

## Article

# Microstructure and Mechanical Properties of Ti6Al4V to Al<sub>2</sub>O<sub>3</sub> Brazed Joints Using Ti-Ag/Cu-Ti Thin Films

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**Abstract:** The processing and characterizing of bonding Ti6Al4V to Al<sub>2</sub>O<sub>3</sub> brazed joints using interlayer thin films was investigated. The brazing was conducted in a tubular furnace with an argon flux at 980 °C for 30 min. The brazing fillers consisted of different combinations of thin Ag/Cu and Ti films with variable thicknesses. The joint interface analysis involved using digital microscopy (DM) and optical microscopy (OM). Microstructural characterization and chemical composition were performed via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Mechanical properties were assessed through microhardness and shear strength tests. Brazing successfully produced interfaces with a combination of titanium films and Ag/Cu as brazing filler. The results revealed that the interface mainly comprises Ti<sub>2</sub>Cu, TiCu<sub>2</sub>Al, α-Ti, and Ti<sub>2</sub>(Cu,Ag). Some segregation of (Ag) was observed at the interfaces, but a decrease in its amount was observed when compared to joints produced using Ag/Cu fillers. The thickness of the titanium film in the brazing filler strongly influenced the integrity of the joints. The amount of (Ag) at the interface diminished as the Ti film's thickness decreased, leading to an improvement in the mechanical properties of the joints. Using a combination of Ag/Cu and Ti thin films revealed a potential approach to reduce the segregation of soft phases at interfaces, promoting a significant improvement in joining metal to ceramic materials.



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**Keywords:** brazing; thin films; Ti6Al4V; alumina; microstructure; mechanical properties

## 1. Introduction

The development and processing of titanium alloys has been intensively researched because of their attractive properties, such as high specific strength, thermal stability, excellent corrosion resistance, and low density. Aerospace, chemical, and automotive applications have the most advantages in using these alloys based on their favorable properties. However, an important aspect of these applications is service temperature, which for these alloys is approximately 500 °C [1–4]. To produce more complex components, especially for the aerospace industry, titanium alloys can be combined with advanced ceramics to extend their applications by producing components with unique properties. This requires the production of reliable joints. Research into joining processes between Ti6Al4V alloys and advanced ceramics such as alumina (Al<sub>2</sub>O<sub>3</sub>) and zirconia (ZrO<sub>2</sub>) has increased significantly in recent years. The effective bonding of these materials will enable the production of diverse components for application in the aerospace, automotive, electronics and nuclear industries, such as missiles, semiconductors, vacuum ducts, energy converters, and satellites [5–8].

There are several challenges in joining metals to advanced ceramics because of the different properties (mechanical, chemical, and physical) of these materials. Conventional bonding techniques make it difficult to obtain joints with favorable bonding, interface

microstructure, and mechanical properties. Typically, solid-state joining methods such as brazing and diffusion bonding are preferred for achieving sound interfaces between these dissimilar materials, as they yield optimal results. However, demanding processing conditions (pressure, temperature, and time) are usually required to obtain high-integrity joints. Another critical factor is the preparation of the contact surfaces, which is very challenging in the case of ceramics. The disparities in coefficients of thermal expansion (CTE) and elastic constants present a challenge when combining metallic and ceramic materials, leading to the formation of residual stresses. New approaches must be developed to reduce such stresses, which are detrimental to the final mechanical properties of the materials [5–8].

Solid-state diffusion bonding is one of the most common joining processes reported in the literature when creating joints between titanium alloys and advanced ceramic materials. However, in these studies it is observed that achieving joint integrity is only possible with high pressures at elevated temperatures [9–23]. The drawbacks of this process are primarily associated with economic concerns, due not only to the required equipment but also the processing of the joints and preparation of the base materials. Additionally, stringent processing conditions can lead to significant changes in Ti6Al4V alloys, especially if the temperature exceeds the  $\beta$ -transus transformation, compromising the mechanical properties of this base material. Nevertheless, this process has the advantage of applying components with highly complex geometries to materials with dissimilar properties. It allows for the application of an interlayer that may enhance the process, improving properties or even reducing the processing conditions.

The use of thin films or multilayers as an interlayer has been demonstrated as a viable approach in bonding Ti6Al4V to  $\text{Al}_2\text{O}_3$  through diffusion bonding [9–12]. This application is attributed to the potential for enhancing diffusivity across the interface, thereby reducing processing conditions, decreasing residual stresses, and improving joint integrity. Barrena et al. [9] explored the utilization of an interlayer composed of Ag/Cu in the diffusion bonding of Ti6Al4V with  $\text{Al}_2\text{O}_3$ . The experiments were performed at 750 °C under 3 MPa, from 10 to 60 min. The results indicated that prolonged bonding times resulted in oxide formation at the interfaces, aligning with increased shear strength. The joint subjected to a 30 min bonding time exhibited the maximum shear strength, with a subsequent decrease in strength observed beyond this bonding time. Other thin films were evaluated by other researchers, such as Silva et al. [10]. In this study, thin titanium film and foils with a thickness of 5  $\mu\text{m}$  were assessed in the diffusion bonding of Ti6Al4V to  $\text{Al}_2\text{O}_3$ . The titanium interlayer facilitated effective diffusion into the ceramic base material, especially when deposited by sputtering. Despite the joint strength being similar, the use of this interlayer led to significant improvements in processing conditions.

Brazing has shown more advantages in joining titanium alloys and advanced ceramics, and for this reason, it has been recognized as one of the main methods for bonding these materials [14–23]. Using a brazing filler that can be selected based on its melting temperature and chemical composition according to a particular system has been identified as a major advantage of this process. Due to the characteristics of this process, there is no need to apply high pressures and temperatures as in the diffusion bonding process. The brazing alloy can also help reduce residual stresses if the selection is performed appropriately. The main brazing fillers reported for the Ti6Al4V and  $\text{Al}_2\text{O}_3$  systems are silver-based and titanium-based. Silver-based alloys have the advantage of having low liquidus temperatures and high corrosion resistance. However, significant segregation of solid silver solution is observed, which reduces the joint's service temperature. Titanium-based alloys have the advantage of producing joints with high mechanical properties, but they require high temperatures, usually above 1000 °C. To overcome the disadvantages of commercial alloys, various researchers are exploring either adding active elements to Ag/Cu alloys or modifying titanium-based alloys to improve the bonding process.

The effect of adding Cu foil to a commercial silver-based alloy in the joining of Ti6Al4V to  $\text{Al}_2\text{O}_3$  was studied by Cao et al. [21]. The brazing experiments were processed at 825 °C

for 10 min using a combination of Ag/Cu and Cu foils with different thicknesses (10, 40, and 120  $\mu\text{m}$ ). The results indicated that adding the Cu foil to the brazing filler significantly improved the shear strength, which increased from  $118.4 \pm 5.4$  MPa with the Ag/Cu alloy alone to 157.4 MPa with the Ag/Cu alloy and the thicker Cu foil. This strength increase was attributed to the diffusion of Cu, which enabled a reaction with the Ti in the titanium alloy that led to an intermetallic that improved the joint's mechanical properties. However, to avoid negative effects the formation of these intermetallics should not exceed 3% [15]. The use of titanium-based alloys results in higher mechanical strength. Alves et al. [16] investigated using a commercial TiCuNi brazing filler in  $\text{Al}_2\text{O}_3/\text{Ti6Al4V}$  brazing. Their results demonstrated that an interface processed at 980 °C consisted of  $\alpha\text{-Ti}$ ,  $\text{Ti}_x\text{O}_y$ , and  $\text{Ti}_2(\text{Cu,Ni})$  with a  $168 \pm 13$  MPa shear strength. The shear fracture is observed through the interface and partially through the interface between the  $\text{Al}_2\text{O}_3$  and the layer with higher hardness. However, titanium-based fillers enable very high properties by increasing the processing temperature [22].

