 72 MPa. The formation of the excessive TiB was introduced as the main reason for the brittleness of the samples with 1.5 wt. % B.

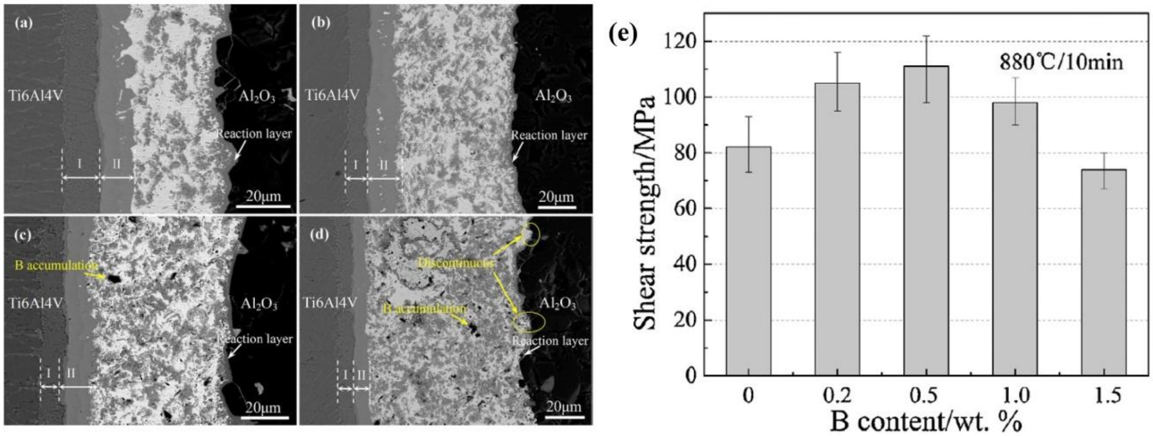

Fig. 3. The SEM images of the Ti6Al4V/Al_2O_3 brazed with Ag-Cu filler with different content B, (a) 0.2 wt.%, (b) 0.5 wt.%, (c) 1.0 wt.%., (d) 1.5 wt.%, and (e) relationship between the shear strength and B content in filler materials, reproduced from [35].

In another study, the effects of titanium contents, by the addition of different contents of TiH_2 (0-0.8 wt.%) in Ag-Cu-Ti brazing filler, was investigated on the brazing of the TiAl/ Al_2O_3 joints was investigated by Niu et al. [36]. The brazing processes were conducted at different temperatures (840- 940 °C) and holding times (0-30 min). Fig. 4 presents the SEM images of the microstructure of the samples with different concentrations of TiH_2. The reaction of the titanium with Al_2O_3 formed the stable $Ti_3(Cu,Al)_3O$ reaction layer that promotes strong chemical bonding at the interface. At the TiAl side, the dissolution of TiAl into the molten filler leads to the formation of $AlCu_2Ti$ and AlCuTi intermetallics. In the case of brazing times and temperature, the highest shear strength value of 102 MPa was obtained at 880°C for 10 min. The study demonstrated that the optimal TiH_2 concentration in the filler metal was 0.2 wt.%, which yielded the highest shear strength in the brazed joints. Microstructural analysis revealed that without adding Ti, only a thin $Ti_3(Cu,Al)_3O$ layer formed, as the active Ti from TiAl dissolution was insufficient to develop a reaction layer of adequate thickness. Increasing the Ti content caused to increase in the thickness of the $Ti_3(Cu,Al)_3O$ reaction layer, which initially enhanced joint strength. However, further increases in Ti led to a significant increase in the formation of brittle $AlCu_2Ti$ compound, causing large residual stresses within the joint. Consequently, excessive Ti content was detrimental, as the overly thick $Ti_3(Cu,Al)_3O$ layer combined with abundant brittle IMCs reduced the mechanical performance of the brazed joints.

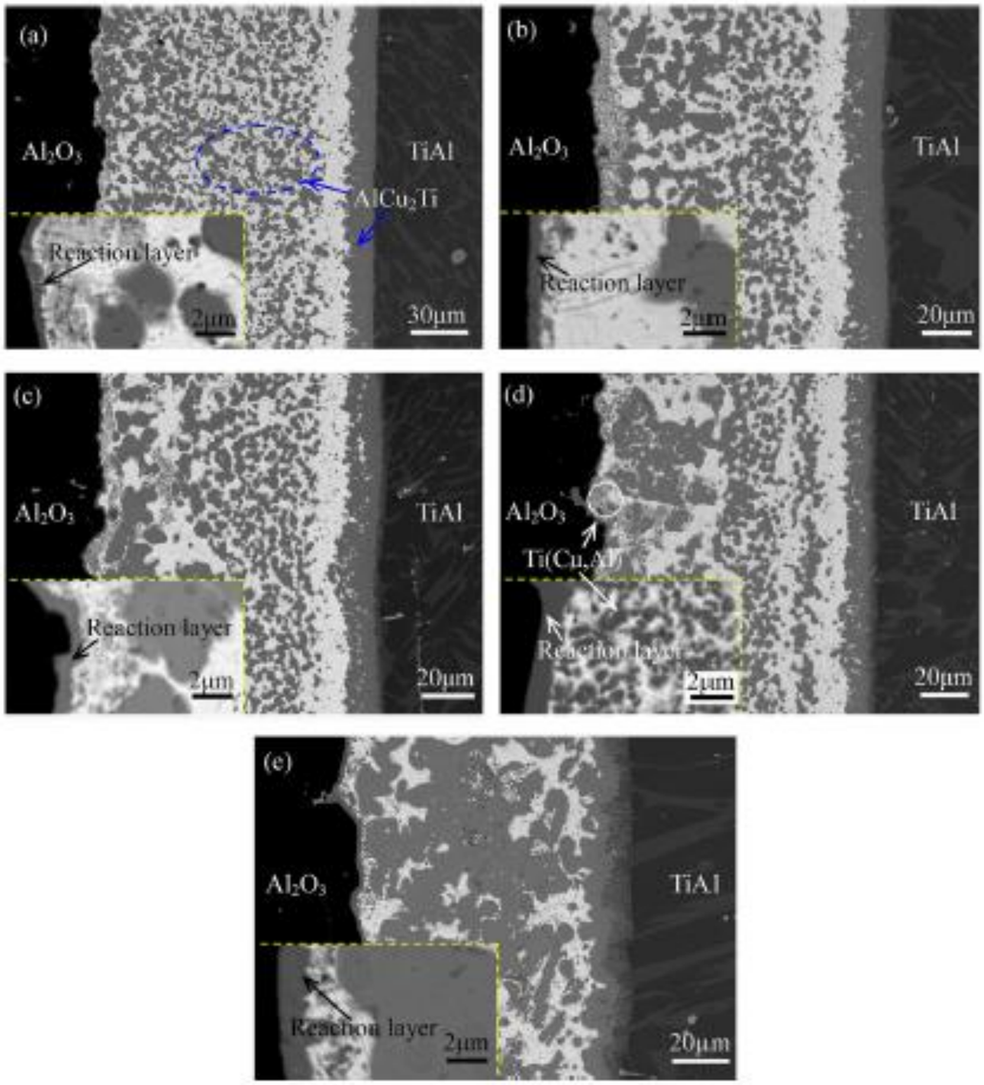

Fig. 4. SEM images of the TiAl/ Al_2O_3 joints brazed with Ag-Cu-Ti brazing with different content of TiH2, (a) 0 wt%, (b) 2 wt.%, (c) 4 wt.%, (d) 6 wt.%, and (e) 8 wt.%, reproduced from [36].

For the investigation of both titanium and Boron, in another study, Yang et al. [38] focused on using Ag–Cu–Ti + B filler to situ synthesize TiB whiskers within the brazing seam. In this work, the fillers were prepared so that the 20 vol.% TiB was in the joint. Moreover, the effects of different contents of the titanium were also investigated in this study. For evaluation of the brazing temperature, the brazing process was done at different temperatures of 850 to 950 °C for 10 min. Moreover, the brazing at 900 °C for different holding times (5 to 30 min) was conducted to evaluate the effects of brazing time. The microstructural evaluations showed that the oxide and intermetallic, such as $Ti_3(Cu,Al)_3O$ and Ti_2Cu + $Ti_2(Cu,Al)$ were formed at the Al_2O_3 side while Ti +Ti_2Cu were formed at the Ti6Al4V side. The results showed that increasing the brazing temperature, time, and content of titanium resulted in an increase of the Ti_2Cu and $Ti_2(Cu,Al)$ and a reduction of the TiCu and Ti(Cu,Al) phases. The increased brazing temperature caused the $Ti_3(Cu,Al)_3O$ to be discontinued at the Al_2O_3 side. In the case of titanium content, there was an increasing trend in the shear strength of samples as a function of titanium content up to 10 wt.%

and reaching to shear strength value of 52 MPa, Further increasing, the shear strength decreased. The maximum shear strength achieved was 78 MPa at 850°C for 10 min with optimal Ti and B content.

