

# Brazing transparent YAG to Ti6Al4V: reactivity and characterization

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## Abstract

The YAG/filler/Ti6Al4V system has been studied for the first time with the aim of producing brazed optical windows. Different fillers (AgCuTi, AgCu, Ag) and temperatures have been taken into account and the interfacial zones of the samples have been evaluated in terms of morphology and compositions. A thin and continuous metal-ceramic layer containing Ti is formed in contact with the YAG ensuring the adhesion between all the joined materials. The best joining results have been obtained at 850 °C, where we have observed **the formation of an interfacial CuTi** layer when AgCuTi and Ag have been used. No intermetallic compound formation was observed using the pure Ag at 970 °C and 1050 °C. The phase formation was interpreted using the CALPHAD method by means of recalculated Ag-Cu-Ti and Ag-Al-Ti isothermal sections. Microhardness tests have been conducted to evaluate the performances of the joints in terms of mechanical properties.

**Keywords:** Transparent YAG; Interface structure; Metal–ceramic joining; Active element.

## 1. Introduction

This investigation aims to define a brazing process that leads to reliable joints between a transparent ceramic (**Yttrium-Aluminium garnet-YAG**) and a structural metal by defining and characterizing a filler alloy, which is capable of promoting interactions and good adhesion between the two different materials to be joined.

Brazing is a flexible and simple process that allows materials to be joined using a metallic interlayer, which has a relatively low melting temperature and promotes the bonding by wetting and reacting with the metal and the ceramic part. In the field of marine applications, new ceramic materials are requested to be used as transparent windows (e.g. for laser sensors). For this reason, the capability of the ceramic part to maintain its transparency after a joining process and during its immersion in the marine water represents a necessary requirement. Many other fields need these particular materials; atomic physics and frequency metrology applications, for instance, require nonmagnetic optical windows for ultra-high vacuum chambers; in this context sapphire and titanium joints were obtained by Ag-Cu-Ti brazes [1]. Jacobs et al have analyzed the silica/PbAg/304 stainless steel interfaces, a material potentially required for various plasma diagnostic systems in the ITER vacuum vessel [2].

Gustarov has investigated how an ITER simulated environment can influence the mechanical stability and the optical characteristics of prototype windows assemblies in which Si<sub>3</sub>N<sub>4</sub>, silica and sapphire are the transmission elements bonded or brazed to a stainless steel or Ti ferrule. They found that the bonds at ceramic-metal interfaces remained leak-tight after irradiation and thermal cycling [3].

A thorough investigation on transparent and gas-tight optical windows in low-temperature co-fired ceramics (LTCC) was conducted three years ago [4]. Thin glasses (borosilicate glasses and fused silica) were bonded by thermo-compression in an LTCC substrate in order to obtain materials used as optical analysis systems, for innovative applications such as observing chemiluminescent reactions. Laser welding techniques for glass-glass and glass-metal joining have recently been considered, including hermetic sealing applications [5].

In this paper, transparent ceramic windows made of sintered **YAG** ( $Y_3Al_5O_{12}$ ) coupled to Ti6Al4V supports have been studied as potential candidates in the marine applications mentioned before. This is due to their transparency, good mechanical properties and to the outstanding corrosion resistance of the individual components. Indeed, Ti6Al4V exhibits an exceptional erosion-corrosion resistance [6-9], a high fatigue strength in air [10-12], as well as in chloride environments [13] and a low coefficient of thermal expansion. This improves the interface compatibility with the ceramic counterpart. Generally, the filler alloys used for joining dissimilar materials contain an active element such as Ta, Nb, Zr, V or especially Ti [14-17] that promotes wetting of the ceramic surface and chemical bonding with the metallic member of the joint by adsorbing or reacting with the ceramic oxide.

In this work, a comparison was performed between joints produced using filler alloys with or without an active element in order to capture the differences in terms of interface reactivity and to find some possible suggestions to be adopted in the potential industrial process.

Different types of metal-ceramic joints YAG/filler/Ti6Al4V (filler=AgCuTi, AgCu, Ag) have been produced under inert atmosphere conditions (Ar), at high temperatures (between 850 °C and 1050 °C), and subsequently assessed in terms of interfacial reactivity by wetting tests and EDS analysis, and in terms of mechanical properties by micro-hardness test.

The wettability and the reactivity of the YAG substrate by the filler alloys AgCuTi, AgCu and pure Ag were previously analyzed **by this Group** and the results reported in [18]. These results showed excellent wettability and interfacial reactivity for the YAG/AgCuTi systems tested at both 850 °C and 950 °C. Indeed, the contact angles for these pairs were significantly below the limit of 90° and two different continuous metal-ceramic layers without defects and pores were observed along the whole contact zone. The microchemistry and the microstructure of new interfacial products represent a crucial point that has to be carefully controlled in order to obtain the desired mechanical performances. Indeed, excessive reactions can create undesirable brittle intermetallic phases compromising the technological quality of the joint. In addition, it is also necessary to consider that the production process of the filler alloys suggests limiting the concentration of the active metals in the brazes for economic (and sometimes, strategic) reasons. In these particular systems, like in several other metal/ceramic ones, the presence of Ti is necessary to wet the YAG surface. We were able to demonstrate that the formation of two metal-ceramic phases at the interfacial zone allows a new interfacial layer to be obtained in contact with the alloy drop and also well wetted by it [18].

Thus, in order to avoid the use of the active element in the filler material with a consequent simplification of the process, YAG/Ag/Ti6Al4V and YAG/AgCu/Ti6Al4V pairs were also tested to demonstrate that the spontaneous Ti migration from Ti6Al4V bulk to the interfacial zone is sufficient to promote the wettability and the adhesion of the metal-ceramic components. Indeed, the Ti6Al4V counterpart could act as an active source of Ti for the brazing alloy.

## 2. Experimental part

### 2.1 Ceramic materials

The ceramic substrates were prepared by CNR-ISTEC following the experimental procedure of Esposito et al [19, 20], starting from extremely pure ( $\geq 99.99\%$ ) and sub-micrometric ceramic oxide powders of  $\text{Al}_2\text{O}_3$  and of  $\text{Y}_2\text{O}_3$  sintered at  $1735\text{ }^\circ\text{C}$  for 16 h under high vacuum conditions ( $10^{-4}\text{ Pa}$ ). Before the brazing process, the substrates (transparency of about 80% [21]) were polished on diamond grinding discs to reach a final surface roughness ( $S_a$ ) below the value of  $1.00\text{ }\mu\text{m}$ , measured by an optical confocal-interferometric profilometer (Sensofar S-neox) on an area typically about  $3\times 3\text{mm}^2$ .

### 2.2 Metals and alloys

Foils of CB4-AgCuTi alloy (Degussa-Germany), AgCu eutectic (99.9% purity, Metalli Preziosi-Milano, Italy) and Ag (99.997%, Goodfellow, Cambridge, UK), used as filler materials in the joining tests, were laminated in order to reach a thickness of  $100\text{ }\mu\text{m}$  and cleaned in an ethanol ultrasonic bath. The CB4-AgCuTi alloy has a density of  $9.9\text{ g}\cdot\text{cm}^{-3}$ , a thermal expansion coefficient equal to  $18\times 10^{-6}/\text{K}$  and a melting range of  $780\text{-}805\text{ }^\circ\text{C}$  [22]. It is considered as a medium-melting-point active filler (melting point between  $700\text{ }^\circ\text{C}$  and  $1000\text{ }^\circ\text{C}$  [23, 24]).

The compositions of the tested alloys are reported in **Table 1**.

**Table 1**- Compositions of AgCuTi and AgCu alloys utilized as filler (at%).

	Ag	Cu	Ti
AgCuTi	57.7	36.8	5.5
AgCuTi	60.2	39.8	-

The metallic support Ti6Al4V (grade 5 Ti, Titalia, Milano, I), at a composition of 6 wt% Al and 4 wt% V (10 at% Al, 3.5 at% V), was cut to obtain parallelepipeds of 1 cm length and polished on diamond grinding discs to reach a final surface roughness  $S_a \ll 1\text{ }\mu\text{m}$ . The YAG/filler/Ti6Al4V sandwiches were brazed after assembling the pieces using a graphite clamp.

### 2.3 Procedure

The joining experiments were performed in a specially designed furnace that can reach  $1600\text{ }^\circ\text{C}$  [25]; the precision of the temperature readings can be estimated to be  $\pm 5\text{ }^\circ\text{C}$ .