The current work presents a new approach to joining metal to ceramic materials. Specifically, it investigated the effect of using a different combination of thin films based on Ag/Cu and Ti as brazing fillers to promote the soundness of Ti6Al4V/ $\text{Al}_2\text{O}_3$  joints. The thin films were selected both to process the brazing below 1000 °C due to the  $\beta$ -transus temperature of the Ti6Al4V and to reduce the segregation of (Ag) at the interface that compromises the service temperature. However, based on previous work [23], a temperature of 980 °C, which is above the liquidus temperature of the Ag/Cu eutectic, was chosen. This selection allowed both the reaction with Ti and diffusion between the liquid phase and the base materials, and it also promoted the formation of strong reaction layers. In addition, the reaction with titanium was expected to reduce or eliminate the segregation of solid solutions at the interface, without compromising the joints' service temperatures.

## 2. Materials and Methods

The Ti6Al4V and  $\text{Al}_2\text{O}_3$  were purchased in rod form from Goodfellow Cambridge Ltd. (Huntingdon, UK). The rods had a diameter of 13 mm for Ti6Al4V and 10 mm for  $\text{Al}_2\text{O}_3$ . Before brazing, the base materials were prepared. First they were cut, and then the surfaces were polished with silicon carbide sandpaper up to 4000 mesh for Ti6Al4V and 1000 mesh for  $\text{Al}_2\text{O}_3$ .

The brazing fillers were produced by combining the Ag/Cu films produced by cold rolling bought from Goodfellow with thin Ti films of different thicknesses (0.075 and 0.015 mm). The films were cleaned with acetone and combined with Ti sheets on the outer layer and Ag/Cu sheets on the inner layer. The base materials were cleaned and assembled as shown in Figure 1, and the entire assembly was fixed with the provided support. Next, contact force was applied. The brazing experiments were conducted in a horizontal furnace at 980 °C for 30 min with a constant argon flow and a heating and cooling rate of 5 °C/min.

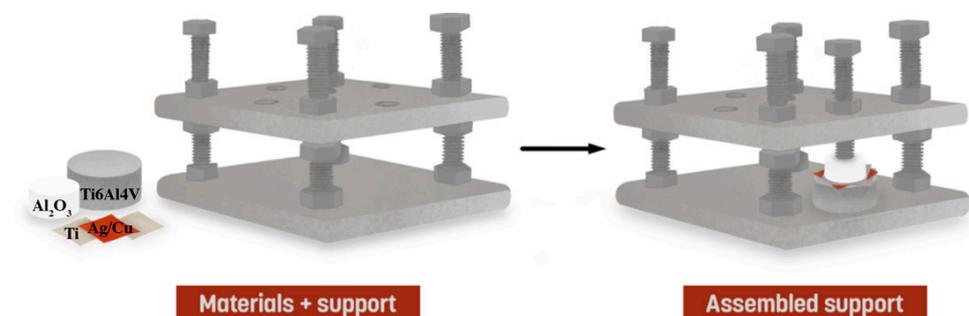


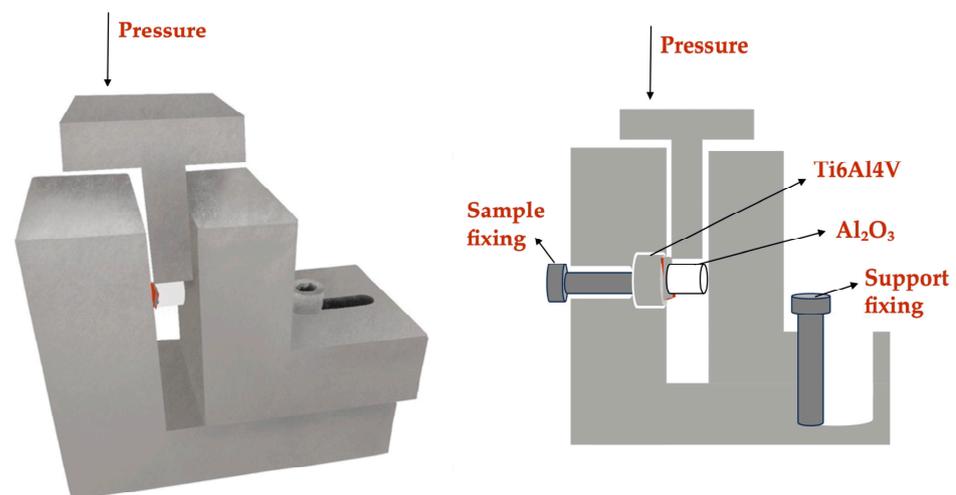
Figure 1. Sample assembly schematic representation of the brazing procedure.

The joints for brazing were produced by combining cold-rolling Ag28Cu eutectic films with a thickness of 0.25 mm and titanium films of 0.015 mm and 0.075 mm, respectively. The microstructure analysis of the joints involved an initial examination using digital

microscopy (DM) and optical microscopy (OM). Joints exhibiting promising characteristics were subjected to more in-depth scrutiny through scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The equipment employed for these characterizations included an optical microscope, M 4000 M, equipped with Leica Application Suite software (version 4.13.0, Leica Microsystems, Wetzlar, Germany), and a Thermo Fisher Scientific QUANTA 400 FEG SEM (Thermo Fisher Scientific, Hillsboro, OR, USA) with EDS capabilities from Oxford Instrument (Oxford Instrument, Abingdon, Oxfordshire, UK).

The evaluation of joint integrity involved conducting hardness and shear strength tests. The hardness tests were performed via Vickers microhardness tests (HV0.01) using a FALCON instrument (INNOVATEST Europe BV, Maastricht, The Netherlands). The applied force for all measurements was 0.09807 N (0.01 kgf). Matrices of indentation, consisting of four columns, were made along the interface, starting at the interface's proximity to the  $\text{Al}_2\text{O}_3$  base material, with a distance of approximately 200  $\mu\text{m}$  between each indentation.

The samples were held in the clamping system illustrated in Figure 2. Four shear strength tests were performed in a tensile machine (AMETEK Test & Calibration Instruments Lloyd Materials testing, West Sussex, UK). Each condition involved testing with four samples, all conducted at 0.5 mm/min and at room temperature. Subsequently, the fractured surfaces of the samples were analyzed using optical microscopy (OM), digital microscopy (DM), and scanning electron microscopy (SEM).