2-2- Brazing of the Ti/Al_2O_3 joints with Cu-based filler materials

Cu-based filler materials are a good material for the brazing of titanium alloys to ceramic materials owing to their various advantages. The Cu-based fillers generally have lower melting points compared to conventional titanium-based fillers, enabling brazing at temperatures below the β-transus of titanium alloys [47-49]. In one of these studies, Yang et al. [39] studied the use of a 65.9Cu–24.4Ti–9.7TiB_2 (wt.%) composite filler to join Al_2O_3 ceramics and Ti–6Al–4V alloy via vacuum brazing. TiB_2 particles react with Ti in the filler to form 30 vol.% TiB whiskers during brazing. In their work, the composite filler was prepared using the milling of the Cu, Ti, and TiB_2 powders. The brazing was conducted at different temperatures (890 to 970 °C) and holding times (5 to 30 min). From Ti6Al4V to Al_2O_3 sides respectively the Ti+Ti_2Cu, TiB whiskers, Ti_2(Cu,Al), and $Ti_4(Cu,Al)_2O$ were formed. Their results showed that by increasing the brazing temperature from 890 to 930 °C, the shear strength of samples increased, while by further increasing the temperature, the shear strength decreased owing to the excessive Ti_3Al formation. The highest shear strength value of 143.3 MPa was obtained for brazing at 930 °C for 10 min, as an optimal brazing condition.

In another study, Yang et al. [37] studied the effects of TiB contents in Cu-TiB composite filler. In their work, the composite fillers were fabricated using the ball milling of Cu and different contents of the TiB_2 powders (5-50 vol.%). The brazing process was conducted at different temperatures of 930 °C to 970 °C for min under a vacuum environment. The microstructural evaluation of the samples with and without TiB_2 showed that the Ti_2Cu/Ti_3Al phases and cracks near Al_2O_3 due to CTE mismatch were observed, while the $Ti_4(Cu,Al)_2O$ phase formed in the case of the addition of TiB_2. They investigated the shear strength values of the samples at different temperatures, and in all cases, the addition of the TiB_2 was effective in increasing the shear strength. The optimal concentration of the TiB_2 was identified as 30 vol.%, and the shear strength values of 96.76 MPa and 115.16 MPa, respectively, were achieved at room temperature and 800 °C. The fracture analysis of samples revealed a change in the fracture mode from brittle in the case without TiB_2 to ductile by the addition of TiB_2. It can be said that the TiB inhibited crack propagation and dispersed brittle intermetallic.

2-3- Brazing of the Ti/Al_2O_3 joints with other filler materials

Although the Ag-based fillers are common for joining the Ti6Al4V/Al_2O_3 joints, they limit the application of the joint for high temperatures. Therefore, recently, other filler materials such as Ti-based and high entropy alloys (HEAs) filler materials have been introduced for brazing of the Ti/Al_2O_3 joints. For example, Alves et al. [41] investigated the microstructure and mechanical properties of Ti6Al4V/ Al_2O_3 brazed joints using a TiCuNi filler. TiCuNi (Ti–15Cu–15Ni wt.%) filler is specifically designed to react with ceramics and metals, promoting strong chemical bonding at the interface. The vacuum brazing was done at 980 °C for 10 min. The microstructure of the samples showed the formation of the Ti_2(Cu,Ni) particles, and lamellar α-Ti + Ti_2(Cu,Ni) regions at both Al_2O_3 and Ti6Al4V sides. The mechanical tests revealed the achievement of the high shear strength of 168 MPa and the hardness value of 1261 HV.

The advantage of the HEAs as filler materials is that the formation of brittle intermetallic compounds can be suppressed by them, and ductile solid solutions can be replaced with it [50-53]. Sharma and Ahn [40] investigated the brazing of the 3D-printed Ti–6Al–4V alloy to Al_2O_3 using AlZnCuFeSi HEA. Owing to the absence of expensive elements in AlZnCuFeSi HEA, it is more cost-effective than Ag-based filler materials. The brazing processes were conducted at different temperatures (990 to 1090 °C) and different holding times (20 to 120 s) under a vacuum environment. The microstructural analyses showed that brazed samples were free of IMCs and included the complex solid solutions and reaction layers, including (Cu–Al + Ti–Fe–Si) solid solutions were formed at interfaces. The presence of the Zn element in the composition of the HEA improved the wetting on both Ti6Al4V and Al_2O_3 sides. The shear strength evaluations showed that increasing the brazing temperature up to 1050 °C resulted in increased shear strength and reached a maximum value of 84 MPa. On the other hand, further increasing the brazing temperature caused the occurrence of grain coarsening and consequently, reduced strength.

3- Brazing of the Ti/ZrO_2 joints

In the case of the Ti/ZrO_2, more studies have been done, and different filler materials, including Ag-based filler, amorphous fillers, Au-based filler, etc., have been used for brazing. Fig. 5 presents a schematic image of the various types of filler materials for brazing of Ti alloys/ ZrO_2 and their general information. The detailed information of the reviewed studies on Ti alloys/ ZrO_2 has also been provided in Table 2.

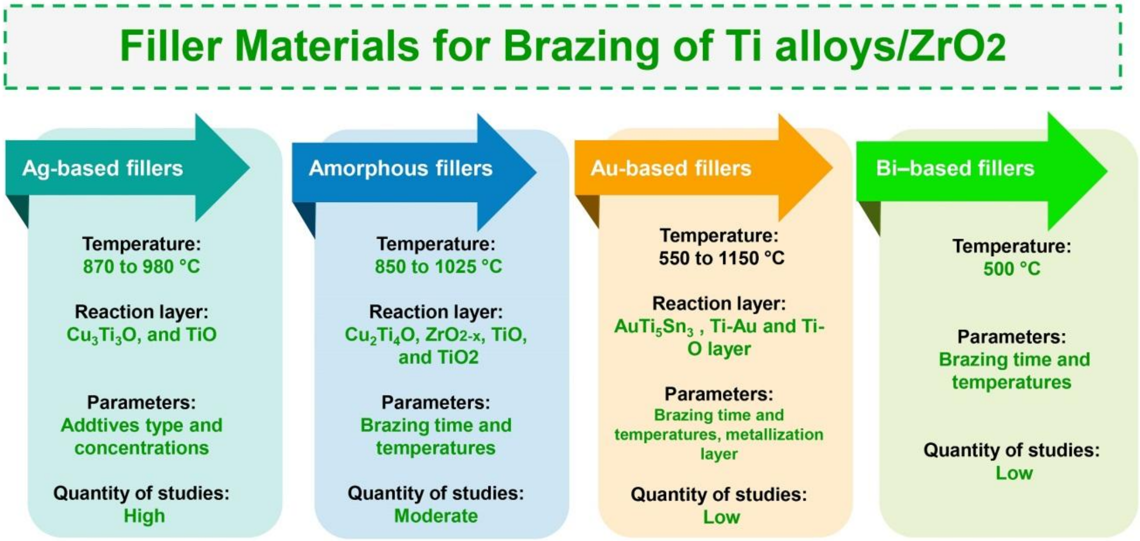

Fig. 5. The main filler materials for brazing of titanium alloys to ZrO_2 and their details.