The oxygen partial pressure  $P_{\text{O}_2}$  in the working atmosphere (Ar with less than 0.5 ppm gaseous impurities, flowing at  $50\text{ cm}^3/\text{min}$ ) was continuously monitored by solid state oxygen sensors at the chamber inlet and outlet. A  $P_{\text{O}_2}$  of about  $10^{-2}\text{ Pa}$  (measured at the gas outlet) was measured and different temperatures were chosen (from  $850\text{ }^\circ\text{C}$  to  $1050\text{ }^\circ\text{C}$ ), depending on the constitution of the filler. The samples in the sandwich configuration were then introduced into the preheated furnace by a magnetically operated push rod, as soon as temperature and  $P_{\text{O}_2}$  reached their pre-set values. The joining samples were tested at different temperatures (YAG/AgCuTi/Ti6Al4V at  $850$  and  $950\text{ }^\circ\text{C}$ , YAG/AgCu/Ti6Al4V at  $850\text{ }^\circ\text{C}$ ; YAG/Ag/Ti6Al4V at  $970$  and  $1050\text{ }^\circ\text{C}$ ).

All the specimens were maintained at the selected temperature for 10 min, cooled at a rate of  $5\text{ }^\circ\text{C}/\text{min}$  and finally extracted from the furnace only when room temperature was reached.

The treated samples were then embedded in epoxy resin, cut for morphological observation after polishing down to  $1\text{ }\mu\text{m}$  grit and cleaning in an ethanol ultrasonic bath.

Accurately polished micrographic sections of our samples were observed by scanning electron microscopy (SEM, model: LEO 1450 VP) with the aim to detect the morphological features, and analysed by electron microprobe (EDS) (Oxford Instruments, 7353 model with Oxford-INCA software v. 4.07, type of detector: Si(Li)). EDS analyses were performed on at least five areas for each sample to determine the local composition. The following parameters were used: -working distance of 15 mm, -live time of 60 s, -acceleration voltage of 20kV, -Co as standard element. By using these parameters, the detection limit is 0.1 wt%, while the precision is 1 wt%. Microhardness of the joints was measured on cross-sectioned samples using a Vickers indenter, with a load of 0.01 kgf (0.098 N) and a dwell time of 12 s.

### 3. Results and discussion

One general result that should be underlined is that all the samples tested during the work **maintain** the same crucial and necessary required characteristics of an excellent grade of transparency.

In the following paragraphs the interfacial microstructure of the different types of the metal-ceramic joints will be accurately analysed and presented.

Thanks to CALPHAD modeling, it is possible to make some hypotheses about the evaluation of the experimental results regarding the high temperature metal/filler/ceramic reactivity of our systems. It is important to underline that to clearly and deeply discuss the experimental results, a quaternary (Ag-Cu-Ti-Al), a quinary (Ag-Cu-Ti-Al-V) or even higher order system (Ag-Cu-Ti-Al-V-O) should be considered. However, at present, no thermodynamic database is available for such a system. Then, in order to interpret our experimental results, we have just focalized our attention on the metallic part of the samples, using the existing database found in the literature for the Ag-Cu-Ti ternary system [26-29] from which Figs.3(a) and 6 have been drawn. In principle, the presence of additional elements such as Al and V, with respect to the calculated ternary system introduces the possibility of new phase equilibria, giving rise to new phases or to the disappearance of some of them stable in the ternary system. These points will be duly addressed. In fact in some cases, as it will be discussed in the following part, it is not possible to explain the microstructures obtained on the basis of the ternary Ag-Cu-Ti isothermal section: the Al and V presence seems to be determinant for the stabilization of the phases found. Even if the interactions in the systems studied, in principle depend also on time, as diffusion phenomena are certainly relevant, the high temperature environment as well as the presence of a metallic liquid phase should drive the system not far from equilibrium conditions. This is demonstrated by the presence of most of the phases foreseen by the phase diagram.

#### 3.1 Tests with AgCuTi as filler

The performances of the joints are closely related to the chemical, chemical-physical and mechanical characteristics of the new phases formed by the reactive interactions between the filler alloy and the adjoining ceramic parts. As far as we know, YAG/AgCuTi/Ti6Al4V joints have not been studied before, but some similarities can be found by observing other metal-ceramic brazing joints in the literature, in particular in the temperature range of 840-870 °C, as will be shown later.

##### 3.1.1 Tests with AgCuTi as filler at 950 °C

Analyzing the YAG/AgCuTi/Ti6Al4V samples tested for 10 **min** at 950 °C, the highest temperature suggested for these filler alloys [22], a few fracture paths were observed along the contact line, due

to the dissimilar thermal coefficients, as well as the formation of some different layers characterized by specific morphology and composition.

Four different layers extended between the joined materials at 950 °C (Fig.1):

- a 1<sup>st</sup> layer in contact with the Ti6Al4V characterized by several light grains of CuTi<sub>2</sub> dispersed inside a dark matrix (TiAlV-modified; Table 2);
- a 2<sup>nd</sup> layer formed of Ti solid solution polygonal grains dispersed in a white Ag solid solution;
- a 3<sup>rd</sup> layer composed of CuTi intermetallic grains and of Cu and Ag solid solutions;
- a 4<sup>th</sup> thin layer grown in contact with the YAG ceramic substrate.

All the layers composition is given in Table 2 (in all Tables, in the text and in the Figures the notation (X) stands for “X-based solid-solution”). The composition of the metallic substrate (Table 2, Fig.1(a); left part) is well confirmed by the SEM-EDS analysis.

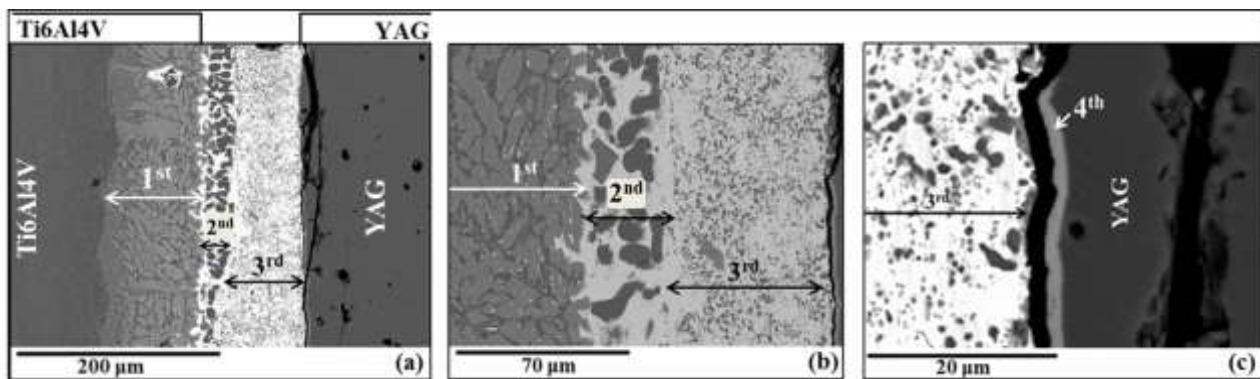


Fig.1- a) Interface microstructure (Back-scattered electrons [BSE] images) of the YAG/AgCuTi/Ti6Al4V samples after test at 950 °C for 10 min and cooled at 5 °C/min; b) and c) the zoomed areas of the different layers .

The 1<sup>st</sup> layer, 100 µm thick, does not appear significantly different in terms of composition from the Ti6Al4V substrate; indeed the Al content of the dark phase (TiAlV-modified in Table 2) of the 1<sup>st</sup> layer remains about 10.0 at% while V increases from 3.5 at% to 12.0 at%. Because of this modified ion distribution, a lower concentration of Ti is found: from 86.0 at% in the Ti6Al4V to 70.0 at% in the 1<sup>st</sup> layer dark matrix. A small amount of Cu (6.0 at%) and Ag traces (2.0 at%) are also detected. The Cu concentration in the light grey grains (CuTi<sub>2</sub> in Table 2) of the 1<sup>st</sup> layer is found to be higher than the Cu amount in the dark matrix, reaching 25.0 at% while both Al and V content decrease from 10.0 at% to 4.0 at% and from 12.0 at% to 1.0 at% respectively. Some Ag traces (< 5.0 at% in CuTi<sub>2</sub> and < 2.0 at% in TiAlV-modified) were also found. The Ag migration is not so significant as the Cu one, however it is more important than in the samples tested at the lowest temperature (850 °C) as shown later.

Table 2- Composition (at%) of the layers (Fig.1) formed at the interface of the YAG/AgCuTi/Ti6Al4V samples (950 °C; Ar<sub>(g)</sub>).