**Figure 2.** Representation of a fixating support used during the shear strength tests.

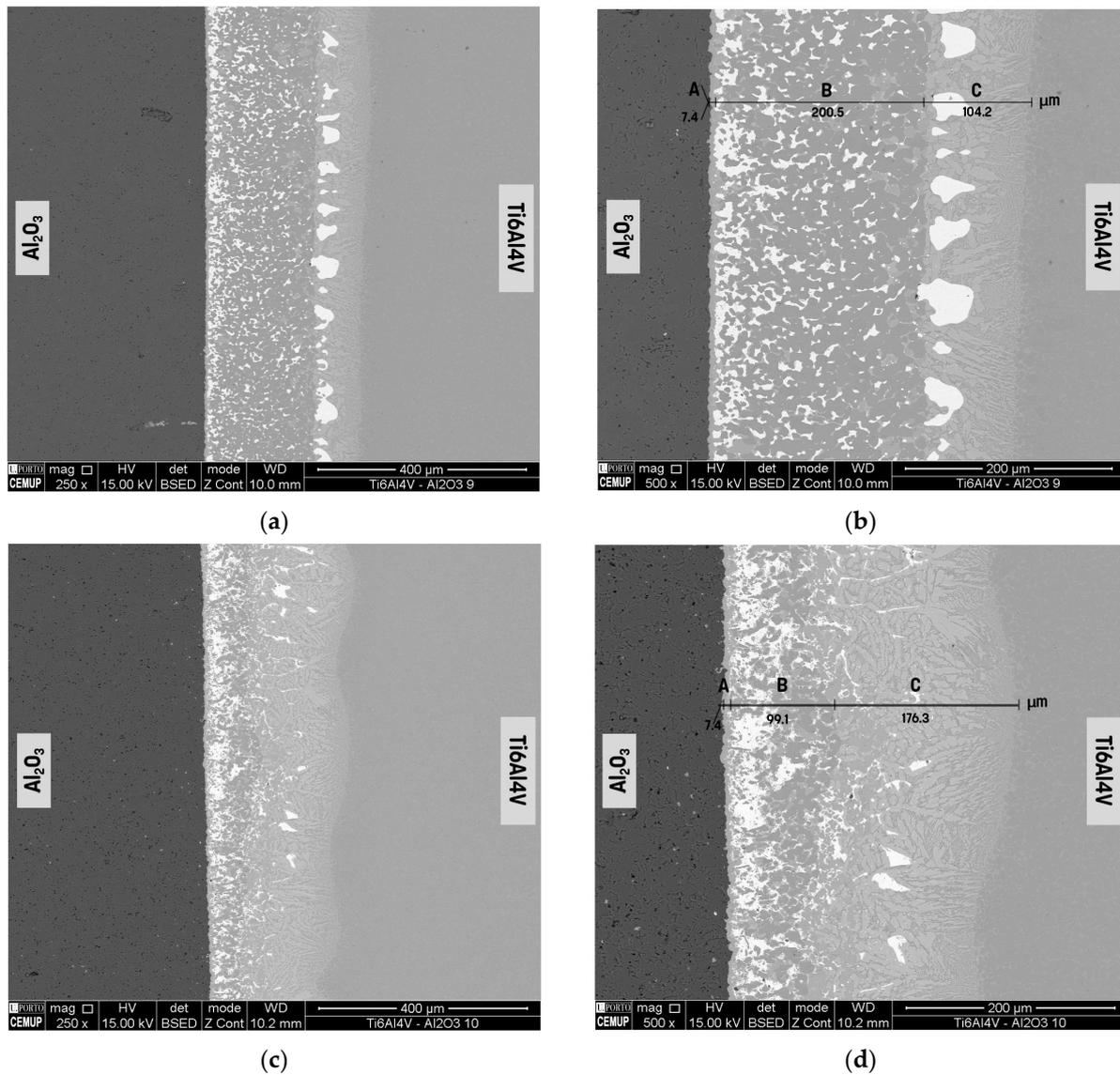
### 3. Results

#### 3.1. Microstructural Characterization

The Ti6Al4V and  $\text{Al}_2\text{O}_3$  brazing was successfully obtained using a combination of Ti and Ag/Cu films as brazing fillers. Microstructural analysis revealed that the interfaces were characterized by three layers that were free of pores, cracks, or unbounded regions. SEM images of the interfaces are presented in Figure 3; they were processed using two thicknesses of Ti films (0.075 and 0.015 mm) in combination with Ag/Cu films (Ti-Ag/Cu-Ti).

The joint interfaces show notable differences but can be divided into three reaction layers (A, B, and C). The thickness of the combined titanium films in the brazing filler (Ti-Ag/Cu-Ti) affected the reaction's thickness at the interface's microstructure. The interface processed using thicker titanium films (0.075 mm) in the brazing filler exhibited a thinner Layer A close to the  $\text{Al}_2\text{O}_3$  base material. Layer B was composed of a gray matrix with brighter dispersed particles. These bright particles had a non-uniform distribution and were larger near the ceramic. Near Ti6Al4V, a dual-phase matrix was observed with larger bright particles at the interface with Layer B. When the thickness of the titanium films used in the filler decreased to 0.015 mm, the interface exhibited a Layer A close to the

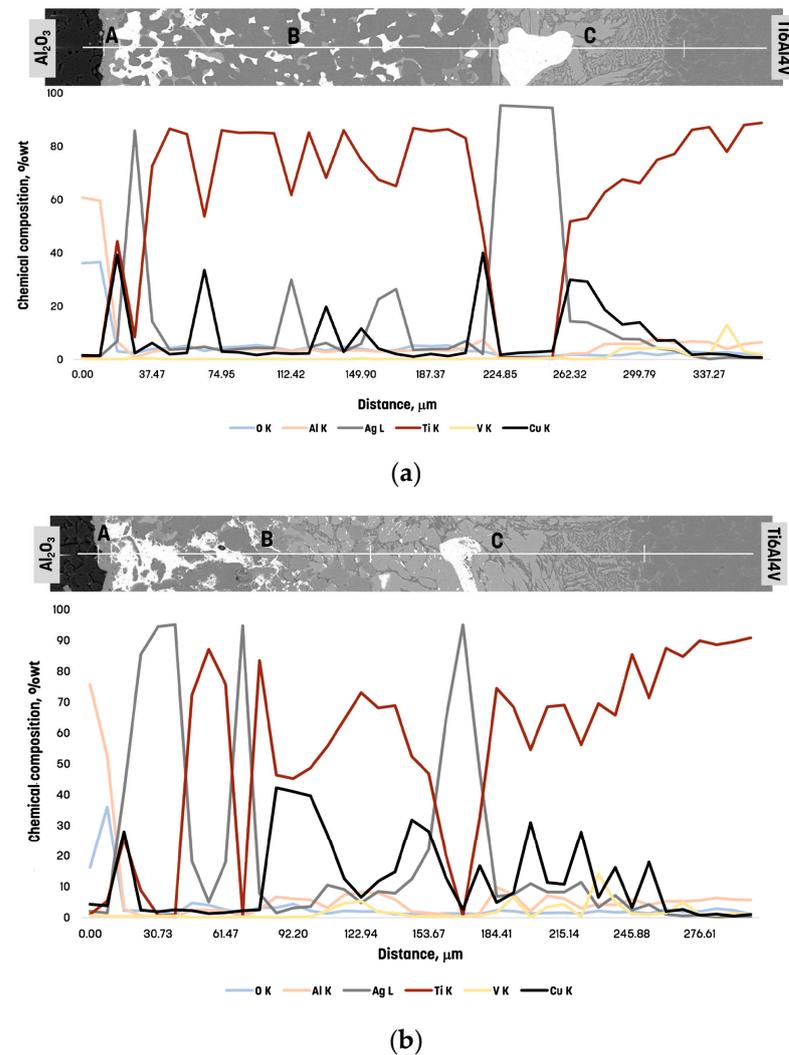
$\text{Al}_2\text{O}_3$ , similar to the one observed for the interface produced with thicker titanium film (0.075 mm)—the main differences were observed at the interface and concerned the thickness and microstructure of Layers B and C. The thickness of Layer B decreased, and although it exhibited a mixture of gray and bright phases, the distribution of the particles was more uniform. Layer C exhibited a similar microstructure but was characterized by a higher but irregular thickness, and the bright particles observed were fewer and smaller.



**Figure 3.** SEM images of the interfaces of the brazing joints processed using (a,b) Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) and (c,d) Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) brazing fillers. The reaction layers are marked as A, B, and C at the interfaces.

The elemental distribution was performed via EDS line profiles across the interfaces. The EDS profiles for both interfaces are presented in Figure 4, which shows the effect of reducing the Ti thickness in the brazing filler. Layer A was made up of Ti, Cu, and Al. Some oxygen was also detected in this layer, which may have originated from the  $\text{Al}_2\text{O}_3$  base material and formed a very thin layer of complex oxides. In the B layers, the Ti element had the highest percentage, with peaks of Ag and Cu observed in the brighter particles that made up this layer. A more uniform composition was observed for the interface produced with the thicker titanium sheet in the filler. In contrast, the interface produced with the

