

## Wettability of transparent YAG ( $Y_3Al_5O_{12}$ ) by molten Ag-Cu-Ti alloys

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### Abstract

The wetting of transparent YAG ( $Y_3Al_5O_{12}$ ) by the AgCuTi brazing alloy has been studied for the first time. The role of the active element Ti in determining the interactions between the brazing alloys and the YAG substrate has been analyzed by CALPHAD method, while the morphology and the composition of phases formed in the alloy/YAG interfacial zone have been evaluated. The low contact angle values ensure very good and fair wettability conditions at respectively 950°C ( $\theta_{eq}=10^\circ$ ) and at 850°C and 820°C ( $\theta_{eq}=73^\circ$  and  $71^\circ$ ) for these systems. Interfacial analyses have shown a significant reactivity at the solid-liquid interfaces and the formation of new phases, such as the  $TiY_2O_5$  at the AgTi/YAG interface. The same metal-ceramic phase was found in the 1<sup>st</sup> layer in contact with the substrate for the all AgCuTi/YAG samples while a second layer, identified as "M<sub>4</sub>X", was found only at the interface of the samples tested at 950°C. Its presence was associated to a significant improvement in the wettability because of its more pronounced metallic behaviour. The different phases formed at 820, 850, 950°C, were identified considering the calculated Ag-Cu-Ti phase diagram and were confirmed by the analyses of the solidified drop sections. This study confirmed the determinant role of the Ti activity for wetting between 910 and 950°C. The obtained excellent wettability and the maintained transparency of the YAG allow these systems to be considered as good candidates for the production of brazed optical windows to be used under extreme conditions.

Active filler metal/ Titanium/ Brazing/ Metal-ceramic joining/ Transparent YAG.

## 1. Introduction

The optical quality of polycrystalline Yttrium Aluminium Garnet-YAG, characterized by transparencies of about 80% [1] and by a good ratio between the Abbe number and the refraction index values [2], makes it an optimal choice to production of lasers [3] and, in general, of optical windows. In particular, due to its high strength and broadband transmission, polycrystalline YAG has the potential to become a significant material of choice for domes and windows for aerospace applications that operate in the midwave infrared. As a stoichiometric compound, YAG has the high index homogeneity necessary for large window applications [4]. Transparent windows often require to be bonded to metal based components and one possibility is to fix them in vacuum-tight devices by brazing processes. The eutectic composition of the system Ag-Cu ( $T_m=780^\circ\text{C}$ ) is widely used as a basis for brazing alloys because it is relatively ductile and therefore able to limit the stresses arising between two materials with different thermal expansion coefficients. But most structural ceramics are not wetted by traditional brazes unless the brazes contain an active element. The wettability and the role of Ti in liquid braze have been discussed by many researchers. Many of them demonstrated that Ti is an active element in Cu and Ag-based braze alloys [5–9]. Paulasto et al. [10] found and confirmed the existence of a miscibility gap which divides the liquid phase into solutions of low and high Ti content in the Ag-Cu-Ti system above a certain temperature; they also found that the Ti activity varies by changing the metal ratio  $\text{Ag}/(\text{Cu}+\text{Ag})$ . Nicholas et al. [11] concluded that the wettability of a ceramic surface ( $\text{Al}_2\text{O}_3$  or  $\text{SiC}$ ) by Ag-Cu-Ti brazing alloys would be improved by increasing the Ag content, because of the low solubility of Ti in the Ag. The thermodynamics of Ti in Ag-Cu-Ti alloy using solid electrolyte sensors was evaluated by Pack et al. [12]; they found that the activity coefficient of Ti showed a positive deviation from an ideal solution behaviour at  $1000^\circ\text{C}$  in the Ag-Cu eutectic system. It was also found that the activity coefficient of Ti in Ag-Cu melts [13] decreases with the increment of Cu

concentration and increases with a higher Ag concentration. Moreover at variance with the segregating interactions between Ag and Cu, both the Ag-Ti and the Cu-Ti systems exhibit high negative values of the heat of mixing leading to spontaneous heteroatomic coordination, which is reflected in intermetallic compounds formation. This fact allows these systems to be classified as compound-forming [14, 15].

While reactivity and wettability data regarding YAG/AgCuTi system are not available from literature, the wetting of other ceramic substrates by AgCuTi has been already widely investigated. For example, materials such alumina [16, 17] or zirconia stabilized with yttria [18] have been studied and discussed. Voytovytsch et al. [19] found that droplets of AgCu alloys without Ti do not wet alumina substrate. At 900°C they form contact angles much higher than 90°, a typical value for noble metal/oxide systems; while additions of 3 to 8 at% of Ti allow a drastic decrease in the equilibrium contact angle thus reaching about 10°, a value typical of metal/metal systems. In this specific cases the improved adhesion and the wettability of the alumina substrates have been attributed to the formation of a  $TiO_x$  and Cu-Ti-O layer at the interface [20, 21].

This paper is aimed at studying the possible use of AgCuTi alloy in order to define the optimal conditions for the production of metal-ceramic joints (YAG/AgCuTi/Ti6Al4V) where the transparent YAG is coupled to the metallic support to form a vacuum tight optical window. Here the focus is on the study of the wetting behaviour of YAG ( $Y_3Al_5O_{12}$ ) transparent ceramic by the eutectic brazing alloys AgCu with Ti as active element. Pure metals (Ag, Cu) and binary alloys (AgCu, AgTi) have been also tested on the same substrate in order to better define the system.

The wettability data, obtained in Ar atmosphere, were elaborated to improve and optimize the YAG/braze adhesion. The contact angle ( $\theta$ ), drop height and drop base diameter of the metals on the YAG substrate were determined by the sessile drop technique allowing the study of their

reactivity and wettability. The Ti role in determining the interactions between the brazing alloys and the YAG has been analyzed by means of modelling by CALPHAD method, while the morphology and the composition of phases formed in the alloy/YAG interfacial zone have been evaluated by optical and electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) analysis.