Layer	Phase	Thickness	Ag	Al	Cu	O	Ti	V	Y
Metallic substrate	Ti6Al4V		-	10.5	-	-	86.0	3.5	-
1 <sup>st</sup>	CuTi <sub>2</sub>	100 µm	5.0	4.0	25.0	-	64.0	1.0	-
	TiAlV modified		2.0	10.0	6.0	-	70.0	12.0	-

2 <sup>nd</sup>	(Ag)	20 $\mu\text{m}$	95.0	-	3.6	-	1.4	-	-
	(Ti)		1.2	3.0	0.8	-	94.0	1.0	-
3 <sup>rd</sup>	(Ag)	80 $\mu\text{m}$	98.2	-	0.6	-	0.2	-	-
	(Cu)		1.5	-	97.5	-	1.0	-	-
4 <sup>th</sup>	CuTi	2 $\mu\text{m}$	0.6	0.4	48.0	-	51.0	-	-
	Ceramic sublayer		-	7.0	2.0	58.0	3.5	-	29.5
Ceramic substrate	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>		-	25.0	-	60.0	-	-	15.0

The 2<sup>nd</sup> layer, about 20  $\mu\text{m}$  thick, is composed of an (Ag) matrix including (Ti) grains. Several Ti polygonal grains are, indeed, detected in contact with the 1<sup>st</sup> layer, showing small traces of the other elements (Ag, Al, Cu, V < 3.0 at% each). In the 3<sup>rd</sup> layer, about 80  $\mu\text{m}$  thick, several small grey CuTi grains surrounded by (Cu) areas (Fig.2) are dispersed inside the Ag matrix that extended to the 4<sup>th</sup> layer in contact with the ceramic substrate.

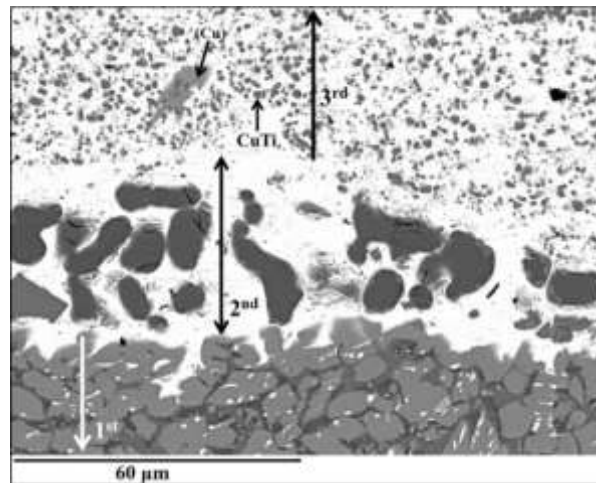
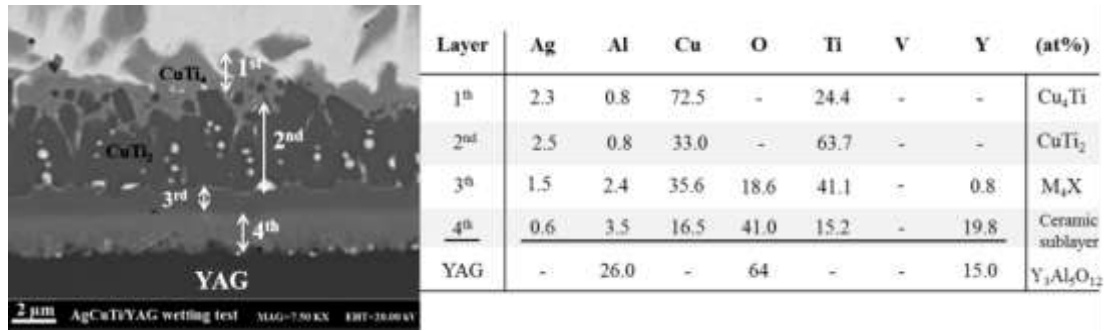


Fig.2- Zoomed interfacial zone of Fig.1(b) close to Ti6Al4V. Samples tested at 950 °C for 10 min and cooled at 5 °C/min.

The 4<sup>th</sup> layer (Fig.1(c)), 2  $\mu\text{m}$  thick, extends as a light grey reaction sub layer on the YAG surface. Because of its small dimensions, it is difficult to obtain accurate EDS quantitative analysis. This layer seems to contain about the same amount of O (58.0 at%) as the YAG (60.0 at%), a lower Al amount (7.0 at% instead of 25.0 at%) because of its high mobility in the molten metal [18] and an enrichment in Y compared to the theoretical stoichiometry of the ceramic (29.5 at% instead of 15.0 at%). The concentration of the active element until the ceramic is related to its presence in the filler material and also to its diffusion from Ti6Al4V.

The Cu and the Ti amounts of the layer in contact with the YAG are larger in the wetting test samples [18] (4<sup>th</sup> layer of Table 2 compared to 4<sup>th</sup> layer in Table 3 in which no metallic counterpart was considered).

Table 3- Interfacial layers of AgCuTi/YAG wetting test system tested at 950 °C for 1 h.



Similarly, comparing the data of **Table 2** and **Table 3** we can observe that:

-the Al amount in the 4<sup>th</sup> layer (**Table 2**, Fig.1(c)) is mainly related to diffusion from Ti6Al4V.

(we can suppose that because the Al concentration in the 4<sup>th</sup> layer of the wetting sections is about 3.5 at% (**Table 3**));

-the Ti amount in the 4<sup>th</sup> layer (**Table 2**, Fig.1(c)) is about 3.5 at%, while it is about 15 at% (4<sup>th</sup> layer; **Table 3**) in the wetting samples.

Considering the thickness of the AgCuTi layer (100 μm) and the absence of Y diffusion from the ceramic part [18], it is possible to locate the original contact surfaces of the starting materials (black lines on the top of Fig.1(a)). On the alloy side, Ti6Al4V extends up to the CuTi<sub>2</sub> grains of the 1<sup>st</sup> layer in the samples tested at 950 °C. According to this consideration, these grains of the 1<sup>st</sup> layer (containing Al and V) are assumed to derive from the modification of the metallic part due to the filler intergranular penetration and diffusion: the grains do not look like solid grains grown from the liquid filler. Cu is the element that migrated most deeply inside the metallic counterpart (**Table 2**, Fig.4): up to about 100 μm from the original Ti6Al4V surface. On the opposite side, we have considered the original surface of YAG corresponding to the limit of the Y presence. The element maps (Fig.4) suggest that Y does not diffuse from the ceramic to the filler as in our previous wettability study of the same systems (YAG/AgCuTi) maintained at 950 °C for 1 h [18]. As underlined in [18], an immiscibility gap is present in the Ag-Cu-Ti liquid (Fig.3(a)). At 950 °C the starting brazing alloy composition falls on the border of the L<sub>1</sub>+L<sub>2</sub> field, then it is mainly formed of liquid L<sub>1</sub> (Fig.3(b)). During the isothermal joining process, the amount of Cu contained in L<sub>1</sub> (36.8 at%) partly migrates inside the Ti6Al4V, promoting the formation of CuTi<sub>2</sub> and partly, as traces, diffuses in the Ti solid solution. This situation is clearly confirmed by the SEM-EDS analysis reported in **Table 4**.

**Table 4-** Composition of the two liquids formed at 950 °C in the Ag-Cu-Ti system.

Comp. at%	Ag	Cu	Ti	ρ [g/cm <sup>3</sup> ]
Starting alloy	57.70	36.80	5.50	9.9
L <sub>1</sub>	57.24	36.72	5.58	8.6
L <sub>2</sub>	11.36	60.45	28.18	6.6

The (Ag) contained in the 2<sup>nd</sup> layer as matrix and in 3<sup>rd</sup> layer together with (Cu) and CuTi traces can be considered as cooling products of a Cu-depleted liquid. However the sequence of solid phases which appeared to be formed during the joining process (CuTi<sub>2</sub> in the 1<sup>st</sup> layer; (Ag) and (Ti) in the 2<sup>nd</sup>; (Ag) and (Cu) as well as CuTi in the 3<sup>rd</sup>) cannot be explained on the basis of the ternary Ag-Cu-Ti isothermal section of Fig.3(a). It is possible that in this case the presence of Al and V in the (Ti) are determinant for its stabilization in 2<sup>nd</sup> layer.