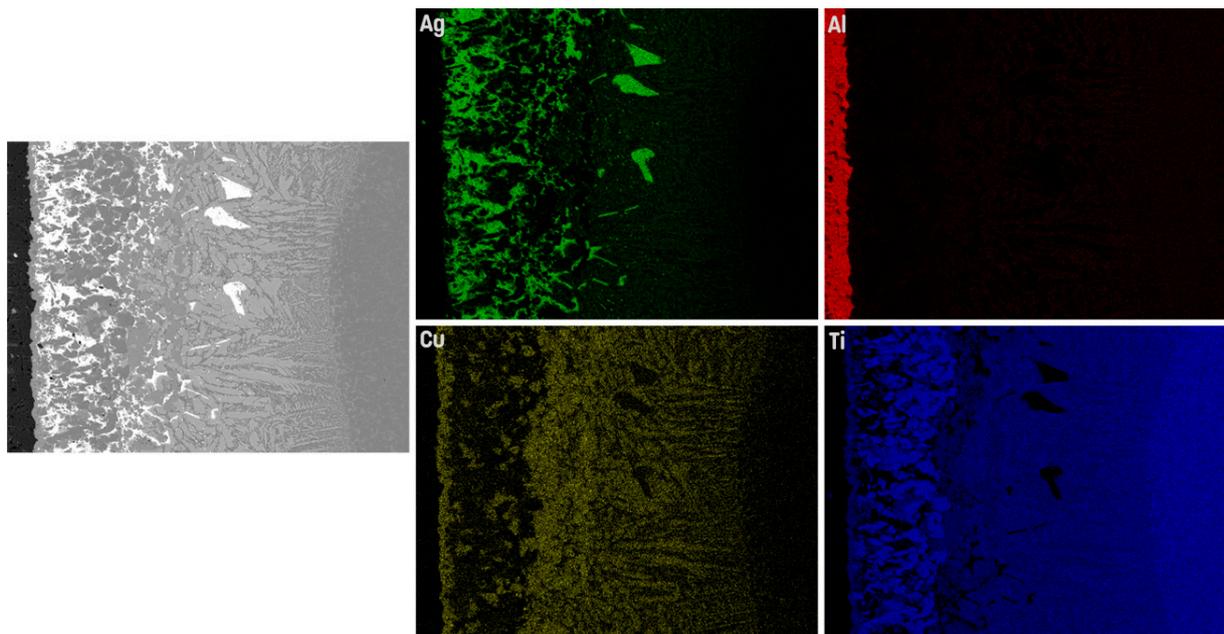
thinner Ti films showed higher concentrations of Ag and Cu in this layer. The C layers were mainly titanium, with Ag-rich bright particles and a Cu-rich light gray phase.



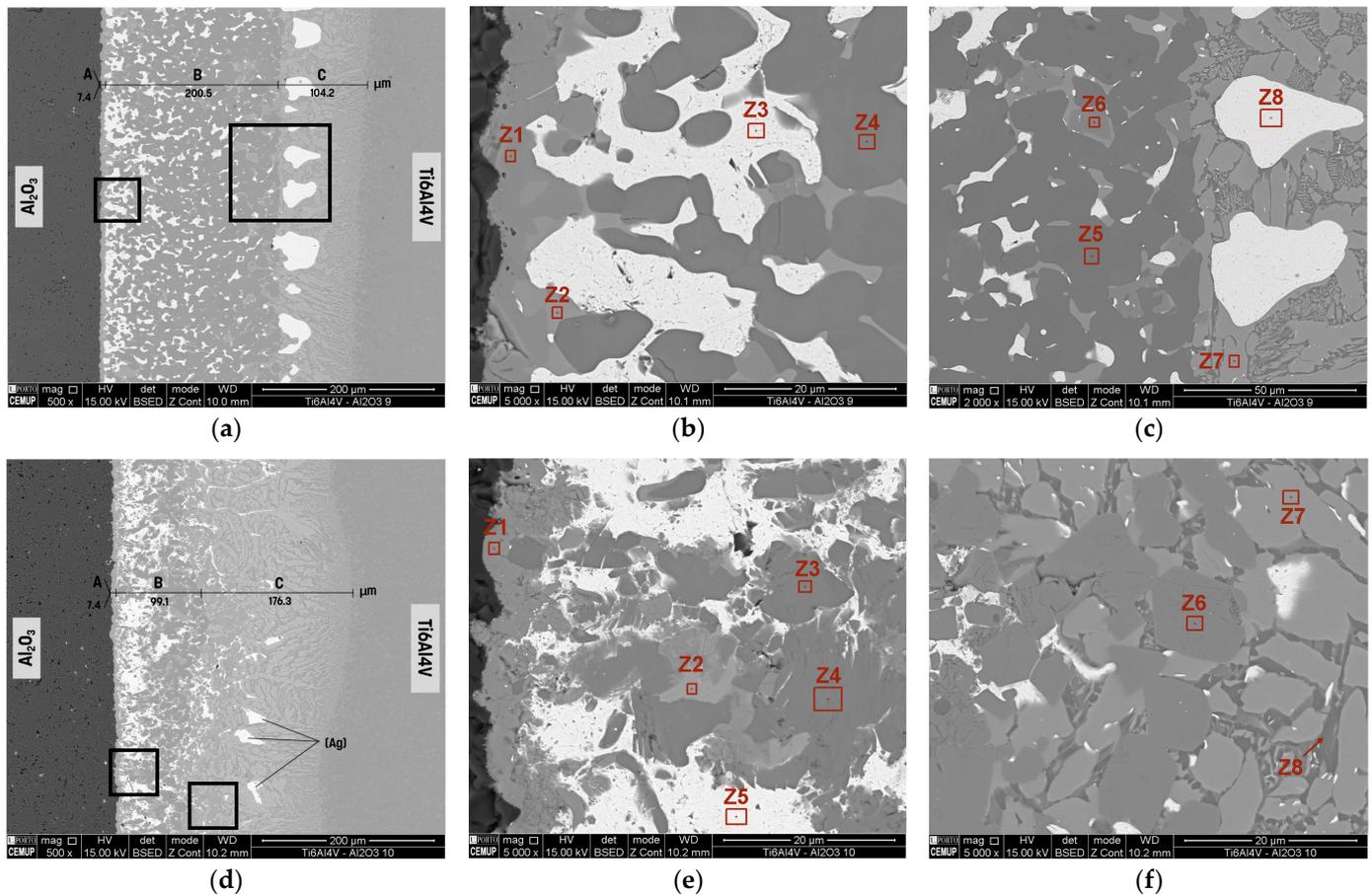
**Figure 4.** EDS chemical composition profile along the interface produced using (a) Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) and (b) Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) brazing filler. The reaction layers are marked as A, B, and C at the SEM images of the interfaces.

The elemental distribution across the interface produced with the Ag/Cu brazing filler combined with Ti at 0.015 mm was also evaluated via EDS maps, as shown in Figure 5. Titanium was present throughout the interface. However, a layer richer in Ti was also observed near  $\text{Al}_2\text{O}_3$ . Cu was detected more predominantly in areas adjacent to Ti6Al4V. Regarding Ag, it was possible to detect that the brightest particles observed in the SEM images corresponded to particles rich in this element. Although the Al map exhibited challenges in readability, the element was observed to be distributed across the interface, with the notable exception of regions rich in Ag.

The identification of reaction layer phases was accomplished via EDS chemical analysis, complemented by SEM observations and information obtained from the Ti-Al-Cu [24], Ti-Ag-Cu [25], Ti-Al [26], and Ti-Cu [27] phase diagrams. Figure 6 displays SEM images of the interfaces with details of the designated regions. EDS was employed to determine the chemical composition of various areas within the reaction layers. Table 1 presents the EDS results corresponding to the marked zones in Figure 6. Due to the EDS volume of interaction and the low thickness of some of the regions, the possible phases were identified from microstructural observation combined with phase diagram data and chemical composition.



**Figure 5.** EDS elemental distribution maps (Ag-green, Al-red, Cu-Yellow and Ti-blue) along the interface produced using Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) brazing filler.



**Figure 6.** SEM images of the interface processed with (a–c) Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) and (d–f) Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) brazing filler. The zones identified (Z1 to Z8) in (b,c,e,f) are the regions where the EDS analysis was performed. The reaction layers are marked as A, B, and C at the interfaces.