## **2. Experimental part**

### **2.1 Ceramic materials**

The ceramic substrates were prepared following the experimental procedure [22] that involves the use of extremely pure ( $\geq 99.99\%$ ) and submicrometric ceramic oxide powders of  $\text{Al}_2\text{O}_3$  (Taimei TM-DAR) and of  $\text{Y}_2\text{O}_3$  (Nanocerox) mixed in stoichiometric ratios and ball milled for 24 h after addition of 0.5 wt% of tetraethyl orthosilicate (TEOS) as sintering agent and 1 wt% of ethanol as dispersant. The suspensions were spray dried in a laboratory spray dryer (Mini Spray Dryer B-290, Büchi) and then the spray dried powders have been shaped in pellets, characterized by a diameter of 1 cm and a thickness of 2–4 mm, by linear pressing at 10 MPa followed by cold isostatic pressing (CIP) at 250 MPa [23]. After a heat treatment at 800°C in order to remove residual organic impurities, the pellets were sintered at 1735°C for 16 h under high vacuum conditions ( $10^{-4}$  Pa). Before the wetting tests, the substrates (transparency of about 80% [24]) were polished on diamond grinding discs to reach a final surface roughness ( $R_a$ ) less than 1  $\mu\text{m}$ .

### **2.2 Metals and alloys**

Pre-formed drops of 4.0-5.0 mm in diameter and of an average weight of about 0.3 g were prepared by arc-melting under purified Ar atmosphere; in order to remove any oxygen contamination a zirconium getter was previously melted. The alloys were remelted several times to ensure homogeneity in their composition. Ag, Ti, Cu rods (purity > 99.9%) or wires of CB4 (Degussa-Germany) alloys were used. The CB4-AgCuTi alloy has a density of 9.9  $\text{gcm}^{-3}$ , a thermal

expansion coefficient equal to  $18 \times 10^{-6}/K$ , a melting range of 780-805°C [25] and is considered a member of a family defined as medium-melting-point active fillers (melting point between 700°C and 1000°C [26, 27]). The compositions of all alloys used are reported in Tab.1.

Tab.1- Composition of the different alloys used in the wetting tests.

	Ag		Cu		Ti	
	wt%	at%	wt%	at%	wt%	at%
AgCuTi (CB4)	70.5	57.7	26.5	36.8	3.0	5.5
AgCu	72.0	60.2	28.0	39.8	-	-
AgTi	96.0	91,4	-	-	4.0	8.6

### 2.3 Procedure

The wetting behaviour of the drops was studied by measuring their contact angle, height and base diameter by the sessile drop technique [28, 29]. The drop profiles were acquired using a high resolution CCD camera and then processed off-line with an *ad hoc* designed ASTRAView image analysis software [30, 31]. The uncertainty in contact angle measurement is given here as  $\pm 2^\circ$ , considering the increased roughness of the solid-liquid interface due to the growth of new phases. Experiments were performed in a specially designed furnace which can reach 1600°C [32]; the precision of the temperature readings can be estimated to be  $\pm 5^\circ C$ . The oxygen partial pressure  $P_{O_2}$  in the working atmosphere (Ar with less than 0.5 ppm gaseous impurities, at 50 cm<sup>3</sup>/min) was continuously monitored by solid state oxygen sensors at the chamber inlet and outlet. Before the tests the metallic samples had been cleaned in a ultrasonic bath and the ceramic supports had been polished down to 1  $\mu m$ . The samples were then introduced, surrounded by a zirconium getter, by a magnetically operated push rod into the preheated furnace as soon as parameters such temperature and  $P_{O_2}$  reached their pre-set values. An Ar atmosphere with a  $P_{O_2}$  of about  $10^{-2}$

Pa (measured at the gas outlet) was measured and different temperatures were chosen (from 820°C to 1150°C), depending on the system. All the samples were extracted from the furnace hot zone after 1 h and left to cool down in the cold part of the furnace. They were then embedded in epoxy resin and cut. The sections obtained, after the polishing process down to 1 μm grit, were observed and analyzed by optical and electron microscopy (LEO 1450 VP) coupled with energy dispersive spectroscopy (EDS) analysis and by FE-SEM (Carl-Zeiss Sigma NTS GmbH, Oberkochen, Germany) coupled with an energy-dispersive X-ray spectroscope (EDS, INCA Energy 300, Oxford Instruments, UK).

### 3. Wettability results and discussion

#### 3.1 AgCuTi/YAG systems

The wettability tests have been performed at various temperatures between 800°C and 950°C to cover the whole range of suggested conditions for brazing processes. The results (Fig.1a) have shown that the wetting process is characteristic of a “reactive” regime, as the contact angle varies quite slowly with time, without reaching an equilibrium configuration after one hour of contact.

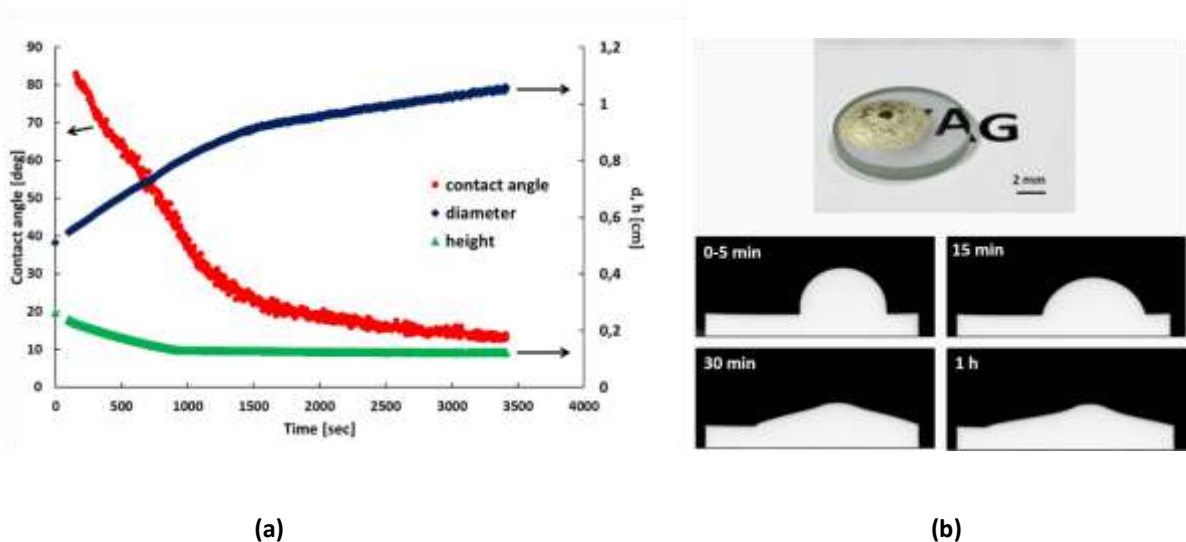


Fig.1- Contact angle, base diameter and height of drop plotted as a function of time (a), the YAG/AgCuTi sample after 1 h test (b, up) and profile images of AgCuTi system at 950°C (b, down). YAG diameter disc: 10 mm.