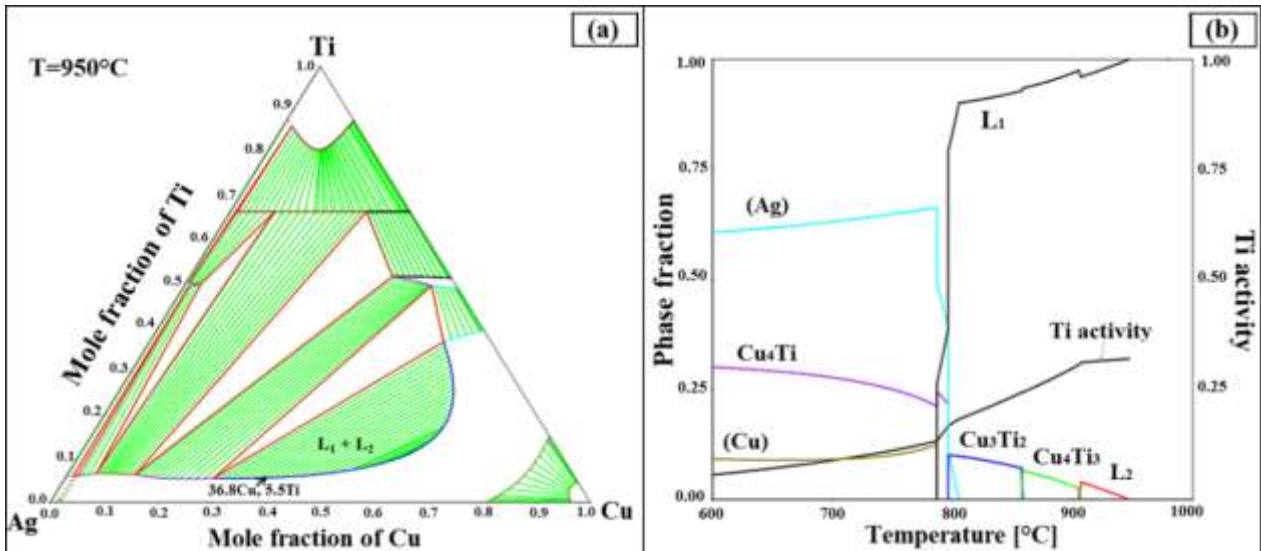


Fig.3- a) Ag-Cu-Ti phase diagram (isothermal section at 950 °C); b) fraction of the different phases formed during the cooling process starting from 950 °C; diagram recalculated from the data of Ref. [26-29].

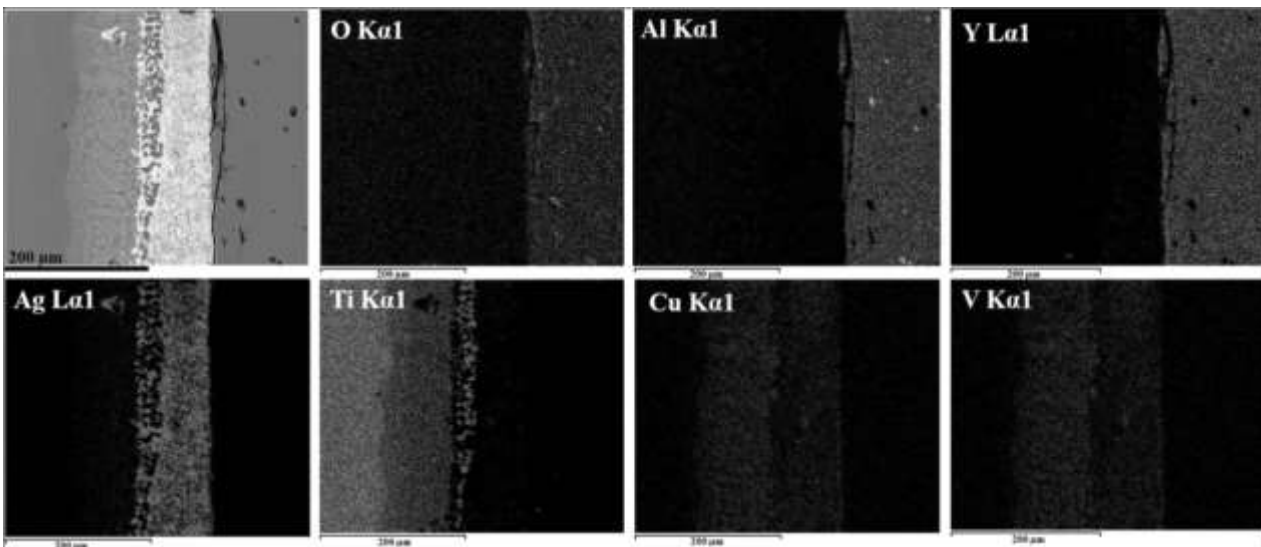


Fig.4- Elements maps at the YAG/AgCuTi/Ti6Al4V samples (950 °C, 10 min, 5 °C/min cooled).

In Fig.1(a) a crack is clearly visible, due to the different thermal expansion coefficients of Ti6Al4V and YAG. In order to overcome this problem, the same systems were tested at a lower temperature (850 °C).

### 3.1.2 Tests with AgCuTi as filler at 850 °C

The wetting behavior of YAG/AgCuTi samples at 850 °C [18] revealed that the contact angle between these materials is 73°, far below the limit of 90° that defines conventionally the non-wettability of a system. So the work of adhesion could assure a good joining at this temperature. Indeed, no fractures or defects were observed along the interfacial layers, which appeared continuous and with a well distributed microstructure (Fig.5).



The YAG/AgCuTi/Ti6Al4V interfacial zone of the samples tested at 850 °C (Fig.5) shows:

- a 1<sup>st</sup> layer in contact with the Ti6Al4V characterized by several grains of **CuTi<sub>2</sub>** dispersed inside a dark matrix (TiAlV-modified; as in the samples tested at 950 °C, this matrix does not appear significantly different in terms of composition from the Ti6Al4V substrate);
- a 2<sup>nd</sup> layer formed of a CuTi intermetallic compound;
- a 3<sup>rd</sup> layer that includes some dark areas of CuTi and (Cu) dispersed inside a light (Ag) matrix (as in the samples tested at 950 °C; **Fig.2**);
- a 4<sup>th</sup> layer grown in contact with the YAG ceramic surface.

The stoichiometry of the Ti6Al4V substrate (Table 5, Fig.5) is well confirmed by the SEM- EDS analysis.

**Table 5-** Composition (at%) of the layers formed (Fig.5) at the metal-ceramic interface of the YAG/AgCuTi/Ti6Al4V samples tested at 850 °C and under Ar<sub>(g)</sub>.

Layer	Phase	Thickness	Ag	Al	Cu	O	Ti	V	Y
Metallic substrate	Ti6Al4V		-	10.5	-	-	86.0	3.5	-
1 <sup>st</sup>	CuTi <sub>2</sub>	10 μm	2.0	10.0	20.0	-	66.0	2.0	-
	TiAlV modified		-	20.0	3.0	-	73.0	4.0	-
2 <sup>nd</sup>	CuTi	10 μm	1.5	1.5	49.0	-	47.0	1.0	-
3 <sup>rd</sup>	(Ag)	80 μm	90.0	-	10.0	-	-	-	-
	(Cu)		3.0	2.0	87.0	-	8.0	-	-
	CuTi		5.3	7.2	42.0	-	45.5	-	-
4 <sup>th</sup>	Ceramic sublayer	2 μm	1.0	-	24.0	44.0	5.0	-	26.0
Ceramic substrate	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>		-	25.0	-	65.0	-	-	15.0

The 1<sup>st</sup> layer, 10 μm thick, appears significantly enriched in Cu particularly in the light phase **formed by CuTi<sub>2</sub>** (Table 5). Comparing the 1<sup>st</sup> layers of the joining samples, tested at higher and lower temperature (950 °C and 850 °C respectively), the main differences consist of:

- a decreased V amount inside the matrix (TiAlV-modified) at 850 °C (V=4.0 at%; Table 5) compared to the V amount found in the interfacial zone maintained at 950 °C (V=12.0 at%; Table 2);
- an increased Al amount at 850 °C in TiAlV-modified phase (Al=20.0 at%; Table 5) compared to the Al amount found in the same areas of the interfacial zone maintained at 950 °C (Al=10.0 at%; Table 2);
- a decreased thickness of this 1<sup>st</sup> layer (Fig.5- T<sub>testing</sub>=850 °C; Fig.1- T<sub>testing</sub>=950 °C).

The 1<sup>st</sup> layer of the samples tested at 850 °C is, in fact, more or less 10 μm thick while the thickness of the same layer in the 950 °C samples is estimated to be more or less 100 μm.

The 2<sup>nd</sup> layer, 10 μm thick too, is formed of the intermetallic CuTi with Ag, Al and V traces (< 1.5 at% each) and represents a sort of barrier for a deeper filler penetration and/or diffusion inside the metallic counterpart. This layer appears very similar to the layer found by Smorygo et al [17], as will be shown in the following part, in terms of composition and morphology. These

observations indicate that the interdiffusion, occurring during the brazing process, between the filler and the base metal led to a depletion of Cu from the molten filler alloy.