**Table 1.** EDS-obtained chemical composition (% at) of the marked zones identified in Figure 6.

	Layer	Zone	Ti	Al	Cu	Ag	Possible Main Phases	
Ti-Ag/Cu-Ti Thickness Ti (0.075 mm)	A	Z1	50.8	14.4	34.8	-	Ti <sub>2</sub> Cu + TiCu <sub>2</sub> Al	
		Z2	62.0	3.8	28.9	5.3	Ti <sub>2</sub> (Cu, Ag)	
	B	Z3	-	-	-	100.0	(Ag)	
		Z4	92.4	6.2	-	1.4	αTi	
		Z5	92.3	5.9	-	1.7	αTi	
		Z6	51.5	13.5	35.0	-	TiCu <sub>2</sub> Al + Ti <sub>2</sub> Cu	
		C	Z7	61.1	4.57	28.0	6.3	Ti <sub>2</sub> (Cu, Ag)
			Z8	-	-	-	100.0	(Ag)
Ti-Ag/Cu-Ti Thickness Ti (0.015 mm)	A	Z1	51.4	13.8	34.8	-	Ti <sub>2</sub> Cu + TiCu <sub>2</sub> Al	
		Z2	62.5	3.2	29.4	4.9	Ti <sub>2</sub> (Cu, Ag)	
	B	Z3	94.2	4.3	-	1.6	αTi	
		Z4	93.9	4.5	-	1.7	αTi	
		Z5	-	-	4.7	95.3	(Ag) + (Cu)	
	C	Z6	51.5	12.7	35.8	-	TiCu <sub>2</sub> Al + Ti <sub>2</sub> Cu	
		Z7	62.3	3.8	27.6	6.4	Ti <sub>2</sub> (Cu, Ag)	
		Z8	73.6	18.1	5.0	3.1	Ti <sub>2</sub> (Cu, Ag) + Ti <sub>3</sub> Al	

In joints formed by combining the thicker Ti film (0.075 mm) with Ag/Cu, Layer A was characterized by Ti<sub>2</sub>Cu + TiCu<sub>2</sub>Al phases. The microstructure of Layer B, spanning a thickness of 200.5 μm, underwent a notable transformation along its length. In proximity to Layer A, there was a higher concentration of Ag-rich particles (Z3) within a Ti-rich phase (Z4) matrix. Conversely, closer to Layer C, an increased prevalence of TiCu<sub>2</sub>Al + Ti<sub>2</sub>Cu particles was observed. Layer C comprised (Ag) particles within a region consisting of Ti<sub>2</sub>(Cu, Ag) + Ti<sub>3</sub>Al phases.

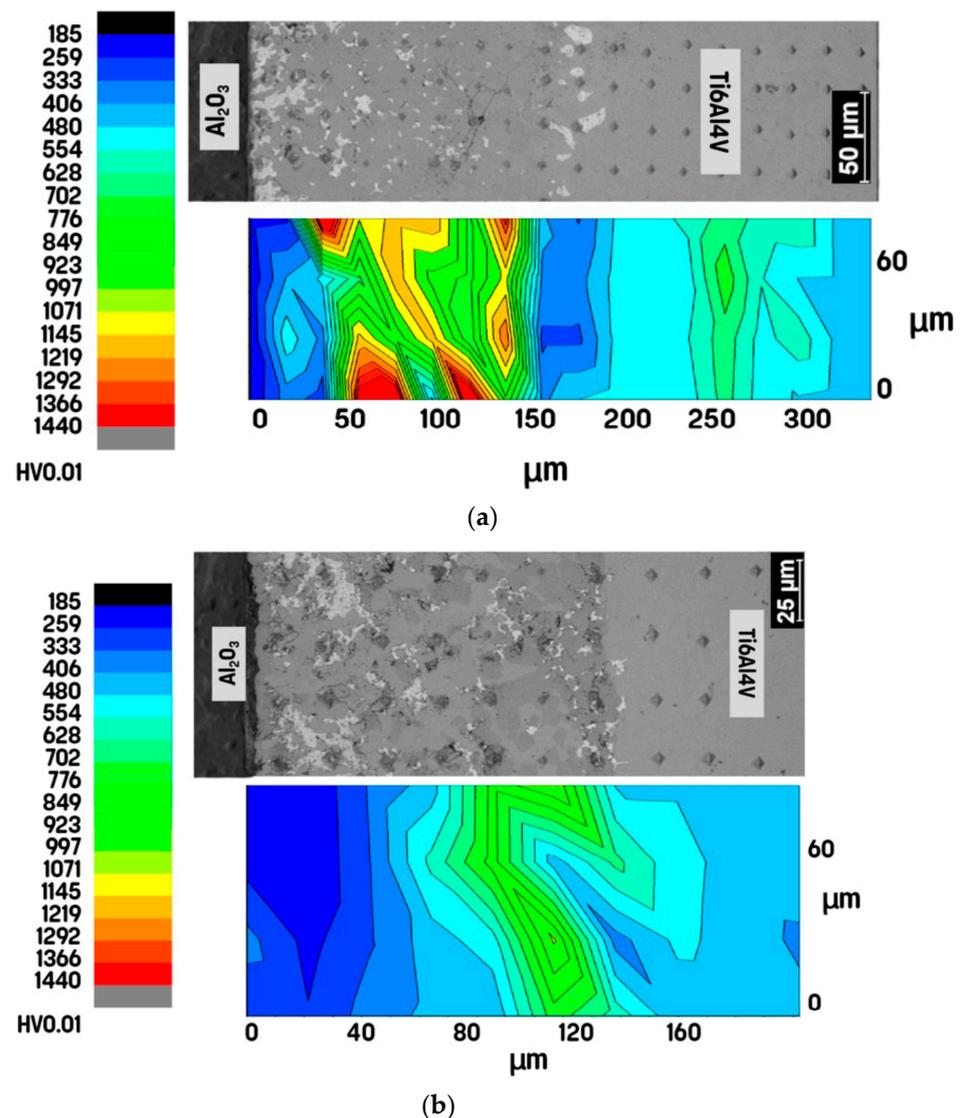
When the thickness of the Ti film in the filler was reduced to 0.015 mm, Layer A exhibited similarities in both thickness and microstructure to the joint produced with the braze filler composed of the combination with thicker titanium film. Phase identification indicated that this layer comprised Ti<sub>2</sub>Cu + TiCu<sub>2</sub>Al phases. Layer B consisted of numerous white (Ag) and (Cu) segregation regions containing Ti<sub>2</sub>(Cu,Ag), Ti<sub>2</sub>Cu + TiCu<sub>2</sub>Al + α-Ti phases. The areas near Layer C showed a reduced presence of (Ag) and (Cu) segregation. Ti-rich phases predominated in the microstructures as the observed brighter (Ag) and (Cu) areas became smaller and more dispersed. Layer C exhibited an extended and markedly different microstructure, characterized by Ti<sub>2</sub>(Cu,Ag) and Ti<sub>3</sub>Al intermetallic phases.

These findings indicate that the reduction in the thickness of the Ti film in the Ag/Cu brazing filler leads to the formation of a more complex interface microstructure, contributing to the elimination or significant reduction of (Ag) segregation. Large (Ag) segregation zones at interfaces can compromise the joint service temperature. Post-brazing heat treatment may be necessary to eliminate or minimize (Ag) segregations and enhance joint performance. Interestingly, combining Ti and Ag/Cu films as a brazing filler demonstrates a trend towards reducing or eliminating (Ag), in contrast to observations in other studies that utilized Ag-Cu and Ag-Cu-Ti interlayers [21,27,28]. The presence of α-Ti, Ti-Cu compounds, and (Ag) segregations aligns with results in other studies that used Ti-Ag-Cu interlayers to bond dissimilar materials [27–29].

### 3.2. Mechanical Characterization

Figure 7 illustrates the hardness distribution maps of the brazed joints, revealing notable variations in hardness evolution for joints produced with different thicknesses