Table 2. The summarized information on the brazing process of Ti/ZrO_2 joints

Joint	Filler	Brazing	Parameter	Shear strength	Reference
TiAl/ZrO_2	Ag-Cu filler	880 °C for 10 min	Brazing time	48.4 MPa	[54]
Ti6Al4V/ ZrO_2	Ag-Cu sputter-coated Ti foil	980 °C for 30 min	Brazing temperature	152 MPa	[55]
Ti6Al4V/ ZrO_2	Ag-28Cu + WB composite filler	870 °C for 10	Concentrations of WB	83.2 MPa	[56]
Ti6Al4V/ ZrO_2	Ag-Cu-Ti with CeO_2 nanoparticles	980 °C for 10 min	Concentration of CeO_2	22.8 MPa	[57]

Ti6Al4V/ZrO$_2$	Ag-Cu/ nanostructured CuO foam/Ag-Cu-Ti	870 °C for 10 min	Interlayer types	95.6 MPa	[58]
Ti6Al4V/ ZrO$_2$	amorphous Ti$_{33}$Zr$_{17}$Cu$_{50}$ active filler	900 °C for 10 min	Brazing time	162 MPa	[59]
Ti6Al4V/ZrO$_2$	amorphous Ti-based filler	850 °C for 30 min	-	63 MPa	[15]
Ti6Al4V/ ZrO$_2$	Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ amorphous filler	900 °C for 10 min	Brazing temperature	95 MPa	[60]
Ti6Al4V/ ZrO$_2$	Ti$_{35}$Zr$_{25}$Be$_{30}$Co$_{10}$ amorphous filler	810 °C for 10 min	Brazing temperature	180 MPa	[61]
Ti6Al4V/ ZrO$_2$	NiCrSiB amorphous filler	1025 °C for 10 min	Ti6Al4V/ ZrO$_2$	284.6 MPa	[62]
Ti6Al4V/ ZrO$_2$	amorphous Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ active filler	860 °C for 60 min	Brazing temperature	186 MPa	[63]
titanium/ ZrO$_2$	Pure Au	1150 °C for 10 min	-	35 MPa	[64]
Ti6Al4V/ ZrO$_2$	Au20Sn	550 °C for 30 min	Thickness of the metallization layer	48.6	[65]
ZrO$_2$/ Ti$_2$AlNb	35Bi$_2$O$_3$-50B$_2$O$_3$-15ZnO	500 °C for 10 min	Brazing temperature	48.75 MPa	[66]
(TA9)/ZrO2	Sn–Zr + AuSn20	550 °C for 30 min	Zr contents in Sn-Zr metallization layer	46.5 MPa	[67]
Ti6Al4V/ZrO$_2$	Al-5wt.%Si	700 °C for 20s	Brazing time	90.68 MPa	[68]

3-1- Brazing of the Ti/ZrO$_2$ joints using Ag-based fillers

The Ag–Cu filler metal is relatively inactive but preferred due to its ductility, which helps relieve residual stresses caused by thermal expansion mismatch between ceramic and metal. Dai et al. [54] studied the brazing of the TiAl/ZrO$_2$ joints using Ag–Cu filler metal. In their work, the brazing was done at a constant temperature of 880 °C for different holding times of 5-25 min. The microstructure of the samples from TiAl to ZrO$_2$ side consisted of AlCu$_2$Ti, Ag-rich solid solution matrix with dispersed granular AlCu$_2$Ti, TiO, and Cu$_3$Ti$_3$O layers. The results showed that by increasing the holding times, the thickness of the reaction layers formed on both sides of the TiAl and ZrO$_2$ increased. The optimal holding time was 10 min so that the highest shear strength of 48.4 MPa was achieved, while increasing the holding time, the thickening of brittle intermetallic caused to reduction in shear strength. In other words, the brittle blocky $AlCu_2Ti$ phase acts as a crack initiation site.

The titanium coating promotes chemical bonding with both ZrO_2 ceramic and Ti6Al4V alloy, enhancing interface adhesion. Sónia Simões et al. [55] studied the effects of brazing temperature on the microstructure and mechanical properties of the Ti6Al4V/ZrO_2 joints by a novel Ag-Cu sputter-coated Ti foil. In their work, the brazing process was conducted at different temperatures of 900-980 °C for 30 min under a vacuum environment. Their results showed an increasing tendency for the shear strength of samples as a function of brazing temperature. In other words, the highest shear strength value of 152 MPa was achieved for the brazed joint at 980 °C. Optimizing the brazing temperature to 980 °C enhances diffusion and phase formation, reducing porosity and improving joint quality.

Literature showed that the addition of particles to the brazing filler can decrease their CTE value. In the study of Dai et al. [56], they used different contents of the WB (5-10 wt.%) with Ag-Cu filler for brazing of the Ti6Al4V/ZrO_2 joints. The Ag-28Cu composite fillers were prepared by the ball-milling method of the Ag-28Cu and WB powders. Fig. 6 shows the SEM images of the brazed joint with different contents of WB in filler and the mechanical properties of the joints. The brazing was done in a temperature range of 870 °C for 10 min under a vacuum environment. As can be seen in Fig. 6a to 6d, owing to the diffusion of the titanium from the Ti6Al4V side, a TiO layer and a Cu_3Ti_3O layer formed on the ZrO_2 side. The brazing seam contained the Ag-rich matrix with randomly distributed TiB whiskers and W particles. The TiB and W act as reinforcement for the joints by the Orawan mechanism. However, evidently, by increasing the concentration of WB to 10 wt.%, the agglomeration of the TiB and W occurred. The results showed that the addition of 7.5 wt.% WB caused to increment of the shear strength to 83.2 MPa which was about 59.4% higher than that of the brazed joint with filler without WB (Fig .6e). Although the CTE value of the joint decreased as a function of the WB content, the aggregation of WB particles and poor fluidity of liquid filler caused the reduction of shear strength (Fig. 6f). Therefore, the optimization of the WB contents for achieving the proper distribution of the in-situ formed TiB is necessary.

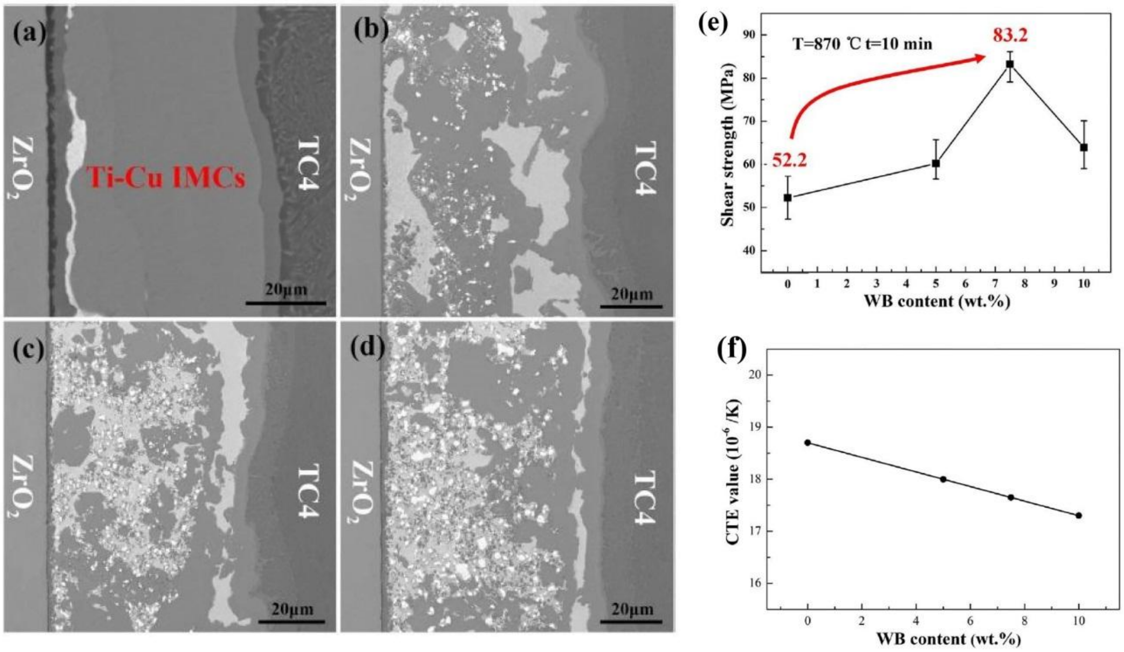

Fig. 6. SEM images of the Ti6Al4V/ZrO_2 joints brazed with Ag-28Cu composite filler reinforced with different contents of WB (a) 0 wt.%; (b) 5 wt.%.; (c) 7.5 wt.%; (d) 10 wt.%, (e) shear strength, and (f) CTE value of the samples as a function of WB contents, reproduced from [56].

In the literature, there are some studies regarding the addition of nanoparticles for improving the properties of the joints. For example, Sharma and Ahn [57] investigated the effect of the addition of different contents of CeO_2 nanoparticles (0.05-0.1 wt.%) in Ag-Cu-Ti filler for brazing of Ti6Al4V/ZrO_2. The CeO_2 nanoparticles contribute to grain refinement, improve toughness, and inhibit grain growth during solidification. The brazing process was conducted at a temperature range of 980 °C for 10 min. The microstructure of the samples consisted of both ductile phases (such as Ag-rich and Cu-rich solid solutions) and intermetallic compounds (such as Ti_2Cu). The presence of fine CeO_2 nanoparticles at grain boundaries caused the grain refinement. Generally, the addition of CeO_2 caused to improvement in the mechanical properties of samples. For example, the shear strength values of brazed joints with 0, 0.03, 0.05, and 0.1 wt.% CeO2 was respectively 19.9, 20.4, 22.8, and 12.6 MPa. The CeO_2 nanoparticles, through various mechanisms of Hall-Petch and Orawan mechanisms, improve the mechanical properties of the joints. The high concentration of CeO_2 can have negative effects on the fluidity and spreadability of the melt and consequently, decrease the shear strength.