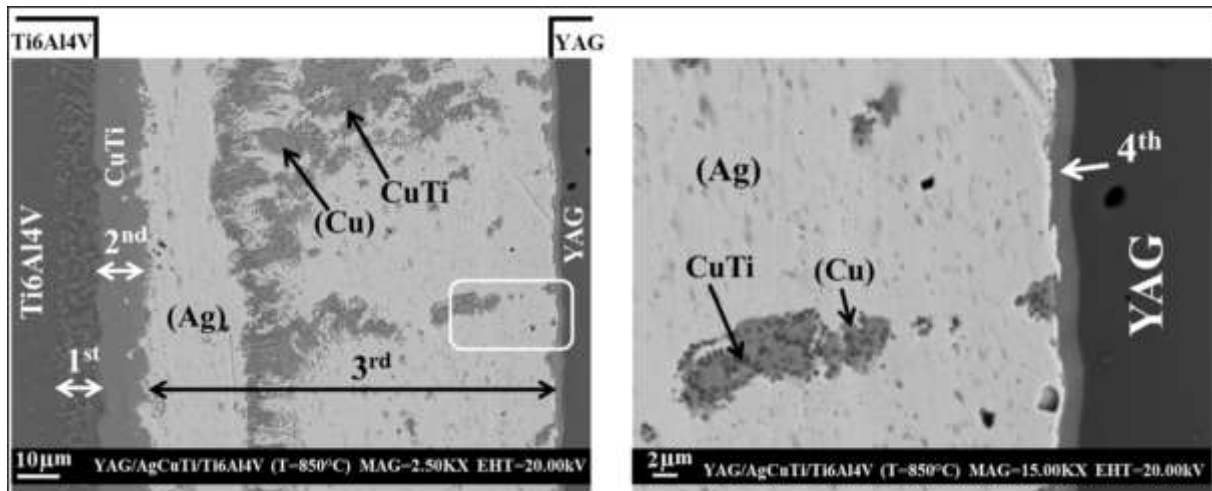


Fig.5- YAG/AgCuTi/Ti6Al4V interface tested at 850 °C; the image is obtained from the SEM-EDS analysis (on the right the zoomed area of the sample part indicated by the white box of the left image).

In the 3<sup>rd</sup> layer, that is 80  $\mu\text{m}$  thick, both Cu solid solution and CuTi, the light and the dark grey areas respectively, are dispersed in a Ag solid solution white matrix extending more or less to the YAG substrate.

The 4<sup>th</sup> layer, **2  $\mu\text{m}$  thick**, formed in direct contact with the ceramic substrate is difficult to analyze precisely by SEM-EDS, like in the case of the previous samples. Nevertheless, this layer seems to contain about 5.0 at% of Ti (Table 5). Therefore, the ceramic sub layer is more enriched in the active element than the ceramic sub layer of the 950 °C samples (Ti= 3.5 at%; Table 2).

The starting composition of the filler alloy is represented by the point shown in Fig.6 (Ag=57.7 at%; Cu=36.8 at%; Ti=5.5 at%) which falls inside the two-phase field L+Cu<sub>3</sub>Ti<sub>2</sub>. During the interaction between filler and metallic counterpart at 850 °C Ti, Al and V diffused into the liquid phase modifying its composition, which is significantly enriched in Ti.

By neglecting Al and V (composition lower than 1.5 at%) we can approximate the liquid phase as a ternary Ag-Cu-Ti.

In this case the appearance of CuTi<sub>2</sub> and CuTi inside the 1<sup>st</sup> and 2<sup>nd</sup> layers respectively may be justified with the Ti-enrichment of the liquid.

The CuTi, already contained in the liquid alloy at 850 °C, promotes the formation of an intermetallic layer (2<sup>nd</sup> layer) along the whole interface profile; this layer is grown in contact to the metallic part considered as Ti source. During the cooling process, the liquid alloy, poor in Ti involved in the intermetallic and sublayer formation, generates first of all **an Ag solid solution** and, after approaching the Ag-Cu eutectic stoichiometry, the Ag and the Cu solid solutions that characterize the 3<sup>rd</sup> layer. These phases extend at the interfacial zone with some CuTi traces.

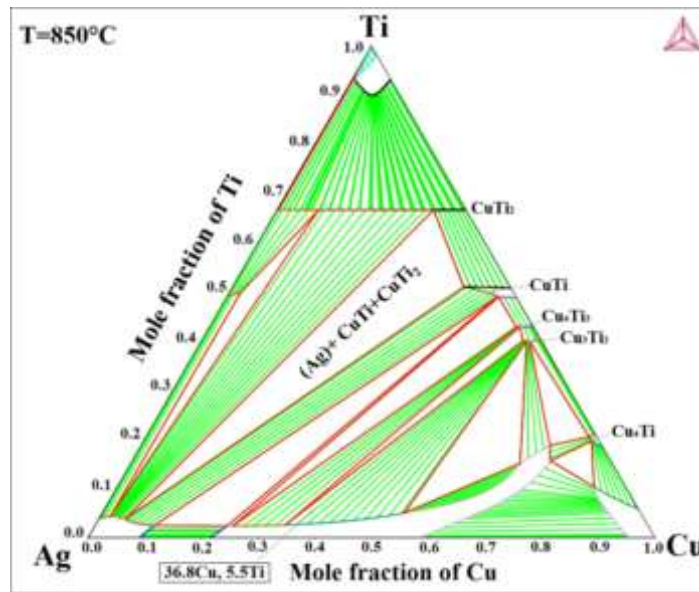


Fig.6- Ag-Cu-Ti (recalculated from the data of Ref. [26-29]) isothermal section at 850 °C.

At 850 °C Cu represents the element that interacts most deeply with the two parts joined. Ag is the least active element of the filler while Cu has a strong tendency to rapidly form intermetallics with Ti [30]. Indeed, Ag has a low diffusivity through the CuTi layer. For this reason, it remains in the central part of the sandwich configuration despite its solubility in Ti and its ability to form intermetallic compounds. The solid solutions of the 3<sup>rd</sup> layer are part of the cooling process (5 °C/min) products. It is important to underline that although CuTi and (Cu) formation occurred at 850 °C, it did not significantly modify the Ti migration at the interface compared to the samples tested at 950 °C. Indeed, the 4<sup>th</sup> layer in direct contact with the YAG is made up of 5.0 at% of Ti, **as already mentioned**. Although YAG/AgCuTi/Ti6Al4V joints have not been investigated before, Smorygo et al [17], for example, analyzed the interface microstructure between zirconia (3Y-PSZ) and Ti joined by active brazing in vacuum in the range of 840-870 °C using 63Ag-35.25Cu-1.75Ti (wt%) as a filler and some similarities can be considered. Analyzing, in particular, the part of the joint closest to the metallic counterpart, they identified and enumerated different layers (Fig.7): a I reaction layer between the filler and the zirconia (3–4 μm), a II bond layer between the zirconia and titanium (45–50 μm) formed by (Ag) with 10–15 at% of the dissolved Cu. Dark intermetallic inclusions of Ti (~40 at%), Cu (~35 at%) and Ag (~25 at%) were also detected; a III reaction layer between the filler and Ti formed of CuTi with Ag traces; a IV diffusive layer containing traces of Ag and with a Cu concentration gradually decreasing inside Ti. Cu must be bound as CuTi<sub>2</sub> in this zone.

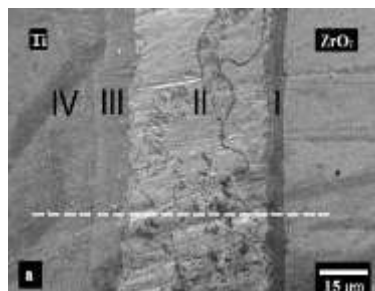


Fig.7- SEM image of Ti/AgCuTi/ZrO<sub>2</sub> joint section (870 °C, 5 min) [adapted from ref 17].

### 3.2 Tests with AgCu and Ag as filler

Samples brazed using alloys without an active metal addition were also tested in order to define a production process as easy as possible and to evaluate how and in what quantity Ti can migrate from Ti6Al4V to the interface.

Among the different elements (Cu, Ge, Si, Sn) capable of forming a homogeneous liquid with Ag, at temperatures lower than its melting point, Cu was considered. Indeed, its use is often related to the best brazing results [31]. For this reason the AgCu alloy ( $T_{eut}=780\text{ }^{\circ}\text{C}$ ) is chosen as potential filler material in joining tests conducted at  $850\text{ }^{\circ}\text{C}$ . The joining tests with pure Ag as filler (YAG/Ag/Ti6Al4V) were also investigated and they were carried out at a higher temperature ( $1050\text{ }^{\circ}\text{C}$ ) compared to the other joining tests reported in the present work, but at the same temperature as the wetting tests reported in our previous work for the Ag/YAG system [18]. The  $T_{exp}/T_m$  (reduced temperature) in the two cases are very similar. Moreover, new wetting tests on Ag/Ti6Al4V samples have been performed to get a full description of all the systems involved. Using Ag as filler will also reduce the global cost of the process, as the source of active element can be the metallic support (Ti6Al4V) itself [32]. Furthermore, a pure Ag filler can reduce the intermetallic compound development at the interface and promote Ti diffusion toward the ceramic part.

#### 3.2.1 Tests with the AgCu as filler

In order to be able to compare the different specimens tested under the same operating conditions, the YAG/AgCu/Ti6Al4V joints were tested at  $850\text{ }^{\circ}\text{C}$ , the lowest of the temperatures used previously for the YAG/AgCuTi/Ti6Al4V samples.