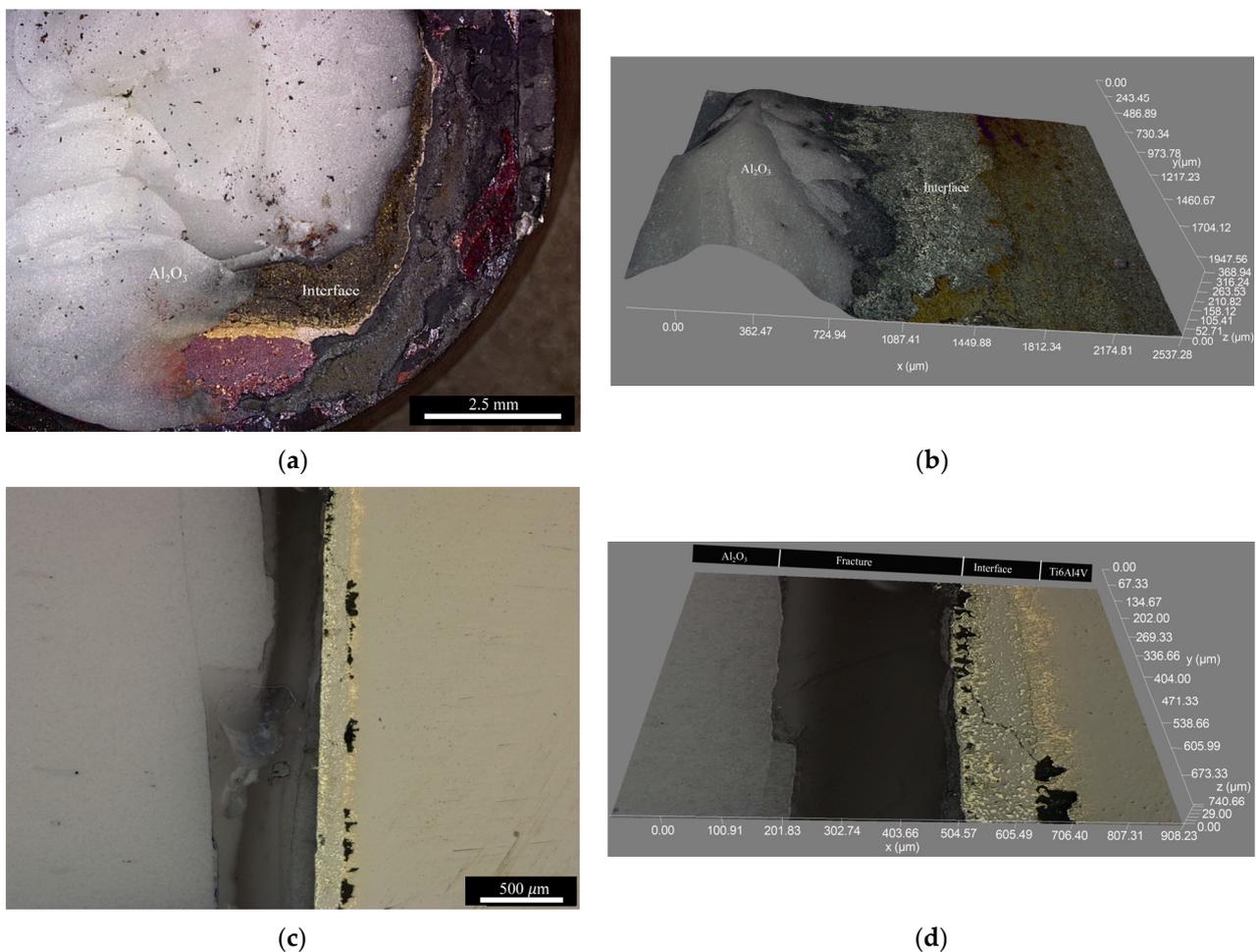
of Ti films in the brazing filler. Although hard phases were expected in Layer A, the limited thickness of this layer prevented hardness measurement. Measurements began near the interface with Layer B. In the case of the sample bonded with a 0.075 mm film, Layer B exhibited a pronounced hardness gradient, with lower values near Layer A, approximately 200 HV0.01, attributed to soft (Ag) segregations. Nevertheless, with the increasing dispersion of (Ag) and a rise in Ti content along the length of Layer B, there was a substantial increase in hardness values, which reached up to 1436 HV0.01. The (Ag)-rich segregations contributed to a decrease in hardness values of approximately 300–450 HV0.01 within Layer B. This reduction may have had adverse effects given that these values fell below the hardness of Ti6Al4V, which is approximately 500 HV0.01.



**Figure 7.** Vickers microhardness distribution maps of the (a) Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) sample and (b) Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) filler.

The values observed for the joint produced with the Ag/Cu brazing filler and the thinner Ti film differed significantly. The different microstructure in Layer B impacted hardness values, with a pronounced hardness gradient being observed along its length. The silver segregations located in layer A at this interface resulted in low hardness values of 180 to 250 HV0.01. An increase in hardness to 500 HV0.01 was observed in the most distant regions of Layer B, due to the Ti phases becoming dominant and the particles (Ag) becoming smaller and more dispersed. Elevated hardness values (900 HV0.01) per-

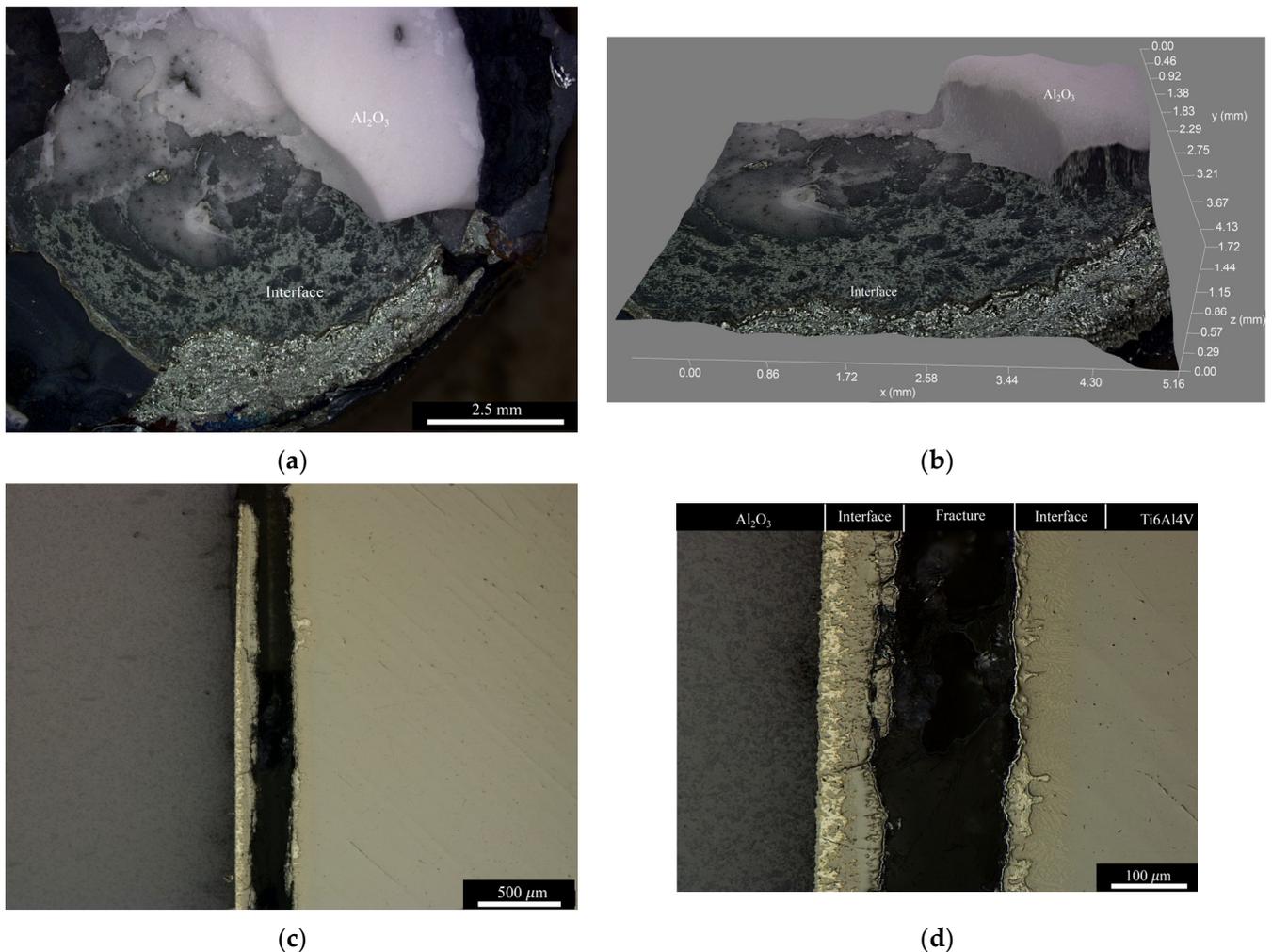
sisted at the interface, likely attributable to intermetallic phases. The sample produced with the thickest film under the load exhibited higher hardness values along the interface, and this increase may be linked to a greater dispersion of content and quantity of intermetallic phases. The integrity of the produced joints was assessed through shear strength tests. The joints formed with the thinner Ti film in the filler achieved the highest shear strength ( $132 \pm 19$  MPa). While this value aligns with some previously reported in the literature [9,21,22], its significance lies in the potential reduction of the solid solution of Ag and Cu, which would enable the maintenance of a higher operating temperature. This value decreased significantly to  $78 \pm 13$  MPa as the thickness of the titanium film increased. Fracture surfaces and cross-sections of each joint fracture were examined using DM, and the results are depicted in Figures 8 and 9.