The morphology and porosity of the filler materials can also have an influence on the properties of the Ti6Al4V/ZrO_2 joints. In a study by Li et al. [58], it was demonstrated that the 3D porous structure of the Cu foam can deform plastically, effectively releasing residual stresses caused by the mismatch in thermal expansion of Ti6Al4V/ZrO_2. In their work, the Ti6Al4V/Ag-Cu/ nanostructured CuO foam/Ag-Cu-Ti/ ZrO_2 sandwich-like assembly was brazed at 870 °C for 10 min (Fig. 7a). For comparison, they also used Cu foam. Their results showed that without using an interlayer, the presence of the Ti-Cu intermetallic caused poor mechanical properties. On the other hand, the application of the Cu foam caused the formation of the Ag/ Cu-based solid solution, improving the ductility of the joints. The application of the nanostructured Cu foam, in addition to the Ag/Cu-based solid solutions, the distributed Cu_3Ti_3O particles, prevents the agglomeration and contributes to both stress relief and strengthening. The average shear strength values of the samples in the case of without Cu foam, with Cu foam, and with nanostructured Cu were respectively 52.2, 78, and 95.6 MPa.

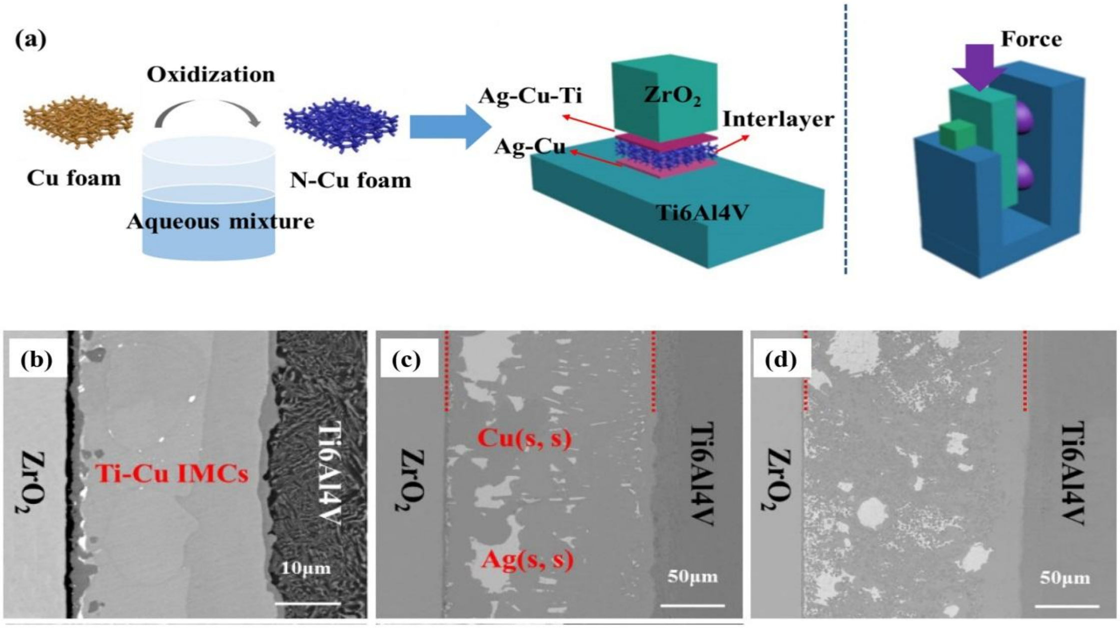

Fig. 7. (a) schematic image of fabrication of N-Cu foam, SEM images of the brazed Ti6Al4V/ ZrO_2 with (b) Ag-Cu filler, (c) Cu foam interlayer, and (d) N-Cu foam interlayer, reproduced from [58].

3-2- Brazing of the Ti/ZrO_2 joints using amorphous filler materials

Amorphous filler materials, owing to their several advantages, are a good material for brazing of the Ti/ZrO_2 joints. The amorphous structure of these filler materials, owing to their glass nature, mostly provides excellent wettability with both metal and ceramic materials, and also, with these materials, the formation of the brittle intermetallic is limited. Moreover, amorphous fillers generally accelerate atomic diffusion and interfacial reactions. Finally, amorphous filler materials generally withstand higher temperatures compared to Ag-based filler materials, making the joint suitable for high-temperature applications [69-73]. Up to now, various types of amorphous filler, including Ti and Zr-based filler materials, have been used for brazing of the titanium alloys to ZrO_2. The main results are summarized in the following.

In the study of Liu et al. [59], the effects of brazing parameters on the microstructure and mechanical properties of Ti6Al4V/ZrO_2 joints using $Ti_{33}Zr_{17}Cu_{50}$ alloy were investigated. Their results showed that at the ZrO_2 side, the Cu_2Ti_4O compound, $(Ti,Zr)_2Cu$ alloy, TiO, and Ti_2O oxides were formed, while at Ti6Al4V side, the $CuTi_2$ alloy was formed. In the brazing seam, the mixture of $CuTi_2$ and $(Ti,Zr)_2Cu$ alloys was observed. Their results showed that by increasing the temperature, the $(Ti,Zr)_2Cu$ intermetallic in the first layer disappeared while the thickness of $TiO+Ti_2O$ and $\alpha\text{-}Ti+(Ti,Zr)_2Cu$ increased. The mechanical tests revealed the achievement of the high shear strength values of 156, 162, and 103 MPa, respectively in brazing at 900 °C for 5, 10, and 30 min. The thickening of the brittle oxide layers was the reason for the reduction of the shear strength at 30 min.

In another work by Liu et al. [15], they studied the effects of different brazing temperatures (850 to 1050 °C) and holding times (5 to 15 min) on the microstructure and mechanical properties of the Ti6Al4V/ZrO_2 joints using amorphous Ti-based filler. The microstructural analyses proved the formation of the TiO_2 and stabilized zirconia phase at the ZrO_2 side and Ti–Ni-Al–intermetallic at Ti6Al4V, indicating the chemical boning. Their results showed that by increasing the brazing temperature, the shear strength decreased, and the highest shear strength of 63 MPa was achieved for the brazed sample at 850 °C for 30 min.

Hu et al. [60] studied the brazing at different temperatures of (900-1000 °C) and different holding times (5-30 min) of the Ti6Al4V/ZrO_2 joint using $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous filler. At the ZrO_2 side, the oxygen-deficient zirconia and TiO phases were formed, while at the Ti6Al4V side, the Widmanstätten structure of Ti alloy was observed. In brazing seam, $(Zr,Ti)_2(Cu,Ni)$, and $(Zr,Ti)_2(Cu,Ni,Al)$ was observed. Their results showed that by increasing the brazing temperature, the thickness of the oxygen-deficient zirconia and TiO phases decreased while the thickness of the Widmanstätten structure increased. Moreover, the $(Zr,Ti)_2(Cu,Ni)$ intermetallic decreased by increasing the brazing temperature. The shear strength of the brazed joint at 900 °C for 10 min was the highest (95 MPa), and it decreased to 65 MPa by increasing the temperature to 1000 °C, owing to the brittleness of the samples. Their results showed that the longer holding times and faster cooling rates caused the respective brittleness and thermal stresses, causing the reduction of shear strength.

Liang et al. [61] investigated the microstructure and mechanical properties of the Ti6Al4V/ZrO_2 joints brazed with $Ti_{35}Zr_{25}Be_{30}Co_{10}$ amorphous filler. In their work, the brazing was done at different temperatures (790-850 °C) and different holding times (5-30 min) under a vacuum environment. Fig. 8 shows the SEM images of the brazed joint at different temperatures and mechanical properties. As can be seen in Fig. 8a to 8d, the microstructure of the samples from ZrO_2 to Ti6Al4V side included of TiO reaction layer, Be_2Ti (dark bulk phase), α-(Ti,Zr) solid solution, and β-(Ti,Zr) and Widmanstätten structure of α and β Ti phases were observed. The TiO layer grows by a reaction-diffusion process exhibiting island growth mode initially, becoming continuous with increased time and temperature. The thickness of this layer is critical, as it influences joint strength. The results showed that by increasing the holding time and brazing temperature, the thickness of the TiO layer increased, and it became continuous. The results showed that the shear strength of the samples was dependent on the thickness of the TiO layer, in which the highest shear strength of 180 MPa was achieved at a temperature of 810 °C for 10 min, while by increasing holding time and temperature, the thicker TiO layer decreased shear strength. Accordingly, it can be said that a thin and continuous TiO layer enhances bonding by providing a graded interface that reduces residual stress and crack initiation.