In this case too, the YAG/AgCu/Ti6Al4V samples tested for 10 min appear with a sound joint interface, visible in Fig.8 with a continuous and defect-free interfacial zone.

The different layers revealed at YAG/AgCu/Ti6Al4V interface (Fig.8, Table 7) are very similar to the layers of the samples with AgCuTi as filler and tested at the same temperature ( $850\text{ }^{\circ}\text{C}$ ):

- a 1<sup>st</sup> layer in contact with the Ti6Al4V characterized by several Ti-rich grains dispersed inside a dark matrix (TiAlV-modified);
- a 2<sup>nd</sup> layer formed of CuTi intermetallic compound;
- a 3<sup>rd</sup> layer that includes some dark areas of CuTi and (Cu) dispersed inside a light (Ag) matrix;
- a 4<sup>th</sup> layer grown in contact with the YAG ceramic surface.

The 1<sup>st</sup> layer, about  $10\text{ }\mu\text{m}$  thick, with the same morphology as the one observed in the other joining systems already shown, presents a lower amount of Al inside the matrix (12.0 at%) and a decreased Cu amount inside the grains (8.0 at%) compared to the 1<sup>st</sup> layer of the samples tested at the same temperature but with AgCuTi alloy as filler (Table 5; Al=Cu=20 at%). A 2<sup>nd</sup> layer of CuTi is formed with the same thickness as in YAG/AgCuTi/Ti6Al4V samples tested at  $850\text{ }^{\circ}\text{C}$ . We can conclude that the presence of this intermetallic compound is related to the testing temperature and it does not depend on the Ti coming from the filler. The CuTi is, in fact, formed in contact to the metallic counterpart. The Cu has a stronger tendency to react with Ti compared to Ag as revealed by the Ti partial enthalpy of mixing in molten copper at infinite dilution ( $-10\text{ kJ/mol}$ ) compared with that in the molten silver ( $39\text{ kJ/mol}$ ) [33].

In the 3<sup>rd</sup> layer, the alternation of **Ag and Cu solid solutions** extends for about 65  $\mu\text{m}$  and again traces of CuTi were detected. The continuous layer in contact with the YAG (4<sup>th</sup> layer, 2  $\mu\text{m}$  thick) shows about the same O amount (60 at%) as the ceramic substrate (65 at%) and the same Ti amount (5 at%) as the YAG/AgCuTi/Ti6Al4V samples tested at the same temperature of 850  $^{\circ}\text{C}$ .

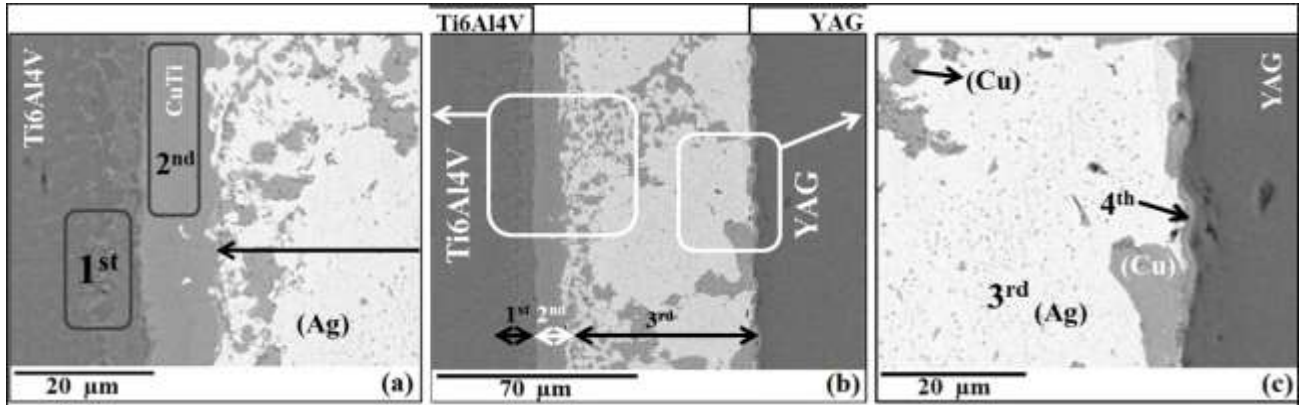


Fig.8- BSE images of the YAG/AgCu/Ti6Al4V interfacial zone tested at 850  $^{\circ}\text{C}$ . In (a) and (c) the zoomed parts of the joint (b) in contact to the Ti alloy support (a) and to the ceramic substrate (c) respectively.

**Table 6-** Composition (at%) of the different layers formed at the metal-ceramic interface of the YAG/AgCu/Ti6Al4V samples (Fig.8) tested at 850  $^{\circ}\text{C}$  and under  $\text{Ar}_{(g)}$ .

Layer	Phase	Thickness	Ag	Al	Cu	O	Ti	V	Y
Metallic substrate	Ti6Al4V		-	10.5	-	-	86.0	3.5	-
1 <sup>st</sup>	Ti-rich grains	10 $\mu\text{m}$	1.0	12.0	8.0	-	72.0	7.0	-
	TiAlIV-modified		-	12.0	-	-	85.0	3.0	-
2 <sup>nd</sup>	CuTi	10 $\mu\text{m}$	1.4	1.6	47.0	-	50.0	-	-
3 <sup>rd</sup>	(Ag)	65 $\mu\text{m}$	96.0	1.0	1.0	-	2.0	-	-
	(Cu)		3.0	4.5	87.0	-	5.5	-	-
	CuTi		1.2	1.5	45.8	-	51.5	-	-
4 <sup>th</sup>	Ceramic sublayer	2 $\mu\text{m}$	2.0	6.5	3.5	60.0	5.0	-	23.0
Ceramic substrate	$\text{Y}_3\text{Al}_5\text{O}_{12}$		-	25.0	-	65.0	-	-	15.0

We can deduce and conclude that the active element inside the filler alloy did not significantly improve the metal diffusion at the joint interface and the metal-ceramic phase formation.

Indeed, the Ti, dissolved and migrated from the metallic counterpart, played an important role in brazing the Ti6Al4V/YAG moving towards the metal-ceramic interface and in forming both the intermetallic compounds and the sub layer on the ceramic substrate. However, as underlined in previous works [30, 31], the possible formation of intermetallic compounds pertaining to the Cu-Ti system is a good way to obtain a stable interface in the metal-ceramic joint. In a work based on the  $\text{Al}_2\text{O}_3/\text{Ti6Al4V}$  [34], for example, diffusion bonded joints at 750  $^{\circ}\text{C}$  with Ag-Cu interlayer present some similarities regarding the interface microstructure after 10 min testing: a 1<sup>st</sup> layer (A) in contact with the Ti6Al4V, composed of a **Ti-rich zone** and  $\text{CuTi}_2$ ; a 2<sup>nd</sup> layer (B) of **CuTi**; a 3<sup>rd</sup> layer (E), **Ag-rich zone**, appeared close to the intermetallic compound and it is made up of Ag (white phase) and Ti and Cu solid solutions (dark phase).

### 3.2.2 Tests with the Ag as filler

The different composition of the YAG/Ag/Ti6Al4V interfacial layers of the samples tested at the higher temperature of 1050 °C (Table 7) and their BSE analysis (Fig.9) are reported below.

Starting from the Ti6Al4V, the following layers can be found:

- a 1<sup>st</sup> layer showing traces of a white Ag solid solution dispersed inside a dark matrix of TiAlIV-modified;
- a 2<sup>nd</sup> layer formed by light Ag and dark Ti solid solutions;
- a 3<sup>rd</sup> thin layer in contact with the ceramic substrate.

**Table 7-** Composition (at%) of the layers formed at the metal-ceramic interface of the YAG/Ag/Ti6Al4V samples (Fig.9) tested at 1050 °C and under Ar(g).

Layer	Phase	Thickness	Ag	Al	O	Ti	V	Y
Metallic substrate	Ti6Al4V		-	10.5	-	86.0	3.5	-
1 <sup>st</sup>	Ti6Al4Vmodified	20 μm	2.6	12.4	-	81.0	4.0	-
2 <sup>nd</sup>	(Ag)	75 μm	97.5	-	-	2.5	-	-
	(Ti)		2.0	10.0	-	87.0	1.0	-
3 <sup>th</sup>	Ceramic sublayer	2 μm	12.5	3.5	60.5	2.0	-	21.5
Ceramic substrate	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>		-	25.0	60.0	-	-	15.0

The 1<sup>st</sup> layer, about 20 μm thick, shows more or less the same composition of Ti6Al4V with Ag traces (on the left side of Fig.9(a)). A continuous, homogeneous and pore-free alternation of (Ag) and (Ti) (respectively the white and the grey zones visible in Fig.9) extends to the ceramic constituting the 2<sup>nd</sup> layer (75 μm). Some small light grey areas can be observed along the contact line with the YAG: in this 3<sup>rd</sup> layer, about 2 μm, the same O amount as in the YAG was found as well as 2.0 at% of the Ti active element (Table 7).