However, given the small slope of the  $\theta$  vs. time curve at the end of the tests, a final “equilibrium” contact angle  $\theta \approx 10^\circ$  can be safely assumed.

The tests at 950°C have shown that the sessile drop profile, after a contact time of about 25 min, evolves from a symmetrical “Laplacian” profile to a perturbed shape with a dome forming at the drop apex (Fig.2) due to the immiscibility of liquids L1 and L2.

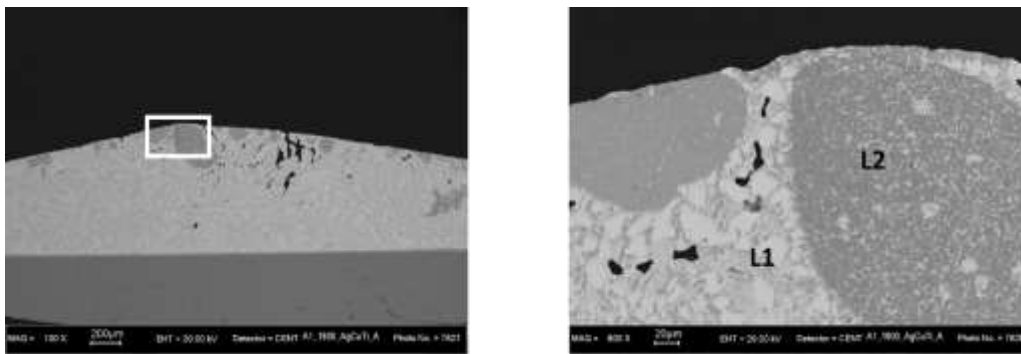


Fig.2- Image of the drop section for AgCuTi/YAG system after testing at 950°C (on the left) and the zoomed area indicated by the white rectangle (on the right).

To analyze the behaviour of this system, reference should be made to the Ag-Cu-Ti phase diagram.

The ternary phase diagrams currently available are essentially based on the extensive work of Eremenko et al. dating back to 1970 [33] and the thermodynamic modelling of Dezellus et al. [34].

We recalculated the Ag-Cu-Ti ternary equilibria by Calphad method using the Dezellus [34] parameters (Fig.3). The resulting isothermal section at 950°C clearly shows that the point representing the Ag-Cu-Ti alloy used in this work should fall just on the border of the L1+L2 two-phase field. This result does not seem to be in full agreement with the experimental results showing the clear presence of a 2<sup>nd</sup> lighter phase in the molten drop. However, calculations made at 940°C show that the two immiscible liquids should exist for this specific AgCuTi composition, with a relative volume fraction of L2 of the order of 10%. Nevertheless, the discussions below will be referred to the temperature of 950°C and to the phase diagram in Fig.3, given the overall

uncertainty due to: a) the inherent approximation of the CALPHAD calculations, b) the measurement uncertainty of the liquid drop temperature, c) the small amount of the second liquid phase.

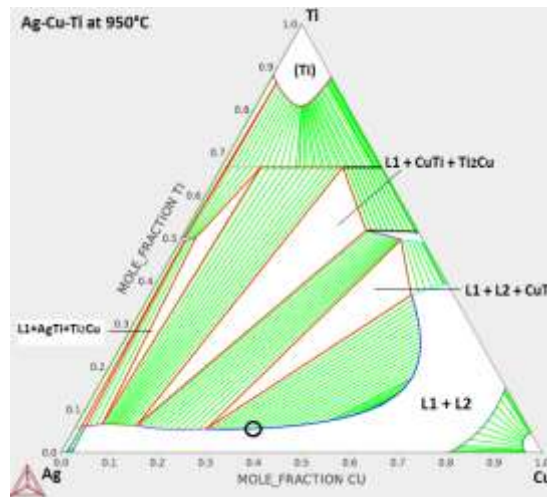


Fig.3- Recalculated ternary phase diagram for the Ag-Cu-Ti system; section at 950°C; the black circle represents the alloy composition used.

Indeed, the L1 and L2 phases co-exist only in the range of 910-950°C, where L2 is present in a quantity less than 10 vol% as shown in Fig.4a where equilibrium phase amounts during solidification path of the alloy AgCuTi are shown as a function of temperature.

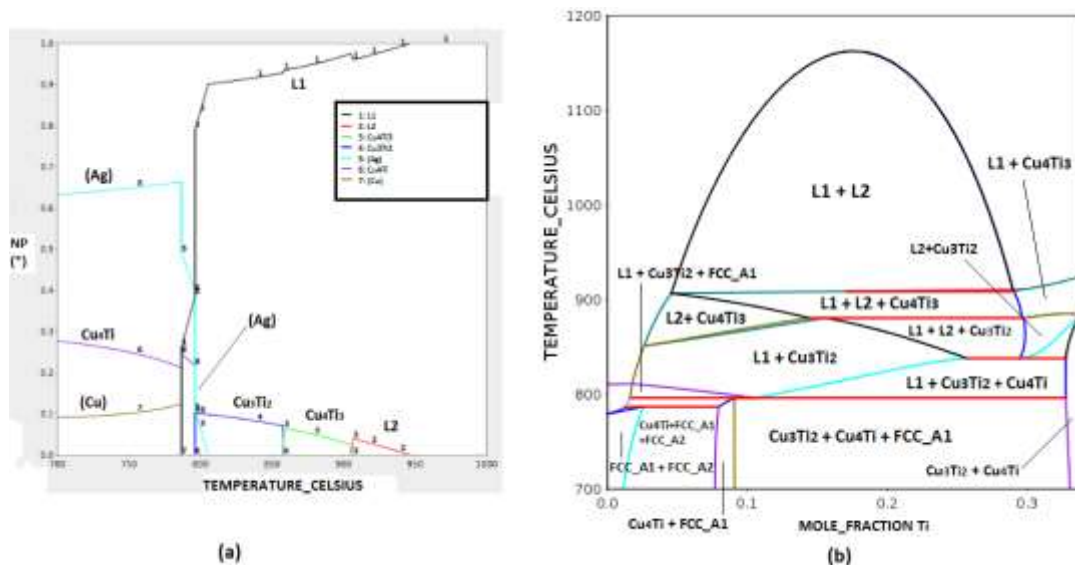


Fig.4- Stability of different phases plotted as a function of temperature (a) and calculated vertical section passing through the L1 and L2 tie line at 950°C (b).