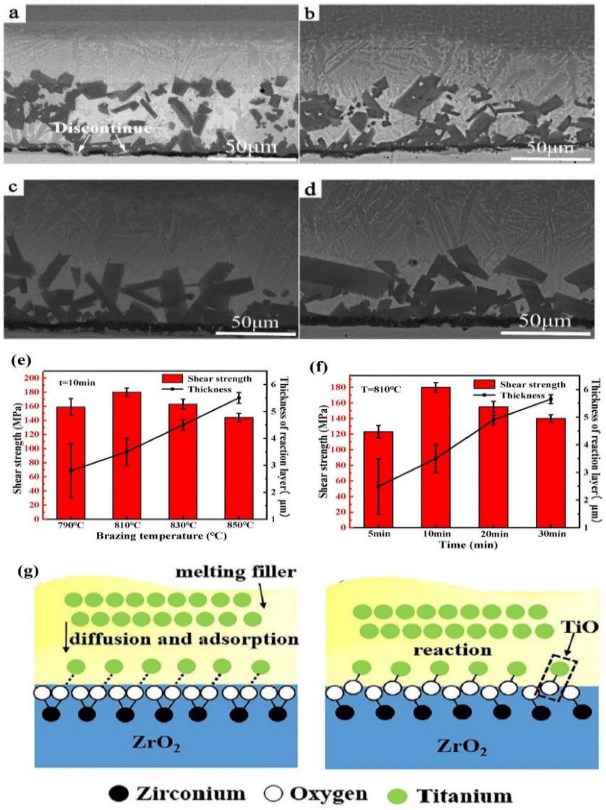

Fig. 8. SEM images of the Ti6Al4V/ZrO_2 joints brazed with $Ti_{35}Zr_{25}Be_{30}Co_{10}$ amorphous filler at different temperatures of (a) 790 °C, (b) 810 °C, (c) 830 °C, (d) 850 °C, (e) shear strength of samples as a function of brazing temperature, (f) shear strength of samples as a function of brazing times, and (g) schematic image of formation mechanical of Ti-O layer, reproduced from [61].

Park et al. [63] studied the effects of brazing parameters on the microstructure and mechanical properties of the Ti-3Al-2.5V/ZrO_2 using amorphous $Zr_{54}Ti_{22}Ni_{16}Cu_8$ active filler. In their work, the brazing process was done at different temperatures of 800 to 860 °C at a constant holding time of 60 min. At low temperatures of 800-820 °C, the thin reaction layer was formed at the ZrO_2 side while at higher temperatures of 840 to 860 °C, more complex interfaces including $(Zr,Ti)_2Ni,Cu)$ intermetallic, ZrO_{2-x}, TiO, and TiO_2 was formed owing to the increased diffusion and enhanced dissolution of elements. By increasing the temperature up to 840 °C, the shear strength increased linearly, while by increasing the temperature to 860 °C, the shear strength increased abruptly and reached the highest value of 186 MPa. The rapid increase in shear strength between 840 °C and 860 °C corresponds to the microstructural transition to the island-type morphology and the reduction of brittle $(Zr,Ti)_2(Ni,Cu)$ phases.

Cao et al. [62] studied the microstructure and mechanical properties of the Ti6Al4V/ZrO_2 joints brazed with NiCrSiB amorphous filler foil. In their work, the brazing process was conducted at different temperatures of 950-1050 °C for 10 min under a vacuum environment. As can be seen in Fig. 9, the microstructure of the samples from Ti6Al4V to ZrO_2 sides includes of β-Ti layer and Widmanstätten structure (at Ti6Al4V), Ti_2Ni, Ti_5Si_3, and β-Ti (at brazing seam), and continuous TiO (at ZrO_2 side). The formation of the continuous TiO at ZrO_2 is caused by the diffusion of the titanium from the Ti6Al4V to the ZrO_2 side. Their results showed that by increasing the brazing temperature, the thickness of the TiO layer and content of β-Ti and Ti_5Si_3 phases increased while the amount of the Ti_2Ni decreased. The shear strength of the samples increased as a function of the brazing temperature up to 1025 °C and reached its maximum value of 284.6 MPa. However, applying a higher temperature of 1050 °C caused to reduction of the shear strength owing to the thicker, brittle intermetallic, and weaker joints.

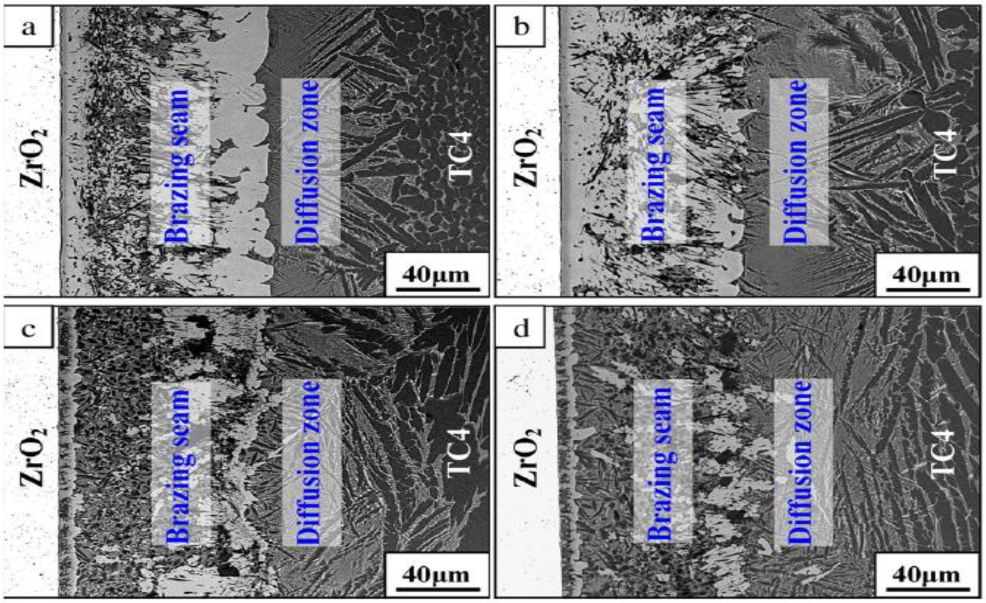

Fig. 9. SEM images of the Ti6Al4V/ZrO_2 joints brazed with NiCrSiB amorphous filler foil at different temperatures of (a) 950 °C, (b) 975 °C, (c) 1025 °C, and (d) 1050 °C, reused from [62].

3-3- Brazing of the Ti/ZrO_2 joints using Au-based fillers

Au is a non-toxic and highly biocompatible material, ideal for medical implants. The low brazing temperature and high ductility of the Au-based filler materials make them suitable materials for brazing the titanium/ZrO_2 joints used for medical implants [74-76]. Lei et al. [64] reported the development of a biocompatible, high-quality brazed titanium/ZrO2 using pure gold. In their work, two groups of brazing were performed. In group 1, the effects of brazing temperature (1110-1190 °C) at a holding time of 10 min were investigated, while in group 2, the effects of different holding times of 5-30 min at a temperature of 1150 °C were studied. The microstructure of the samples from titanium to ZrO_2 side included Ti_3Au, TiAu, $TiAu_2$, TiAu4, and Ti-O layer. The formed Ti-O layer that is essential for metallurgical bonding is caused by the diffusion of titanium to the ZrO_2 side. Their results showed that there is an optimal brazing temperature at which the highest shear strength of 35 MPa was achieved at 1150 °C for 10 min. Moreover, the optimal holding time was 10 min, in which the higher times caused to thicknessing of the intermetallic layers.