**Figure 8.** Digital microscopy (DM) images of the shear-tested sample of the joint produced with Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) brazing filler: (a) image of the fracture of the Ti6Al4V base materials, (b) 3D image of the region in (a), (c) cross-section of the shear-fractured sample, and (d) 3D image of image (c).

Regarding the samples, all fractures originated from the ceramic base material and propagated along it, eventually reaching the interface. These results confirm that using this brazing filler allows a sound joint to be obtained, assuring the bonding of  $\text{Al}_2\text{O}_3$ . Figure 8 shows the images of the surface and cross-section of the fractured sample produced with the brazing filler composed of Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm). The fracture occurred mainly through the ceramic material, propagating through the interface between Layer A and this base material. This result indicates that this joint has an interface with high mechanical strength. The regions where the fracture was observed corresponded to the

regions of higher hardness. This may be due to the formation of complex oxides next to the alumina. Significant differences were observed for the sample produced with the brazing filler with thinner Ti films. Although fracture nucleation occurred in the ceramic material, propagation occurred mainly at the interface between layers B and C. This result can be explained by the difference in hardness between these two layers and the formation of intermetallic, which may negatively affect the mechanical properties.



**Figure 9.** DM images of the shear-tested sample of the joint produced with Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) brazing filler: (a) image of the fracture of the Ti6Al4V base materials, (b) 3D image of the region in (a), (c) cross-section of the shear-fractured sample, and (d) a detailed view of image (c).

## 4. Discussion

### 4.1. Effect of the Titanium Film Thickness in the Brazing Filler

The results show that the titanium film's thickness significantly affects the interface's microstructure and mechanical properties, as seen in Figures 3 and 7. A thin film with a finer microstructure promotes greater interdiffusion between the Ti6Al4V base material and the brazing filler. This is because, for lower thicknesses, the diffusivity of the elements increases, as well as with thinner microstructures. A more substantial reaction layer C is evident at the interface established with the Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) brazing filler, as depicted in Figure 5. This layer is essential to ensure the bonding of this base material. Due to more intense interdiffusion, the interface shows a lower extent of (Ag) and (Cu) at the interface, which may allow the maintenance of the service temperature properties of the joint (Figure 5). When the titanium film increases on the braze alloy, the interface mainly comprises a central layer (B layer) composed of Ti and hard intermetallic

from the Ti-Cu and Ti-Cu-Ag systems (Figure 5). The dissolution of Ti with Cu is more intense than that observed for the Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) braze filler due to the high Ti content of this joint. Therefore, a more pronounced reaction is noted between the layers of the brazing filler. The thickness of the Ti in the brazing filler also plays a role in influencing the mechanical properties of the joints. The interface was formed using Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) braze filler, which is characterized by a more uniform hardness distribution and with the value close to that of Ti6Al4V (Figure 7b). This is due to the formation of a thinner reaction layer of soft phases and less formation of hard intermetallic resulting from the reaction between the brazing filler films. The thickness of the Ti in the brazing filler also affects the formation of  $\text{TiCu}_2\text{Al}$ . The increase in Ti content in the brazing filler using a higher thickness promotes an intense dissolution of Cu and the formation of a greater amount of Ti-Cu and Ti-Cu-Al intermetallic phases at the interface. Other authors also observed and reported the strong influence of the Ti amount in the Ag/Cu brazing filler in the interface microstructure during the brazing of alumina and Ti alloys [27].

The thickness of the Ti film in the brazing filler film combination also significantly affects the joint's mechanical properties. When the film thickness is reduced, an increase in shear strength is observed, which means that the bond between the base materials and the brazing filler is ensured via assisted diffusion.

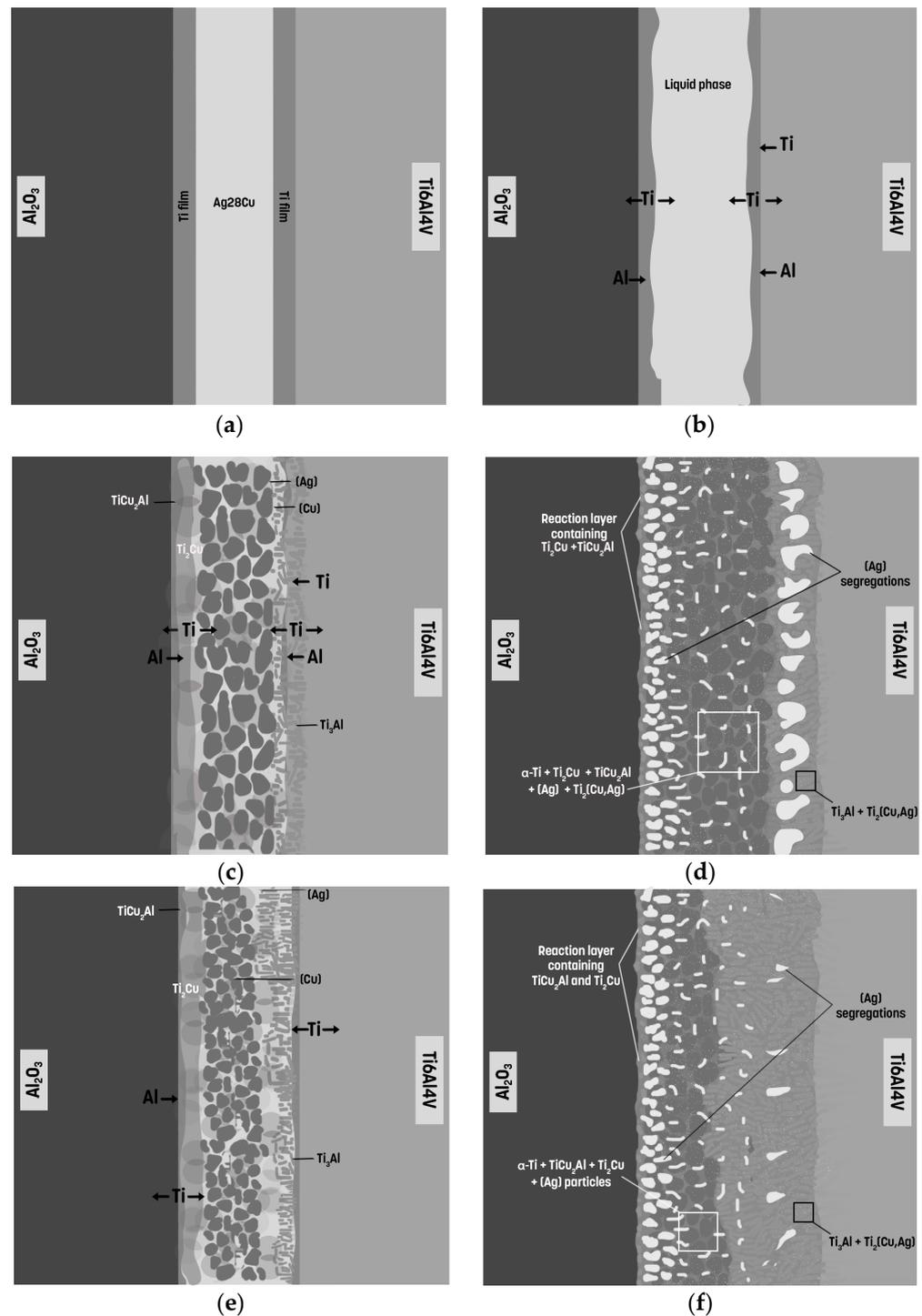
#### 4.2. Mechanism of Interface Formation

Derived from both preceding research involving Ag/Cu interlayers and the current experimental findings, Figure 10 delineates a plausible mechanism for forming the interfaces' microstructure using different Ti film thicknesses in the brazing filler.