The formation of the two liquids, already known, and its effect on the wetting process, has been discussed by other authors. In particular, Hinryj and Indacochea [25] have addressed this specific item from a thermodynamic point of view. Extending their analysis, on the basis of our CALPHAD calculations, it can be seen (Fig.4a) that, above 900°C, the starting alloy demixes into two liquids, whose compositions, recalculated by CALPHAD, are reported in Tab.2 (T= 950°C).

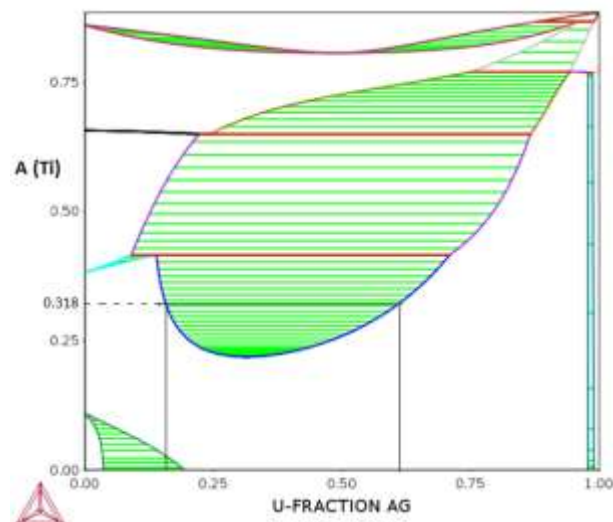


Fig.5- Ti activity (A) plotted as the Ag function  $u = \frac{x_{Ag}}{x_{Ag} + x_{Cu}}$  at 950°C.

In Tab. 2 the estimated densities of the two alloys are also reported: even if this is an estimate on the basis of published data for the binary systems, it is clear that L1 is much denser than L2 (L1≈ 1.30 L2), so that L2 should float on top of L1.

Comp. at%	Ag	Cu	Ti	$\rho$ [g/cm <sup>3</sup> ]	u	a <sub>Ti</sub>	$\Upsilon_{Ti}$
Starting alloy	57.70	36.80	5.50	9.9	0.612		
L1	57.24	36.72	5.58	8.6	0.606	0.318	5.70
L2	11.36	60.45	28.18	6.6	0.158	0.318	1.13

Tab-2. Compositions of the L1 and L2 liquids at 950°C, their estimated densities  $\rho$  (values for Ag-Cu and Cu-Ti alloys interpolated from data reported in [35] and [36] and the Ag fraction  $u = \frac{x_{Ag}}{x_{Ag} + x_{Cu}}$ .

Thus, the wetting between 910°C and 950°C should be governed by the L1 liquid, which represents the major phase. As underlined in [25] it has often been argued that the L2 liquid should wet the underlying oxide much better than L1, due to its much higher Ti content. However, as the L1 and L2 liquids are in equilibrium, the Ti chemical potential and its activity in the two phases must be the same and sufficient to make the phase L1 a good wetting liquid even if at a much lower Ti concentration, as demonstrated by the experiments performed on the Ag-Ti system. Therefore the compositions of the corresponding L1 and L2 liquids with the same Ti activity can be evaluated (Tab.2, Fig.5) confirming a much higher activity coefficient  $\gamma_{Ti}$  in L1 than in L2 which is due to a higher Cu content.

Other tests have been made at 820°C and 850°C.

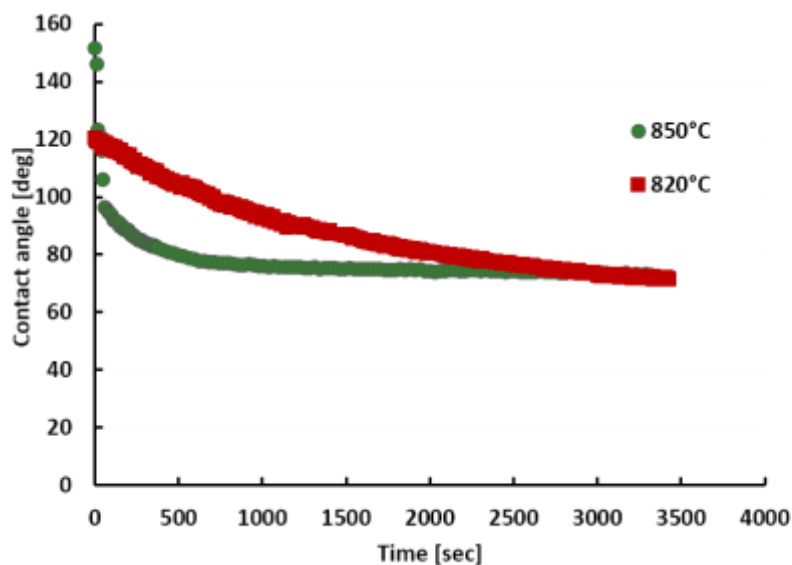


Fig.6- Contact angle as a function of time for AgCuTi system at 820, 850°C.

The observed sessile drop profiles are quite regular, the spreading kinetics tends to reach an equilibrium value before the end of the tests, giving final contact angles less than 90° at both temperatures (Fig.6, Tab.3). However it should be noted that at 820°C the spreading is much slower than that at 850°C reaching a “final” contact angle close to the one at 850°C only after 1 h

contact. These differences confirm that the extent of interfacial reactions between Ti (and Cu to a minor extent) with the underlying YAG substrate depends certainly on the temperature (slower diffusion kinetics) but, to a large extent, on the Ti activity in the liquid phase. Indeed at both temperatures the concentration of Ti in the liquid phase is about half that at 950°C (Fig.4b).

Tab.3- Contact angles of the AgCuTi/YAG system after 1 h testing.

Alloy/metal	T [°C]	$\theta_{eq}$ [°]
AgCuTi	820	71
AgCuTi	850	73
AgCuTi	950	10

At these temperatures most of the drop volume should consist of the liquid L1 co-existing with the intermetallic compound  $Cu_3Ti_2$  to a max of 10 vol%.