In another work, Jiang et al. [65] studied the brazing of the Ti/ZrO_2 joints using Au-20Sn filler material. Firstly, the Sn-xTi (x = 2, 3, 4 at.%) alloys with different thicknesses of 75 to 200 μm were metalized on the ZrO_2 surface, and then the brazing process was done at 550 °C for 30 min in a vacuum environment. Fig. 10 shows the schematic illustration of metallization and brazing assembly, the microstructure of the sample with different thicknesses of the metallization layer, and the mechanical properties of the samples. By metallization, the Ti-Sn and Ti-Sn-O phases, including + Ti_2Sn_3, Ti_6Sn_5, and $Ti_{11.31}Sn_3O_{10}$ were formed. As can be seen in Fig. 10b to 10g, by increasing the titanium content from 2 to 4 at. %, the thickness and homogeneity of the Ti-O layer increased. In the brazing seam, the $AuSn_2$ + $AuSn_4$ was formed, while at Ti6Al4V, the $AuTi_5Sn_3$ phase was observed. Their results showed that by increasing the thickness of the metallization layer, the $AuTi_5Sn_3$ phase formed at the Ti6Al4V side increased. Fig. 10b to 10g reveals a direct correlation between Au-Sn-Ti layer thickness and metallization layer dimensions in titanium brazing systems. During the brazing process, Sn from the metallization layer diffuses into the molten AuSn20 filler, while Ti dissolution from the substrate contributes to Au-Ti-Sn intermetallic phase formation. Thinner metallization layers (75-150 µm) limit Sn availability, producing only trace Au-Ti-Sn phases with minimal thickness variation in the $AuTi_5Sn_3$ layer. As metallization thickness increases beyond 150 µm, higher Sn release into the filler metal elevates liquid phase Sn content, driving rapid Au-Ti-Sn layer thickening. As can be seen in Fig. 10i, this structural evolution critically impacts mechanical performance, in which samples with 150 µm metallization achieve peak shear strength (48.6 MPa) through the optimal distribution of $AuSn_2$ and AuSn4 phases. Beyond this threshold, excessive growth of the brittle Au-Ti-Sn layer near the Ti substrate reduces load-bearing capacity, causing strength decline. The study demonstrates a crucial balance between metallization parameters and joint integrity, with 150 µm representing the optimal thickness for maximizing strength while minimizing brittle phase dominance.

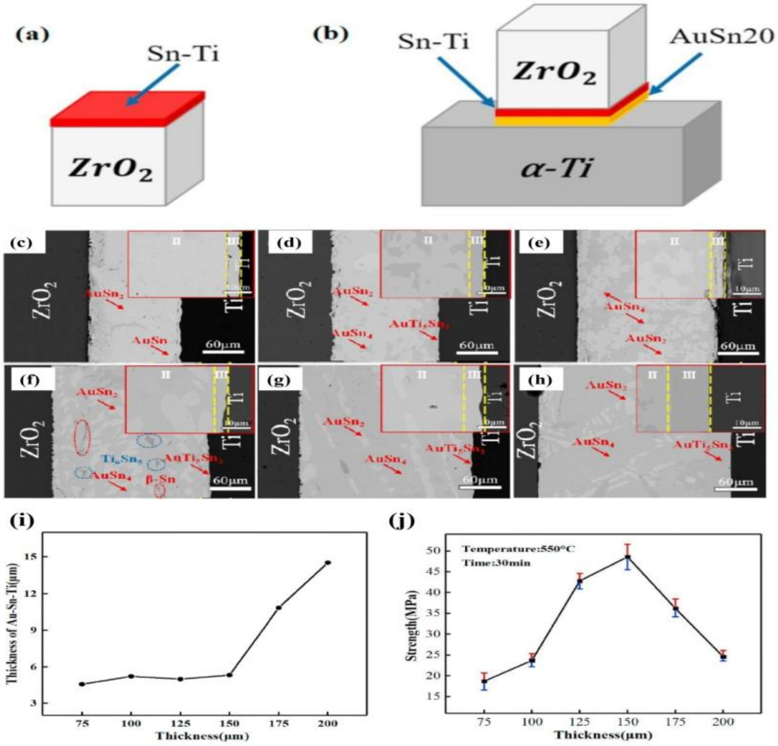

Fig. 10. (a) schematic images of the metallization step and brazing assembly, SEM images of the Ti/ZrO_2 joints with different thicknesses of the metallization layers, (b) 75 µm, (c) 100 µm, (d) 125 µm (e) 150 µm (f) 175 µm, (g) 200 µm, (h) relationship between the thickness of the Au-Sn-Ti layer and (i) shear strength of joints with thickness of metallization layer, reproduced from [65].

3-4- Brazing of the Ti/ZrO_2 joints using Bismuth filler materials

Bismuth-based fillers, owing to their attractive properties including low melting temperatures, crystallization strengthening, and excellent wettability with both metals can ceramics be proper filler materials for brazing of the metal/ceramic joints [66, 77-79]. Sun et al. [66] investigated the microstructure and mechanical properties of the Ti6Al4V/ZrO_2 joints using 35Bi_2O_3-50B_2O_3-15ZnO glass brazing filler. In their work, the effects of different brazing temperatures from 420 to 520 °C for 10 min were evaluated. The microstructure analyses (Fig. 11a to 11f) of the samples showed that the diffusion of the titanium from the Ti6Al4V side and reaction with $35Bi_2O_3$ resulted in the formation of the $Bi_4Ti_3O_{12}$ as a bonding strengthening phase, while no reaction of the ZrO_2 and filler was observed. Results showed that at lower brazing temperatures, the filler was in the amorphous state and therefore, was not affected by the formation of strong bonding. This study proved that there is an optimal brazing temperature for brazing, in which the highest shear strength value of 48.75 MPa was achieved at 500 °C. At lower temperatures, weak bonding, and at higher temperatures, the excessive crystallization and pore formation lead to a reduction of the shear strength value. The fracture analyses showed that an excessive increase in the brazing temperature caused the change of the failure mode from cohesive failure to interfacial one.

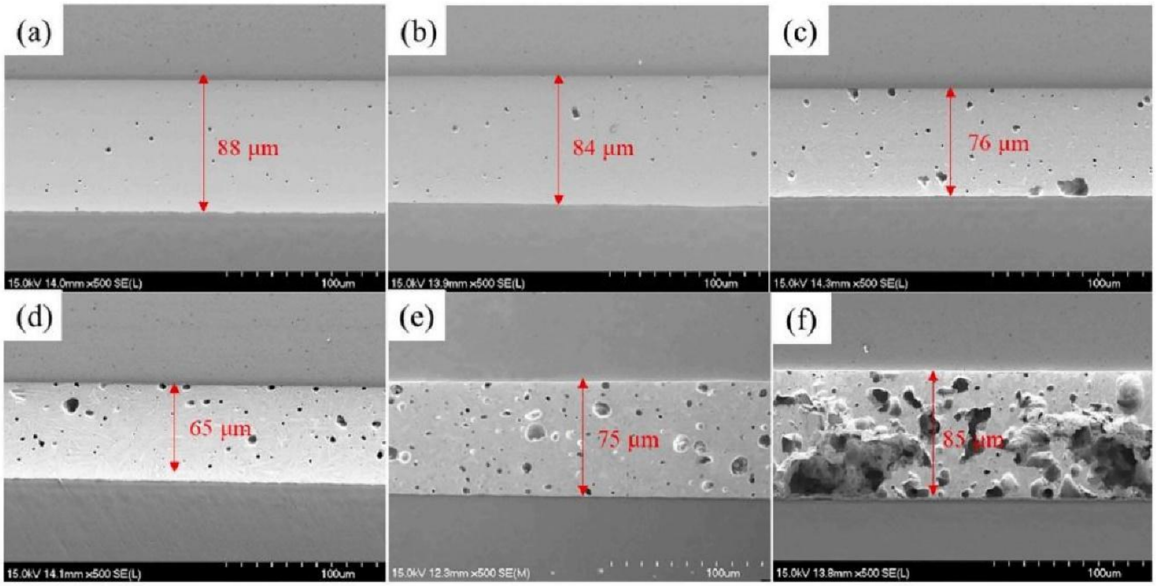

Fig. 11. The SEM images of the Ti6Al4V/ZrO2 joints brazed with $35Bi_2O_3$-$50B_2O_3$-15ZnO glass brazing filler at temperatures of (a) 420 °C, (b) 440 °C, (c) 460 °C, (d) 480 °C, (e) 500 °C, and (f) 520 °C, reused from [66].

3-5- Brazing of the Ti/ZrO_2 joints using other filler materials

In addition to the introduced filler materials, other fillers such as Sn–Zr + AuSn20 and Al-Si alloy have also been used for the brazing of titanium to ZrO_2. In the case of Sn–Zr + AuSn20, it is biocompatible with a low brazing temperature, which, owing to the good wettability with both metals and ceramics, can be used in joining the titanium/ ZrO_2 joints. Chen et al. [67] studied the microstructure, mechanical, and biocompatibility of the Ti-0.2Pd (TA9)/ZrO2 joints using Sn–Zr + AuSn20 brazing filler. In their work, Zr content in the Sn–Zr filler (2, 4, 6, 8 at.%) was changed. Firstly, the Sn–Zr powders were metalized on the surface of the ZrO2, and then, the pre-metalized ZrO_2, AuSn20, and TA9 were brazed at 550 °C for 30 min. Fig. 12 presents the schematic image of heating curves for metallization and brazing, and the microstructure of the samples. As can be seen in Fig. 1b to 1i, the microstructure of the samples from TA9 to ZrO_2 side consisted of $AuTi_5Sn_3$, Sn–Zr/$AuSn_4$, $AuSn_2$, Au–Sn–Zr, $ZrSn_2$, $AuSn_4$, monoclinic ZrO_2, and tetragonal ZrO_2. The $AuTi_5Sn_3$ at TA9 provides good bonding. The mechanical tests showed that increasing the content of Zr up to 6 at.% caused to improvement of the shear strength from 13.8 MPa to 46.5 MPa, while further increments of Zr had negative effects and resulted in a shear strength of 38 MPa. In samples with high Zr content (8 at.%), the unreacted Sn_2Zr and wider seams caused to reduction in shear strength. In low content of Zr content, owing to the insufficient m-ZrO2, the failure occurred at ZrO_2, while by increasing the Zr content, failure shifts to IMC layers ($AuSn_4$ and $AuTi_5Sn_3$).