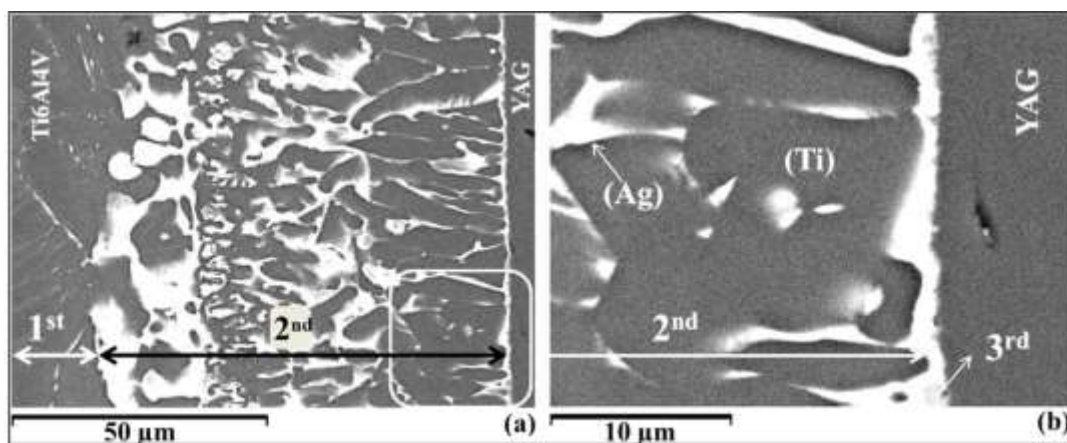


Fig.9- a) BSE image of the YAG/Ag/Ti6Al4V interface; b) the zoomed area (white box) of Fig.(a); (T=1050 °C; t=10 min).

At 1000 °C (Fig.10(a)) we have not detected the AgTi intermetallic compound which is in equilibrium with the liquid phase in a small temperature range (Fig.10(b)).

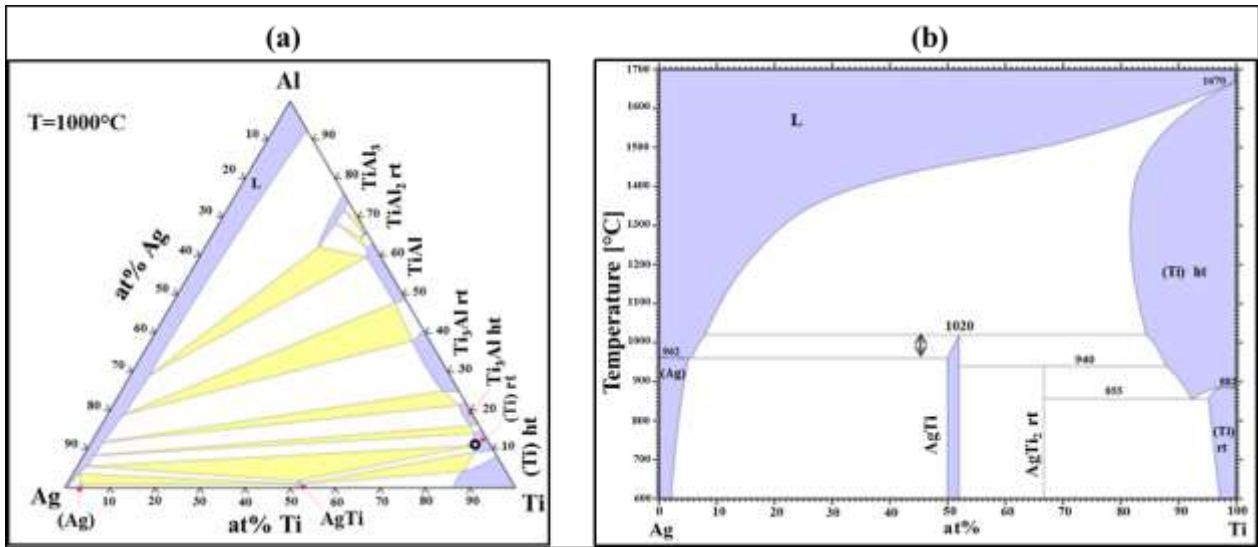


Fig.10- Isothermal section of the Ag-Al-Ti system at 1000 °C (a) [35]; Ag-Ti binary phase diagram [36].

We can suppose that the Ti counterpart remains in the solid state throughout the test and that below 962 °C the Ag-rich liquid phase disappears, preventing the AgTi from forming anymore.

In order to observe the interdiffusion phenomena which can occur at the Ag/Ti6Al4V interface, specific wetting tests have been carried out at a temperature (970 °C) just above the Ag melting point. At this temperature a complete and ideal wetting of the Ag on the Ti6Al4V occurs (Fig.12(b) and (c)). The wetting behavior of this system was followed between 800-970 °C, waiting for 20 min at each temperature (800, 850, 900, 950, 960 and 970 °C) in order to detect whether Al (max solubility 18 at% above 777 °C; Fig.11), diffusing into Ag solid solution, could decrease the temperature, giving rise to contact melting. However, Ag spreading started just above its melting point and, after 5 min from the melting, the substrate was totally covered by the molten metal (Fig.12(b) and (c)): observing the compositions of the Ag/Ti6Al4V interfaces, no (Ag) containing Al is found at all (Fig.13(a); Table 8).

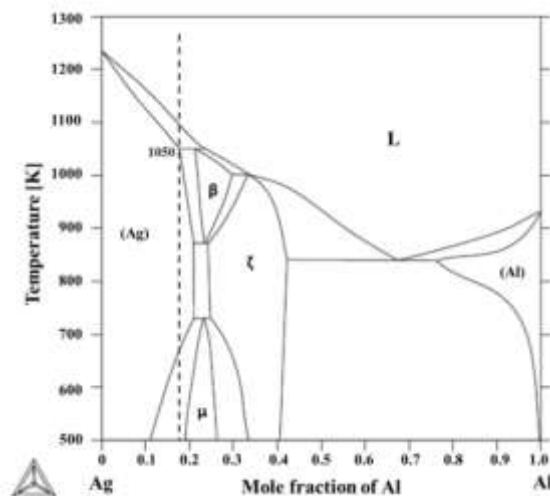


Fig.11- Binary phase diagram of Ag-Al system [37]; the dotted line indicates the maximum solubility the Al has in the Ag solid solution in the presence of a liquid phase.

The Ag, indeed, first of all entered inside the Ti6Al4V bulk (point 3 in Fig.13(a)) and formed a solid solution with the Ti (dark areas detected in point 5 Fig.13(a)).

Al was found in the grey layer close to the metallic support in which the Ti6Al4V composition is maintained (point 3 in Fig.13(a)). YAG/Ag/Ti6Al4V samples were also brazed at 970 °C for 1h. Observing the phase composition at the interfacial zone (Fig.13(b); Table 9), we did not find significant differences in terms of microstructure and composition compared to the same samples tested at 1050 °C (Table 7 compared to Table 9).



Fig.12- Ag/Ti6Al4V profiles of the sample step-heated: at 850 °C (a) and at 970 °C (b); image of a sample after the wetting test at 1050 °C (c).

Table 8- Composition (at%) of the different zones (Fig.13(a)) at the metal-ceramic interface of the Ag/Ti6Al4V samples tested at 970 °C and under Ar(g).

Analysed zone	Ag	Al	Ti	V
(1) Ag	100.0	-	-	-
(2) Ti6Al4V modified	-	10.0	86.1	3.9
(3) Ti-rich zone	9.5	7.1	79.5	3.8
(4) Ag-rich	95.0	-	5.0	-
(5) Ti-rich	4.1	8.3	85.2	2.4

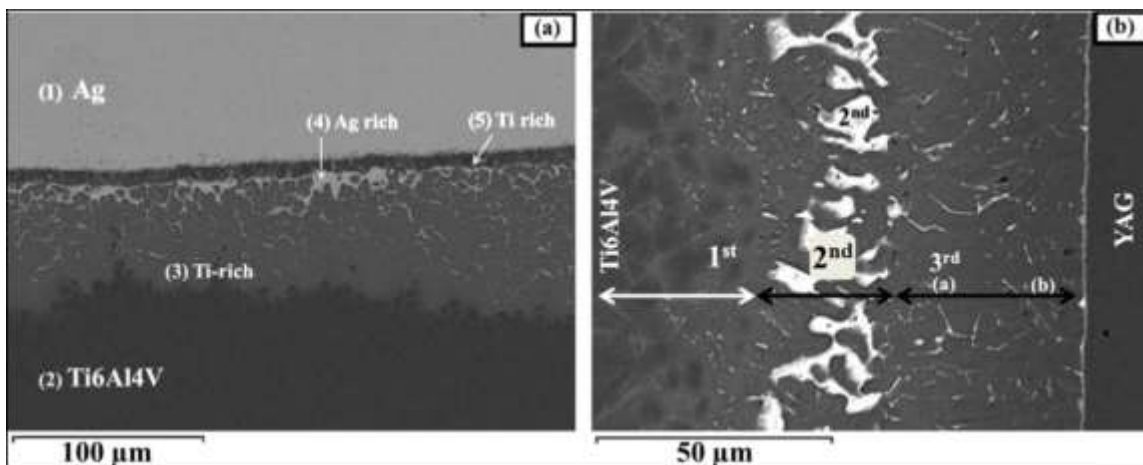


Fig.13- Section microstructure of the Ag/Ti6Al4V samples after the wetting tests conducted at 970 °C (a) and of the YAG/Ag/Ti6Al4V samples after the joining tests at 970 °C for 1h.