### 3.2 Pure metals/YAG and binary alloys/YAG systems

Reference tests using Ag, Cu and AgCu, AgTi alloys have been made at various temperatures (close to  $T=1.05 T_m$  K) to clarify the role the different elements have on the wetting when in contact with the YAG substrate. From the wetting and kinetics study of pure metals/YAG and binary alloys/YAG samples (Tab.4) it is observed that only the AgTi/YAG system does reach a contact angle value ( $\theta_{eq}=64^\circ$ ) which is characteristic of the wetting region. The role of Ti as active element and the increase of Ti activity coefficient by the presence of molten Ag are confirmed [12]. No wettability was obtained for the Ag/YAG and Cu/YAG systems; even if a strong decrease of contact angle values was observed after the first 5 min. In particular, the equilibrium contact angles measured after 1 h are  $116^\circ$  and  $127^\circ$  for Ag/YAG and Cu/YAG systems respectively (Tab.4).

Tab. 4- Values of contact angles at the testing temperatures, Ti concentrations  $x_{Ti}$ , activity  $a_{Ti}$  and activity coefficients  $\gamma_{Ti}$  of the metal/YAG and binary alloy/YAG systems after 1 h testing.

Alloy/metal	T [°C]	$\theta_{eq}$ [°]	$x_{Ti}$	$a_{Ti}$	$\gamma_{Ti}$ (ref.Ti hcp)
Ag	1050	116	-	-	-
Cu	1150	127	-	-	-
AgCu	850	107	-	-	-
AgTi	1050	64	0.086	0.74	9.25

### 3.3 Work of adhesion

The wetting behaviour of the different alloys can also be interpreted in terms of the Work of Adhesion, defined, after Young-Dupré [28], as:

$$W_a = \sigma_{LV} (1 + \cos \theta) \quad 1)$$

Thus, the thermodynamic value of the work necessary to separate the liquid phase from the solid surface at a certain temperature ( $W_a$ ), is a direct function of the liquid surface tension ( $\sigma_{LV}$ ) and of the experimentally determined contact angle. For alloys pertaining to the AgCuTi system, the liquid surface tension has been evaluated both theoretically [37] and experimentally [14] at various temperatures. Taking into account that small Ti additions (of the order of 5 at%) to the Ag-Cu eutectic alloy cause an increase of the liquid surface tension lower than about 1% [37], an extrapolation of the values reported in [14] can be safely applied. The results are shown in Table 5.

Table 5. Work of adhesion ( $W_a$ ) calculated from experimental contact angles ( $\theta$ ) and surface tension ( $\sigma^*$ ) values extrapolated from [14, 37]. The  $\sigma^*$  is the surface tension of the pure metal or of the Ag-Cu alloy and the  $\sigma^c$  the corrected one (5 at% of Ti addition).

	T [°C]	$\theta$ [°]	$\sigma^*$ [mN/m]	$\sigma^c$ [mN/m]	$W_a$ [mJ/m <sup>2</sup> ]
	820	71	969	979	1298
AgCuTi	850	73	967	977	1262

	950	10	955	965	1914
<b>Ag</b>	1150	116	898	-	504
<b>Cu</b>	1150	127	1274	-	506
<b>AgTi</b>	1050	64	907	952	1904

These data underline that in this specific case the liquid surface tension does not play a central role in the adhesion; rather, that the interfacial structure is the determining parameter that, through an important decrease of the interfacial tension, causes a drop in contact angle and thus the large increase of the Work of Adhesion found at 950°C. The reasons for this decrease in the interfacial tension value are linked to important changes in the chemical nature of the solid-liquid interface, that will be discussed in the next paragraphs.

#### **4. Reactivity results and discussion**

A first important result of this investigation is that all the systems analyzed retain the full transparency of the ceramic substrate after high temperature wettability tests, at least outside the metal-ceramic contact zone. However, at the solid-liquid interface, except for the pure metals and the AgCu alloy, interactions took place with the formation of new phases (Fig.1b, up)..

##### **4.1 Pure metals/YAG systems**

The analyses of the Ag/YAG and Cu/YAG interfaces show that no layers containing new phases or compounds grew between the substrate and the alloy, demonstrating that no significant interactions took place between the ceramic and the metallic material. In the AgCu/YAG system the eutectic structure extends in the whole drop, from the top to the metal-ceramic interface, while there is a total absence of visible interactions between the ceramic and the metal.

## 4.2 AgTi/YAG system

The situation is more complex at the AgTi/YAG interface in which two layers are found at the solid-liquid interface: the compositions of the various layers are reported in Tab.6, Fig.7.

The YAG bulk substrate was not affected by the contact with the liquid alloy and its composition corresponds to the theoretical one: 60 at% O, 25 at% Al, 15 at% Y.

Tab.6- Composition of the interface in AgTi/YAG system.

At%	Ag	Al	O	Ti	Y
YAG substrate	-	24.7	59.7	-	15.6
1° layer TiY <sub>2</sub> O <sub>5</sub>	4.4	6.2	53.8	10.5	25.1
2° layer (Ti)	1.2	-	-	98.8	-
drop	100	-	-	-	-

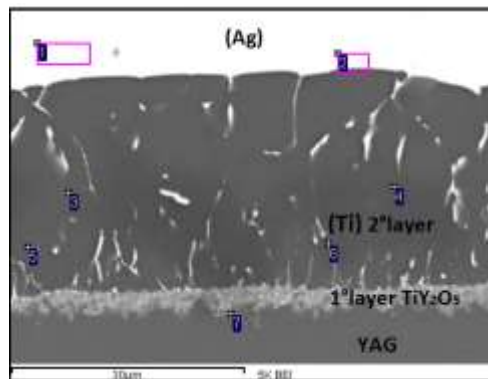
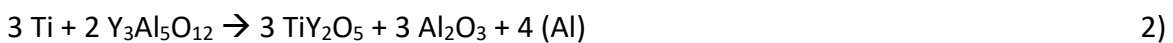


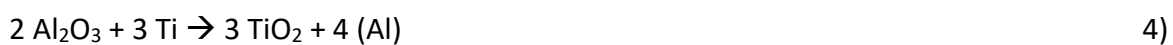
Fig.7- AgTi/YAG cross section after testing at 1050°C.