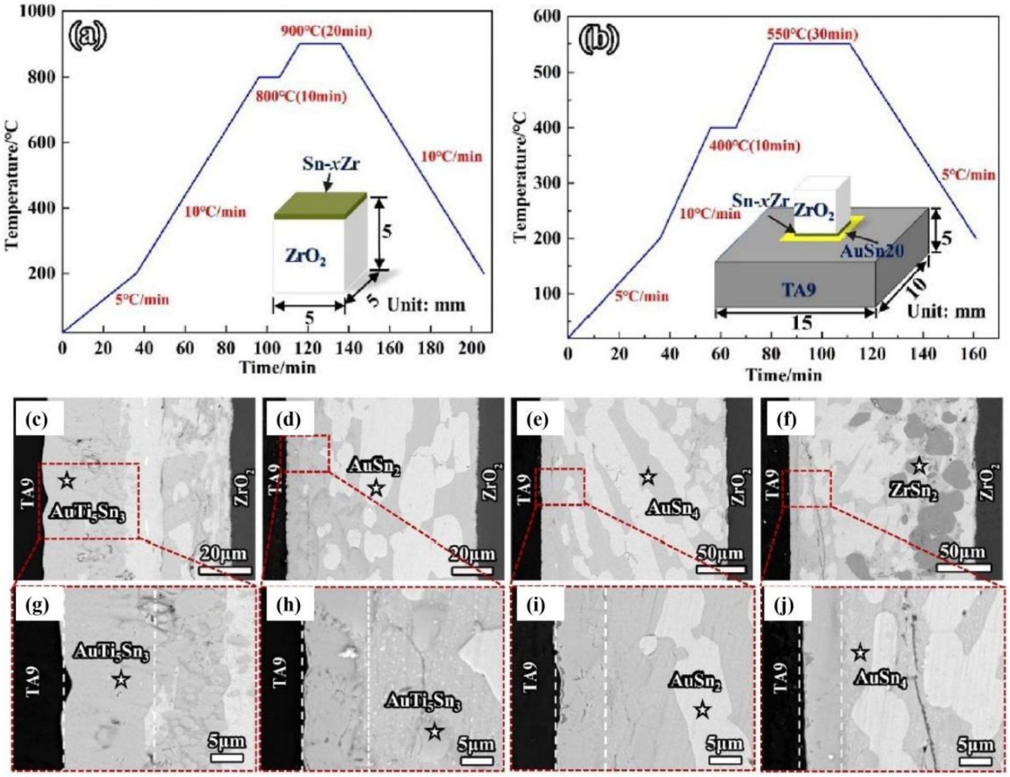

Fig. 12. Process curve and assembly diagram, (a) metallization, (b) brazing, SEM images of TA9/AuSn20/Sn-xZr/ZrO_2 joint at 550 °C for 30min, (c), (d) Sn-2 at.%Zr, (e), (f) Sn-4 at.%Zr, (g), (h) Sn-6 at.%Zr, (i), and (j) Sn-8 at.%Zr, reproduced from [67].

Al-Si alloy is another filler material that can be used for joining metals to ceramics owing to its good wettability with them [80-82]. Zhang et al. [68] studied the microstructure of the Ti6Al4V/ZrO_2 joints by ultrasonic brazing with Al-5wt.%Si filler. For this aim, the joints were heated to 700 °C, and then the ultrasonic vibration was applied for different times of 5 to 30 s under constant pressure of 0.1 MPa. The microstructure of the samples from Ti6Al4V to ZrO_2 sides included $Ti_7Al_5Si_{12}$ and lamellar $Ti(Al,Si)_3$ (at Ti6Al4V), pure Al matrix with isolated Al-rich islands (at brazing seam), and discontinuous flocculent ZrO_2 (at ZrO_2 side). Ultrasonic action: Promotes dissolution of Ti from the alloy, increases Si chemical potential gradient, and causes Si segregation at the interface and within the joint. Increasing the ultrasonic brazing time up to 20 s caused an increasing tendency for the shear strength of samples and reached to highest value of 90.68 MPa. In lower brazing time, the poor wetting, and at higher brazing time, the excessive growth of the intermetallic caused the reduction of shear strength. In summary, it can be deduced that the ultrasonic energy can remove surface oxides, enhancing filler wetting on ZrO_2, and promoting the dissolution and diffusion of Ti and Si.

4- Brazing of the Ti/SiO_2 joints

Up to now, very few studies have been done on the brazing of the Ti alloys/SiO_2 joints. Table 3 presents the main information regarding the Ti alloys/SiO_2 joints reviewed in this study.

Table 3. The summarized information on the brazing process of Ti/SiO_2 joints

Joint	Filler	Brazing	Parameter	Shear	Reference

				strength	
Ti/ SiO_2-BN	Ag-Cu-Ti + BN	870 °C for 15 min	Concentrations of BN	31.4 MPa	[83]
Ti6Al4V/SiO_2	AgCuNi + Al_2O_3	950°C for 10 min	-	40 MPa	[84]
Ti6Al4V/ SiO_2f/SiO_2	AgCuTi + Cu foam	900 °C for 10 min	Interlayer	59.6 MPa	[85]
Ti6Al4V/ SiO_2-BN	TiZrNiCu	970°C for 10 minutes	Surface treatment	29.7 MPa	[86]
Ti6Al4V/SiO_2-BN	TiZrNiCu + CNT-Ni	970°C for 10 minutes	Interlayer	50 MPa	TiZrNiCu filler

4-1- Brazing of the Ti/SiO_2 joints using Ag-based filler materials

Unlike the Ti/Al_2O_3 and Ti/ZrO_2 joints, very lower investigations have been done on the brazing of the Ti/SiO_2 joints. The main studies have been focused on Ag-based filler materials. In the following, the affecting parameters on the brazing of the Ti/SiO_2 joints are reviewed. As mentioned earlier, the addition of micro/ nanoparticles to the filler materials can reduce the CTE and thermal mismatch. Yang et al. [83] studied the addition of different contents of BN (1.5-6 wt.%) for Ag-Cu-Ti filler for brazing of the titanium/ SiO_2-BN joint. The brazing process was done at 870 °C for 15 min under a vacuum environment. The microstructure of the brazing seam comprised Ag and Cu solid solutions with dispersed TiB whiskers and TiN particles, while the reaction layers were mainly composed of Ti-Cu intermetallic. Their results showed that more fine-grained and thinner reaction layers were formed by the addition of the BN particles. The results proved that the highest shear strength of 31.4 MPa was achieved for the samples with 3 wt.% BN particles, which were about 340% higher than those without BN.

In another work, BIAN et al. [84] investigated the effectiveness of the addition of nano-Al_2O_3 particles to AgCuNi filler for brazing of Ti6Al4V/SiO_2 joints. The brazing process was done at 950°C for 10 min under a vacuum environment. The microstructure of the samples brazed with micro-sized filler was Larger, with less uniform phases and with more defects. However, the presence of nano-Al_2O_3 acted as the nucleation sites, refining the interfacial structure. By the diffusion of the titanium from Ti6Al4V, the Ti_4O_7 and $TiSi_2$ formed at the SiO_2 side. Results showed that the addition of nano-Al2O3 caused to increment of shear strength from 19 MPa to 40 MPa (110.5%).

The use of the interlayer can absorb the diffusion of the titanium from titanium alloys, preventing the formation of thick and brittle intermetallics. In another study, Lin et al. [85] studied the application of Cu foam as an interlayer for brazing of the Ti6Al4V/ quartz fiber reinforced silica (SiO_2f/SiO_2) using AgCuTi brazing filler. The brazing process was done at 900 °C for 10 min. Their results showed that without an interlayer, the thick reaction layers composed of the Ti-Cu compounds, $TiSi_2$, and Cu_3Ti_3O phases were formed at the interface. However, using the Cu foam reduced the thickness of the reaction layers and caused to formation of fine-grained microstructure. The mechanical tests showed that the shear strength increased from 5 MPa (in the case without an interlayer) to 59.6 MPa by using a Cu foam interlayer.