The diffusion of Ti plays a crucial role in influencing the microstructural evolution of joints when employed as a brazing filler with varying thicknesses of Ti. As indicated in other studies [29,30], as the temperature increases during the brazing process, a liquid phase enriched in Ag and Cu begins due to the lower liquidus temperature of this film that constitutes the brazing filler (Figure 10b). According to previous research, at 780 °C a eutectic reaction occurs, which results in the formation of a liquid in the center of the interface [31]. The liquid phase incorporates constituents from the closest regions surrounding a Ti film. As the brazing temperature increases, there is greater diffusion of Ti from thin films, Ti and Al from Ti6Al4V, and Al from  $\text{Al}_2\text{O}_3$ . The diffusion and dissolution of Al and Ti in the liquid phase begin with the layer forming at the interface. Close to  $\text{Al}_2\text{O}_3$ , this liquid phase dissolves the Al from  $\text{Al}_2\text{O}_3$  and the Ti from the brazing filler, facilitating the formation of Layer A composed of  $\text{Ti}_2\text{Cu}$  and  $\text{TiCu}_2\text{Al}$  (Figure 10c,e). This occurs when the maximum solubility limits are reached, and different intermetallic precipitates appear, forming continuous layers that guarantee bonding between the base materials and the brazing filler. Based on previous research, a thin layer composed of Ti-Cu-Al-O may form between Layer A and alumina [28]. Complex oxides were also observed in the interface ceramic and Layer A. Figure 11 shows the fracture surface of the sample tested via the shear test, which was analyzed as fracture zones. Table 2 shows the EDS chemical composition of the marked regions of the Figure 11.

**Table 2.** EDS-obtained chemical composition (% at) of the marked zones identified in Figure 11.

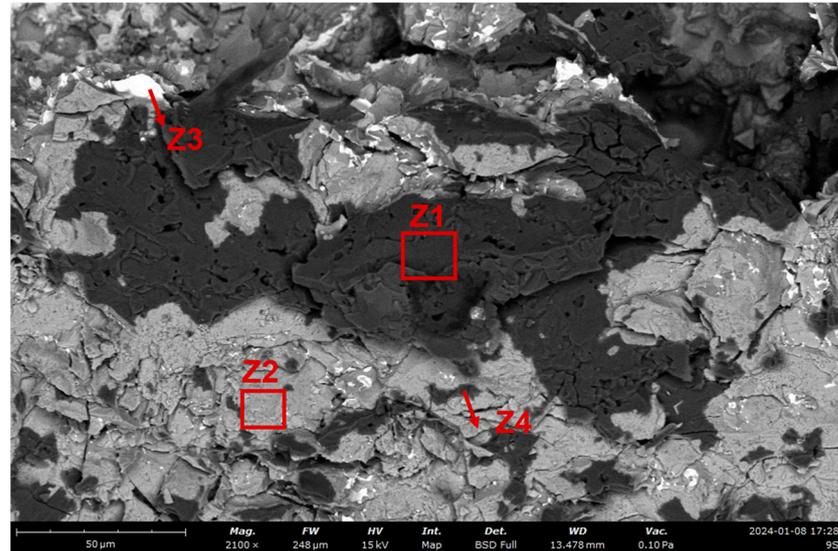
Zone	Ti	Al	Cu	O	Ag	Possible Main Phases
Z1	-	42.6	-	57.4	-	$\text{Al}_2\text{O}_3$
Z2	50.7	20.3	28.9	-	-	$\text{Ti}_2\text{Cu} + \text{TiCu}_2\text{Al}$
Z3	16.5	8.0	15.9	-	59.6	(Ag)
Z4	41.6	13.4	24.2	20.8	-	Ti-Al-Cu-O



**Figure 10.** Schematic illustration of a possible mechanism for the microstructural evolution of the interface of the joint processed with (a) initial configuration of the brazing filler, (b) evolution with an increase in the brazing temperature up to 780 °C, (c,d) evolution of the interface using a Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) sample, and (e,f) evolution of the interface using Ti (0.015 mm)-Ag/Cu-Ti (0.015 mm) filler.

$\text{Ti}_2\text{Cu}$  and  $\text{TiCu}_2\text{Al}$  can be considered complex oxides consisting of Ti-Cu-Al-O. In the proximity of the titanium alloy, the interaction between the brazing filler and the base material forms a Layer C, which, due to the incorporation of Ti and Al from  $\text{Ti6Al4V}$ , forms  $\text{Ti}_3\text{Al}$ . Particles from the Ti-Cu-Ag and Ti-Cu-Al systems are also present in this region. Segregations of (Ag) and (Cu) are observed in specific areas. The center of the interface

is characterized by a mixture of Ti and particles from the Ti-Ag-Cu system with some segregations of (Ag); these result from the intense diffusion of Ti at the brazing temperature. The formation of  $Ti_2(Cu,Ag)$  and  $Ti_2Cu$  particles at the interface is due to the high reactivity of Ti with Ag and Cu.



**Figure 11.** SEM image of the surface of the shear-tested sample of the joint produced with Ti (0.075 mm)-Ag/Cu-Ti (0.075 mm) brazing filler. The zones identified (Z1 to Z4) are the regions where the EDS analysis was performed.

Extending the time at the brazing temperature facilitates the growth of the formed reaction layers due to the Ti diffusion and reaction. When the thickness of the Ti is reduced, a notable contrast is observed in the evolution of interface formation.

In the reaction between the brazing filler and the Ti6Al4V base material (Layer C), the interdiffusion of Ti and the diffusion of Al contribute to forming a thicker reaction layer with less segregation of the solid solution of Ag and Cu (Figure 10c,d). An increase in Ti thickness in the brazing filler may considerably impede the dissolution of Ti from Ti6Al4V. This diffusion of Ti into both base materials impacts the joining process significantly. The thinner the film, the easier the diffusion, due to both the shorter distance and its structure, which are favorable factors in forming interface reaction layers (Figure 10e,f).

#### 4.3. Integrity of Brazed Joints

The integrity of the brazed joints between Ti6Al4V and alumina is an issue for service performance in aerospace applications. In the current study, the maximum shear strength was obtained using the brazing filler composed of Ti films with 0.015 mm and Ag/Cu eutectic cold rolling films. However, the fracture nucleates at the ceramic base material and propagates through Layers B and C, which then present some hard intermetallics. Using Ti films combined with Ag/Cu eutectic filler is a useful approach for obtaining joints without significantly compromising service temperature. Using Ag/Cu films makes it possible to reduce the processing conditions of joints between metals and ceramics. Still, a major disadvantage is the formation of solid solutions of Ag and Cu, which affect service temperature [9]. Using Ti foils or Ti-based brazing fillers is a good approach for overcoming the joint's service temperature challenges. However, it is necessary to use high processing temperatures, which can damage the mechanical properties of titanium alloys. Combining the two approaches in a single brazing filler has been shown to significantly reduce the extent of (Ag) while maintaining guaranteed high-temperature properties and, at the same time, allow for the use of processing conditions below which significant changes in the microstructure and properties of the Ti6Al4V alloy are observed.

## 5. Conclusions

This study aimed to introduce an innovative method for brazing Ti6Al4V to Al<sub>2</sub>O<sub>3</sub> by developing a new brazing filler. A combination of Ag/Cu and thin Ti films was employed to achieve this goal. This combination aimed to combine the characteristics of both films to result in solid joints with low processing conditions and high mechanical properties. The use of this brazing filler promotes a sound joint.

The thickness of the Ti film in the brazing filler influences the joints' microstructure and mechanical properties. The microstructural characterization revealed that the interface mainly comprises Ti<sub>2</sub>Cu, TiCu<sub>2</sub>Al,  $\alpha$ -Ti, and Ti<sub>2</sub>(Cu,Ag). The thickness of the thin titanium films in the brazing filler affects the reaction layer close to the Ti6Al4V, composed of Ti<sub>3</sub>Al and the amount of (Ag) at the interface. The interface obtained for the joint produced with thinner Ti film exhibits a more heterogeneous layer thickness and microstructure with respect to the distribution and amount of (Ag) particles. This promotes a more homogeneous hardness distribution across the interface and a higher shear strength value. The joints exhibiting higher shear strength show fractures that begin within the ceramic base material, extending along or towards the interface. This approach effectively achieves robust joints characterized by minimal (Ag) at the interface. It ensures the endurance of the joints at service temperatures while maintaining a high shear strength value.

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