The 1<sup>st</sup> layer in contact with the ceramic material has an average thickness of about 7 μm and it extends along the whole interface profile. Its composition analyzed by SEM-EDS analysis is very close to the stoichiometry TiY<sub>2</sub>O<sub>5</sub>.

This compound should come from the reaction:



This reaction is meant to formalize that Ti, migrating to the solid-liquid interface, partially reacts with the Al contained in the YAG, entering into the solid structure to substitute a certain number of Al places, while causing the separation of small quantities of Al<sub>2</sub>O<sub>3</sub> and of metallic Al which enters into the liquid metallic phase, as proved by the Al traces found in the bulk drop after solidification. In other words, this process could be formally depicted through the following reaction cycle:



The sum of these reactions gives reaction 2), allowing the formation of a ceramic phase with fixed stoichiometry, stable at low temperature and with a hexagonal or orthorombic structure [38], the first found in the Y<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> phase diagram for increasing Ti contents [39, 40].

The 2<sup>nd</sup> layer with a thickness of about 30 μm (Fig.7) extends also over the whole interfacial area. While the bulk drop is essentially constituted of Ag, the active element (Ti) is concentrated at the interface, in particular in the 2<sup>nd</sup> layer, formed by columnar grains of (Ti) separated by several white silver rich phase zones. The reduced dimension of this last phase does not allow to carefully define its composition. The growth of columnar grains at the solid-liquid interface should take place in two steps: 1) at the temperature of the experiment, the Ti migrated to the YAG surface gives rise to the TiY<sub>2</sub>O<sub>5</sub> compound, followed by the nucleation of metallic nuclei on top of it; 2) during cooling due to its decreased solubility in Ag, the columnar grains develop producing a metallic layer of the Ti solid solution which is very diluted in Ag with its maximum thickness at the center of the solid-liquid interface. It is clear that step 1) is the relevant process promoting the observed good wettability. Silver shows also a tendency to accumulate close to the interface

between the 1<sup>st</sup> and the 2<sup>nd</sup> layers, while Al is a component, at low concentration, of the 1<sup>st</sup> layer but it can also be found as traces in all the metal drop.

### 4.3 AgCuTi/YAG systems at 950, 850 and 820°C

The results obtained with the Ag-Cu systems already described can be used as a basis to interpret the complex interactions found in the AgCuTi/YAG system. The attention is focused on the evaluation of the interfacial zone where most of the phenomena related to the wetting process take place. The section of the AgCuTi/YAG sample, tested at 950°C, confirm the system reactivity and show four different layers grown at the metal-ceramic interface (Fig.8). The light grey and continuous 1<sup>st</sup> layer of the interface zone shows a composition (Tab.7) demonstrating that both Cu and Ti migrated at the interface while a small quantity of Al diffused from YAG into the molten drop, entering at different concentrations in various phases. The Al diffusion in the liquid phase is compensated by Cu and Ti migration to the interface zone. Traces of Ag (0.6 at%) can be found also in the 1<sup>st</sup> ceramic-metal layer.

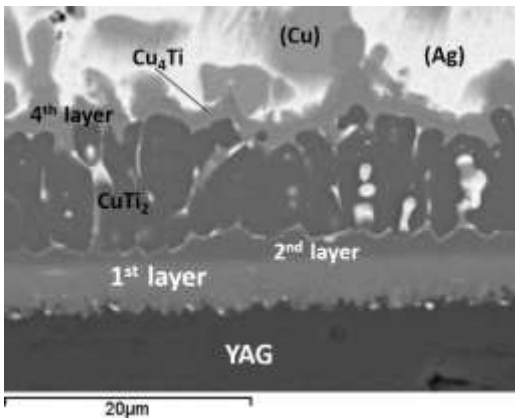


Fig. 8- Interfacial layers of AgCuTi/YAG tested at 950°C after 1 h.

Layer	Composition (at%)						
	Ag	Al	Cu	O	Ti	Y	
YAG	-	26	-	64	-	15	
1 <sup>st</sup>	0.6	3.5	16.5	41	15.2	19.8	
2 <sup>nd</sup>	1.5	2.40	35.6	18.6	41.1	0.8	M <sub>4</sub> X
3 <sup>rd</sup>	2.5	0.8	33	-	63.7	-	Cu Ti <sub>2</sub>
4 <sup>th</sup>	2.3	0.8	72.5	-	24.4	-	Cu <sub>4</sub> Ti

Tab. 7- Composition of the layers of AgCuTi/YAG tested at 950°C.

In the 2<sup>nd</sup> layer, which is continuous and thinner than the 1<sup>st</sup> one, the amount of O decreases from 41 at% to 18.6 at% while the concentration of Ti and Cu increases. The presence of Y in this layer is drastically less than in the 1<sup>st</sup> one, while Al composition does not change significantly. However, Ag



traces vary from 0.6 at% to 1.5 at%. It is possible to suppose, regarding the composition shown, that this 2<sup>nd</sup> layer is mainly formed by an intermetallic compound with stoichiometry  $M_{23}X_6$  (shortly:  $M_4X$ ) known as  $\tau$  phase [21, 41].

This phase is one of a class of dilute ceramic compounds that are metal-rich compared to the conventional ceramics and which have properties in-between those typical of ceramics and those typical of metals. This 2<sup>nd</sup> layer seems to be perfectly adherent to the 1<sup>st</sup> layer: in fact no defects or pores are formed along the contact line. It has an increased metallic character that probably improves the wetting behaviour significantly. The 3<sup>rd</sup> layer, with a thickness of about 10  $\mu\text{m}$ , is constituted by columnar grains in which it is possible to identify the intermetallic compound  $\text{Cu Ti}_2$  dissolving small quantities of Ag (2.5 at%) and Al traces (0.8 at%). The existence and the stability of  $\text{Cu Ti}_2$  under our experimental conditions are confirmed by literature data [42]. This phase, stable at room temperature, is often used in chemical industry because of its outstanding corrosion resistance which is considerably higher than that of pure Cu or Ti. Its presence can be beneficial for a sector in which transparent windows should withstand highly corrosive environments, such as in case of deep sea applications. No ternary compounds have been found in the Ag-Cu-Ti system but it is known that in the  $\text{Cu}_x\text{Ti}_y$  compounds the Ag solubility decreases continuously as Cu content increases [34]. The white regions of the 3<sup>rd</sup> layer, placed inside the Ti-rich dark grey columnar grains, are too small to be quantitatively defined by SEM-EDS but they are Ag-rich as demonstrated by element maps (Fig.9).