4-2- Brazing of the Ti/SiO_2 joints using TiZrNiCu filler materials

TiZrNiCu is a suitable filler material for brazing of Ti to ceramic materials. The presence of the active elements of Ti and Zr can improve the wettability and promote bonding with ceramics. Furthermore, the presence of Ni and Cu contributes to eutectic formation, lowering the brazing temperatures [87-89]. Ba et al. [86] used a novel approach to brazing Ti6Al4V/ SiO_2-BN joints with a TiZrNiCu filler. In their work, the SiO_2-BN ceramics were etched using 20wt.% Hydrofluoric acid (HF) for different times of 3-10 min (Fig. 13a). Then, the assembled joints were brazed at a temperature of 970°C for 10 minutes under a vacuum environment. Their results showed that the surface without etching was composed of brittle, continuous, mainly $Ti_2(Cu,Ni)$. However, by etched samples caused to diffusion of the B and N and the formation of the in-situ TiB and TiN phases. Their results showed that the optimal time of etching for achieving the highest density of TiB whisker was 5 min, while the over-etching caused to reduction in whisker formation and composite layer integrity. As can be seen in Fig. 13g, the shear strength evaluations revealed that the general etching caused to increment of shear strength, while the highest shear strength of 29.7 MPa was achieved for the etched sample for 5 min, which is 2.3 times higher than that of the untreated sample.

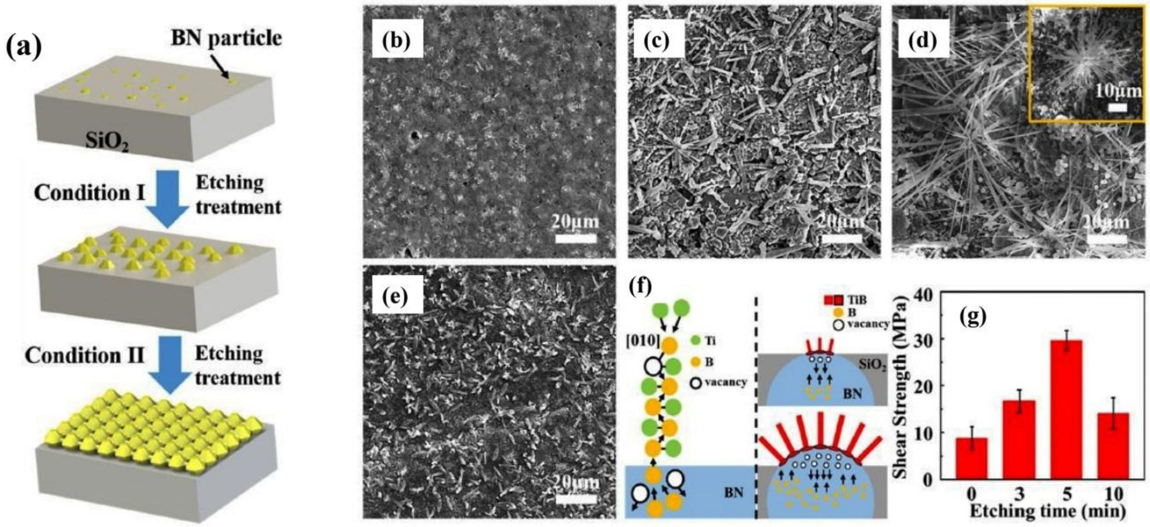

Fig. 13. (a) Schematic diagram of ceramic etching treatment, Morphology and distribution of TiB whiskers on SiO2-BN interface etched for (b) 0 min (c) 3 min (d) 5 min, and (e)10 min; The inset of (d) is TiB forming on single BN particle. (f) Schematic diagram of TiB whiskers formation mechanism and (g) Shear strength of SiO2-BN/Ti6Al4V joints treated with various times, reproduced from [86].

The application of the interlayers in the brazing seam can reduce the titanium intermetallic formation and also solve the thermal mismatch and residual stresses. Ba et al. [90] used in-situ grown CNTs on Ni foam as an interlayer for brazing of the Ti6Al4V/SiO_2-BN joints using TiZrNiCu brazing filler. In their work, the plasma-enhanced chemical vapor deposition (PECVD) method was used for coating the carbon nanotubes on the Ni foam. Three assemblies of TiZrNiCu, TiZrNiCu + Ni foam, and TiZrNiCu + CNT-Ni foam were used in their work for brazing at 970 °C for a holding time of 10 min. In the case without an interlayer, their work showed that excessive titanium IMCs formed on both SiO2-BN and at the brazing seam. By using Ni foam, the titanium solid solutions with Ti_2Ni, $(Cu,Ni)_{10}Zr_7$ were observed in brazing seams, which have higher ductility. In the case of using CNT-Ni interlayer, the formation of brittle intermetallic was limited, and a more refined structure was observed owing to the presence of

CNTs. CNTs acted as barriers, impeding the reaction between Ti and the ceramic and further reducing residual stress. The mechanical tests showed that the shear strength of the samples with TiZrNiCu, TiZrNiCu + Ni foam, and TiZrNiCu + CNT-Ni foam was 10, 30, and 50 MPa.

5- Summary and perspectives

In this study, the microstructure and mechanical properties of the joining of the titanium alloys with oxide ceramics (Al_2O_3, ZrO_2, SiO_2) through brazing methods were reviewed and compared. However, the dissimilar joining of metal and ceramics presents several challenges that make it difficult to obtain the microstructural and mechanical soundness of the joints. The results showed that the integration of titanium alloys with advanced ceramics like Al_2O_3 and ZrO_2 through brazing requires careful optimization of filler materials, interfacial reactions, and stress management.

In the case of Ti/Al_2O_3 joints, Ag-based fillers form critical $Ti_3(Cu,Al)_3O$ and TiO phases at the interface, which enable adhesion but become detrimental if excessively thick. The addition of boron mitigates detrimental Ti-Cu IMCs by forming TiB whiskers. Ti-based fillers produce joints with the highest reported shear strength, though they require higher brazing temperatures compared to Ag-based systems. The optimal $Ti_3(Cu,Al)_3O$ layer continuity ensures metallurgical bonding, while excessive TiO formation reduces mechanical integrity.

In the case of titanium/ZrO_2 joints, Ag-Cu fillers generate TiO and Cu_3Ti_3O layers, with TiB whisker formation (via boron/WB additives) reducing brittle IMCs. Nanoparticle reinforcement through various mechanisms (e.g., through Hall-Petch/Orowan mechanisms) enhances joint strength. Ti/Zr amorphous fillers form $(Zr,Ti)_2(Cu,Ni)$, oxygen-deficient zirconia, and TiO phases. A continuous TiO layer improves stress distribution and crack resistance. Cu foam integration effectively dissipates residual stresses caused by thermal expansion mismatch.

The brazing of Ti/SiO_2 joints has been less studied compared to Ti/Al2O3 and Ti/ZrO2, with most research focusing on Ag-based fillers. Adding micro- or nanoparticles such as BN or nano-Al_2O_3 to Ag-based fillers significantly improves joint properties by refining microstructure, reducing thermal mismatch, and increasing shear strength. Using interlayers like Cu foam further enhances joint quality by limiting brittle intermetallic formation and residual stresses, boosting shear strength dramatically. TiZrNiCu fillers, containing active elements Ti and Zr, improve wettability and bonding with ceramics and lower brazing temperatures. Surface treatments like HF etching promote in-situ formation of reinforcing TiB and TiN phases, increasing shear strength by over twofold. Additionally, employing interlayers such as Ni foam coated with carbon nanotubes (CNTs) can further reduce brittle intermetallic and residual stress, resulting in highly refined microstructures and shear strengths up to 50 MPa.

In summary, for all joints, it can be said that Ag-based fillers offer low-temperature processing but lower shear strength, while Ti-based systems and high-entropy alloys (HEAs) require higher temperatures for superior mechanical performance. The additive engineering that includes the addition of nanoparticles and ductile phases (e.g., Cu foam) is critical for balancing interfacial reactivity, residual stress, and joint durability.

For future works, the following items it is suggested for the future works:

- Very limited studies have been done regarding the application of HEAs as fillers for brazing of the titanium alloys to oxide ceramic materials.
- More studies should be done on the brazing of the titanium alloys to SiO_2.
- More studies should be done on the Surface metallization techniques to enhance the wettability of the oxide ceramics to titanium alloys.
- The application of engineered interlayers, such as porous interlayers, for the brazing of oxide

ceramics to titanium alloys should also be considered for future work.

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