Table 9- Composition (at%) of the different layers formed at the metal-ceramic interface of the YAG/Ag/Ti6Al4V samples (Fig.13(b)) tested at 970 °C and under Ar(g).



Layer	Phase	Thickness	Ag	Al	O	Ti	V	Y
Metallic substrate	Ti6Al4V		-	10.5	-	86.0	3.5	-
1 <sup>st</sup>	Ti6Al4V modified	100 $\mu\text{m}$	1.0	12.5	-	84.0	2.5	-
2 <sup>nd</sup>	(Ag)	25 $\mu\text{m}$	95.5	-	-	4.5	-	-
3 <sup>th</sup>	(Ti) zone (a)	50 $\mu\text{m}$	4.0	14.0	-	80.0	2.0	-
	(Ti) zone (b)		2.0	8.0	-	90.0	-	-
Ceramic substrate	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>		-	25.0	65.0	-	-	15.0

It is possible to underline an increased amount of Ti in the solid solution closer to the YAG (zone (b)) and a modified distribution of the Ag-rich white areas. Silver diffusion seems to be more pronounced at higher temperature (Fig.9(a)); a significant amount of Ag was also found very close to the ceramic. The layer in contact with the ceramic maintained the same composition and thickness as that already found in the samples tested at 1050 °C.

#### 4. Microhardness evaluation

Microhardness measurements performed on the different interfaces exhibited a general high dispersion because of the complex and interspersed structures.

The Ag-based zones show a lower value (Fig.14, zone A) compared to the surrounding metallic phases with HV0.01 ranging from 110 to 132 ( $1.1 \cdot 10^3$ - $1.3 \cdot 10^3$  MPa). For all the systems considered, the increased plasticity and ductility associated to the presence of Ag-based phases is considered to have a role in mitigating the residual stresses, which arise upon cooling of the joint because of the CTE mismatch. Moreover, in the case of YAG/Ag/Ti6Al4V joints the **Ag and Ti solid solutions** are concentrated close to the metallic and the ceramic part respectively and no intermetallic compounds are found as underlined before. This fact plays a positive role in terms of the mechanical performances of the materials, as the growth of thick intermetallic layers generally leads to a significant loss in ductility. The Cu–Ti intermetallics, formed when using AgCu and AgCuTi filler alloys, have a higher hardness than Ti6Al4V (Ti6Al4V: 359 HV0.01;  $3.5 \cdot 10^3$ MPa). These compounds are homogeneously placed inside the Ag matrix except for the thin (10  $\mu\text{m}$ ) and continuous layer in contact with the metallic part.

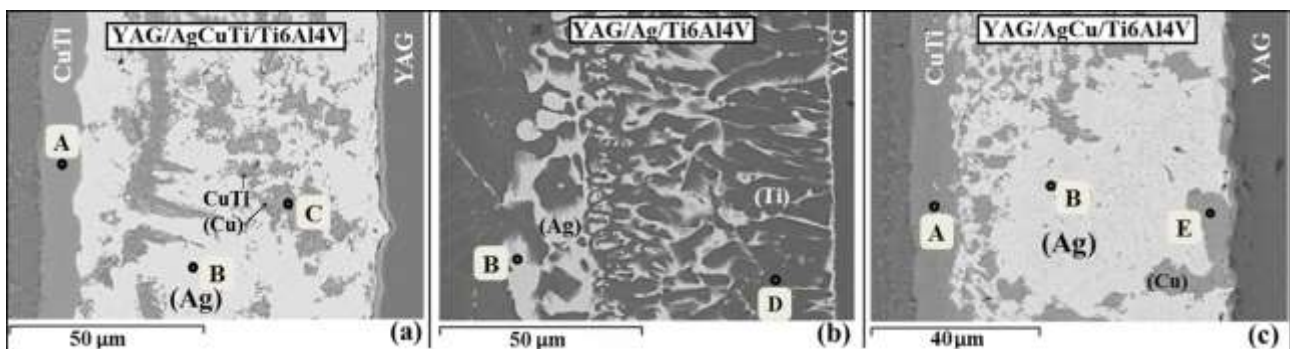


Fig.14- Interfacial zone of the samples YAG/AgCuTi/Ti6Al4V tested at 850 °C (a), YAG/Ag/Ti6Al4V tested at 1050 °C (b) and YAG/AgCu/Ti6Al4V tested at 850 °C (c) selected for the hardness test. The capital letters represent the zones in which more than 10 microindentations were made.

**Table 10-** Microhardness values (all values have an error of  $\pm 50$ ) in the areas indicated in Fig.14.

Filler	ZONE A:CuTi		ZONE B:(Ag)		ZONE C:CuTi/(Cu)		ZONE D: (Ti)		ZONE E: (Cu)	
	HV 0.01	MPa	HV 0.01	MPa	HV 0.01	MPa	HV 0.01	MPa	HV 0.01	MPa
AgCuTi	570	$5.6 \cdot 10^3$	118	$1.2 \cdot 10^3$	542	$5.3 \cdot 10^3$	-	-	-	-
AgCu	550	$5.4 \cdot 10^3$	110	$1.1 \cdot 10^3$	-	-	-	-	356	$3.5 \cdot 10^3$
Ag	-	-	-	-	-	-	350	$3.4 \cdot 10^3$	-	-

The hardness tests conducted on the YAG ceramic substrate revealed an average and reliable value 1750 HV0.01 ( $17.2 \cdot 10^3$ MPa) that did not change significantly with the distance of the ceramic from the interface as a further evidence that the material was not affected by the process. No macro-cracks or pores were detected inside the interface of the samples (Fig.14) and in all the interfacial Ag-matrix zone: this fact indicates that the joints are sound and promising in view of the envisaged applications.

## 5. Conclusions

Different types of metal-ceramic joints were prepared with the aim of producing optical windows with possible applications in marine environment. The previous wetting evaluations [18] related to the same filler /YAG systems significantly support and complete the present work.

Transparent YAG ( $Y_3Al_5O_{12}$ ) and Ti6Al4V, an excellent corrosion resistant alloy, were chosen.

The joining tests conducted in Ar using 3 different fillers (AgCuTi, AgCu, Ag) and different temperatures, were thoroughly analyzed in terms of microstructure and composition of the interfacial zone.

The metal-ceramic interactions were interpreted on the basis of thermodynamic arguments: the high temperature isothermal sections obtained by CALPHAD methods allowed us to study and to predict the phases formed during each specific process and to compare the theoretical results to the experimental ones.

In all the systems a thin and continuous metal-ceramic layer, containing more than 2 at% of Ti, was formed at the metal-ceramic contact zone. Important fractures at the filler/YAG interface were observed in the samples tested at 950 °C using AgCuTi as filler. On the contrary, the samples tested at a lower temperature (850 °C) with AgCuTi and with AgCu as fillers show a continuous defect-free interface and the formation of CuTi as a homogenous layer on the alloy side. This is considered to play the role of diffusion barrier for the filler's components.

In particular, although the CuTi formation may not represent a negative point for the brazed samples performances, it is worth noting that no brittle and discontinuous intermetallic compounds were detected at the YAG/Ag/Ti6Al4V interface.

This point, as well as the homogenous and pore-free interfacial zone, makes this sound and promising joint a favorite candidate for the applications under investigation.

The different phases formed between the ceramic and the metallic counterpart were also evaluated in terms of micro-hardness. In particular, in the case of the YAG/Ag/Ti6Al4V samples, the plasticity of the Ag matrix represents an advantage for the brazed products, as it reduces the interfacial stresses between the two different materials, thus improving the joint performances.

The corrosion resistance of the joined materials in marine water, simulating the possible real operation, is currently under way and will be reported in a forthcoming paper.

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