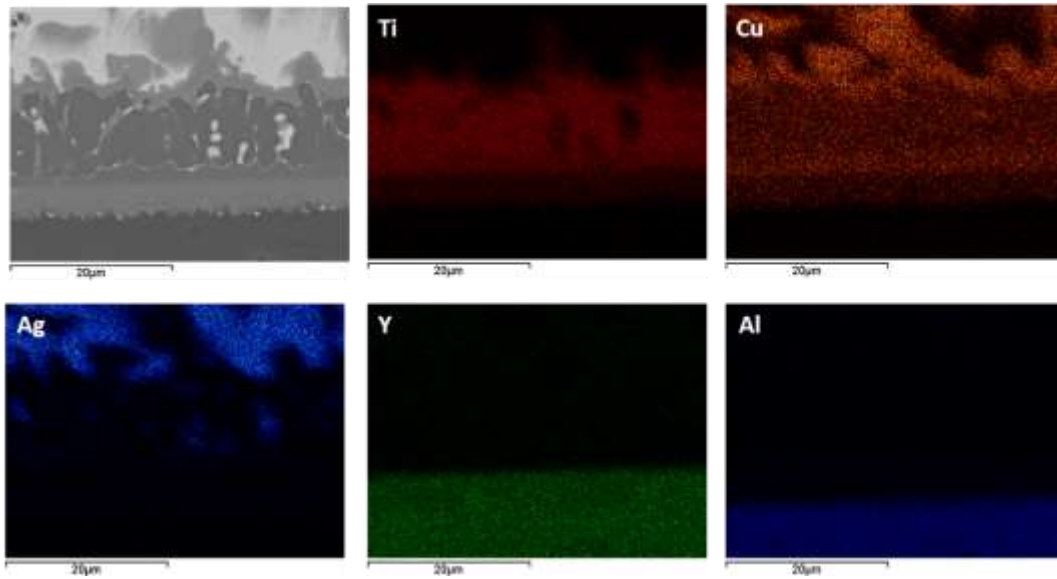


Fig.9- Element maps of the AgCuTi/YAG interface layers (T=950°C).

The composition of the 4<sup>th</sup> layer, shown in Tab.7, exhibits the same Ag and Al concentrations of the 3<sup>rd</sup> layer. The reaction allowing the formation of Cu<sub>4</sub>Ti intermetallic compound occurs at 808°C (at equilibrium condition; Fig.4a) and it is the most important reaction with respect to the amount of liquid transformed into solid [25]:



During this transformation, both at equilibrium or not, most of the alloy is liquid; for this reason this is a crucial point for the wetting behaviour. It is known from literature data that there are three equilibrium phases at low temperature: Ag- and Cu-based solid solutions and Cu<sub>4</sub>Ti. In the present work the system tested at high temperature is cooled quickly following non-equilibrium paths, especially at lower temperatures. The presence of Cu<sub>3</sub>Ti<sub>2</sub>, for example, was reported in previous works and proves that the alloy was not at equilibrium [43]. In the alloys tested during our experimental work, part of the CuTi<sub>2</sub> intermetallic formed the interface zone at 950° and the rest is involved in the reactions leading to the formation of Cu<sub>4</sub>Ti as predicted from the equilibrium path. It is important to underline that the adhesion, as it is shown (Fig.10), is obtained also in the

sample tested for only 15 min at 950°C; the liquid metal is infiltrated inside the YAG pores allowing the formation of a continuous and homogeneous interface.

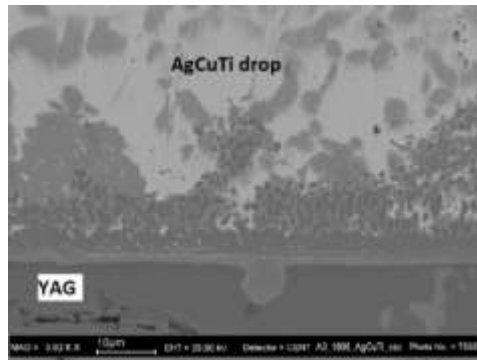


Fig.10- Cross section of AgCuTi/YAG sample tested at 950°C for 15 min.

The AgCuTi/YAG systems tested at 850°C and 820°C for 1 h show a worse wettability than that found at 950°C, even if the values obtained (Tab.3) are still useful for brazing processes and the reactivity at the interface zones is similar for both the temperatures (850, 820°C).

At 850°C the 1<sup>st</sup> layer of the interface zone is thinner (4 μm) than the corresponding layer found in samples tested at 950°C (Fig.11), with similar compositions (Tab.8). A 20 μm thick 2<sup>nd</sup> layer, in which a bright phase of (Ag) and a dark phase of CuTi, can be observed on top of the first metal-ceramic layer. Moreover a 2 μm layer of CuTi extends between the 2<sup>nd</sup> layer and the eutectic structure that characterizes the whole drop.

Tab. 8- Composition of the layers of AgCuTi/YAG tested at 850°C.

Layer	Composition (at%)					
	Ag	Al	Cu	O	Ti	Y
YAG		25.3	0.3	58		16.4
1 <sup>st</sup>	0.4	3.1	15.7	44	17.2	19.6
2 <sup>nd</sup>	83.6		12.9		3.5	(Ag)
2 <sup>nd</sup>	3	2.3	50.5		44.2	CuTi
3 <sup>rd</sup>	2.5	2.7	45		49.8	CuTi
4 <sup>th</sup>	60		39.1		0.9	Ag-Cu

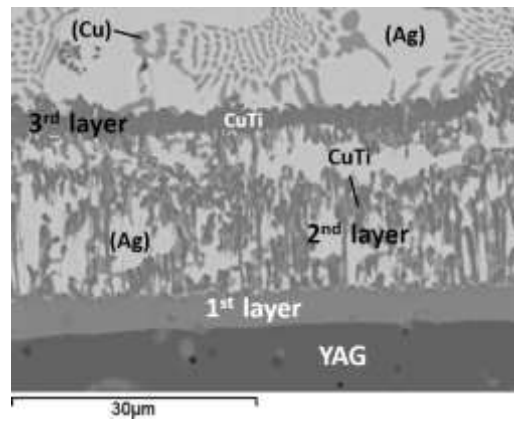


Fig.11- Interfacial morphology of AgCuTi/YAG tested at 850°C for 1 h.

The small quantity of Ti in the 4<sup>th</sup> layer (eutectic structure) is justified by the Ti migration to the interface zone. A map of the different distribution of elements is presented in Fig.12.

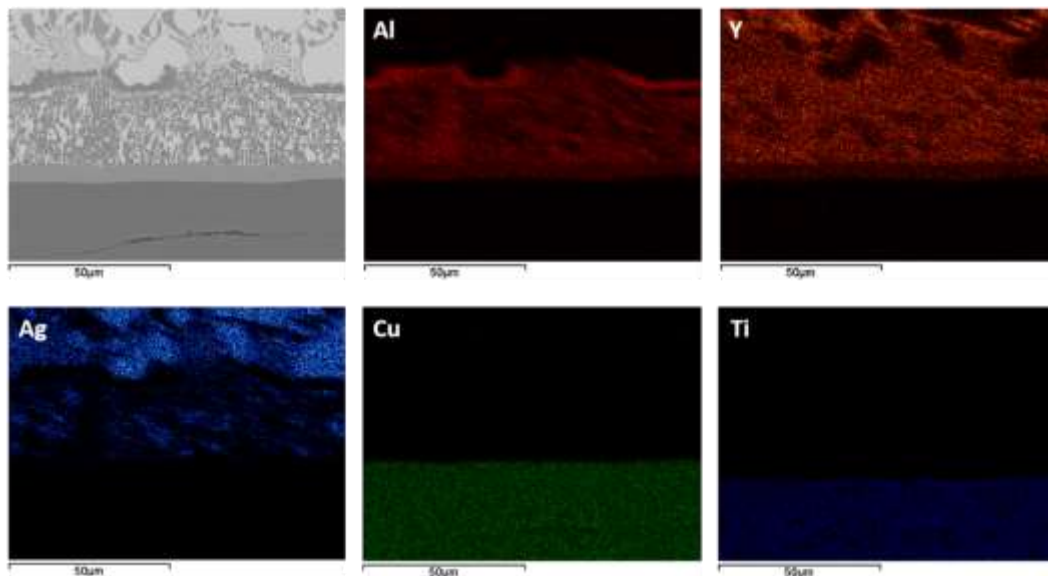


Fig.12- Elements map of the AgCuTi/YAG interface layers after testing at 850°C for 1 h.

The AgCuTi/YAG samples tested at 820°C show the same layers of the samples tested at 850°C, regarding both thickness and composition. The general overview offered by the elemental maps (Figs.9, 12), together with the quantitative analyses already discussed, allow us to state that: 1) at all temperatures Ti migrates from the bulk AgCuTi molten alloy towards the YAG/alloy interface, modifying a thin layer ( $\approx 5-8 \mu\text{m}$ ) of the YAG substrate into a new compound which is more complex than the  $\text{TiY}_2\text{O}_5$  found in the AgTi system due to the presence of Cu atoms at a concentration close to that of Ti; 2) a striking difference between the structure of the 950°C

samples and the ones treated at lower temperature is that, on top of the complex first layer, the specimens treated at a higher temperature show the presence of the so-called  $M_4X$  layer, a promoter of wettability which is absent in the specimens treated at 850°C and 820°C. In addition, the Ti concentration  $x_{Ti}$  in the liquid phase is much lower than  $x_{Ti}$  in L1 at 950°C. These differences are directly reflected into the values of the work of adhesion and thus in the wetting behaviour of the AgCuTi alloy which is very good at 950°C, lower but still acceptable for brazing applications, at 850°C and at 820°C; 3) the elemental maps show that Ti segregates close to the solid-liquid interface, leaving the core of the molten drop formed by the “nearly pure” Ag-Cu eutectic. Al diffuses into the 1<sup>st</sup> layer and, as traces, into molten drop, while Y does not leave the original YAG substrate, however it takes part in the formation of the above mentioned Ti-Cu containing interfacial structure.

## 5. Conclusions

This study reports a thorough investigation of the wetting interactions of the AgCuTi/YAG system, for which no data exist, as far as we know. The low contact angle values ensure these systems very good wettability conditions at 950°C ( $\theta_{eq}=10^\circ$ ) and fair conditions at 850°C and 820°C ( $\theta_{eq}=73^\circ$  and  $71^\circ$ ). That makes them promising candidates for the use in metal-YAG ceramic joints.

Thermodynamic calculations by CALPHAD methods allowed us to highlight the relevant role of the Ti activity in the liquid alloy to determine the final contact angles, as well as to clarify the interplay the L1 and L2 liquids, coexisting in the miscibility gap between 910 and 950°C, with respect to the wetting process. Interfacial analyses conducted by SEM-EDS have shown a significant reactivity at the solid-liquid interfaces with the formation of new metal-ceramic phases without any pores and defects. The different phases, formed at 820, 850, 950°C, were identified considering the calculated Ag-Cu-Ti phase diagram and were confirmed from the analyses of the solidified drop sections. From the analyses of the binary alloys/YAG interfaces, it was possible to evaluate the

different role the elements have in the wetting phenomena. Although the amount of Ag in the layer in contact with the ceramic substrate was not significant (<1 at%), its presence in the rest of the drop is absolutely determinant for the final wettability, as it increases the activity of Ti to a large extent. From the analyses of AgTi/YAG systems the formation of  $TiY_2O_5$  phase at the interface zone was observed and its formation mechanism hypothesized. The same metal-ceramic phase was found in the 1<sup>st</sup> layer in contact with the substrate for the all AgCuTi/YAG samples while a 2<sup>nd</sup> layer, identified as a “ $M_4X$ ” metal-ceramic compound, was found only at the interface of the samples tested at 950°C. Its presence was associated to the significant improvement in the wettability because of its more pronounced metallic behaviour. This layer presented the same amount of Y (19 at%) in all the samples and a decrease of the Al amount compared to YAG stoichiometry (from 25 at% to 3 at%). Moreover it was observed that Cu and Ti have migrated in about the same quantities to this 1<sup>st</sup> layer. The excellent reactivity, wettability and the maintained transparency of the YAG obtained allow these systems to be considered as good candidates for the production of brazed optical windows to be used in extreme conditions like the ones found in marine environments or aerospace applications. An extended study of the specific brazing processes will be reported soon.

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