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**CHARACTERIZATION OF Al<sub>2</sub>O<sub>3</sub>/TA6V AND ZrO<sub>2</sub>/TA6V CERAMIC-METAL INTERFACES**

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**Résumé** - Des liaisons par brasage actif ont été réalisées entre l'alliage de titane Ti-6Al-4V (TA6V) et les céramiques Al<sub>2</sub>O<sub>3</sub> et ZrO<sub>2</sub>. L'alliage de brasage utilisé a la composition Cu-40Ag-5Ti. Des réactions chimiques complexes se produisent dans la zone interfaciale et conduisent à la formation de phases de différentes compositions. Le composé Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O est observé à l'interface brasage/céramique. A proximité du métal de base, des phases intermétalliques Cu-Ti sont observées. Les microstructures des interfaces TA6V/Al<sub>2</sub>O<sub>3</sub> et TA6V/ZrO<sub>2</sub> sont très semblables alors que les propriétés mécaniques présentent des différences notables : la résistance à la traction mesurée pour le joint TA6V/Al<sub>2</sub>O<sub>3</sub> (3 MPa) est très inférieure à celle du joint TA6V/ZrO<sub>2</sub> (150 MPa).

**Abstract** - Alumina and zirconia were joined to a Ti-6Al-4V alloy (TA6V) using an active braze of composition Cu-40Ag-5Ti. The interface region is shown to be very complex, consisting of numerous layers of varying composition and thickness. The chemical interaction of the braze with the ceramic results in a Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O layer. Adjacent to the Ti-6Al-4V base metal, a series of Cu-Ti intermetallic phases is observed. The TA6V/Al<sub>2</sub>O<sub>3</sub> and TA6V/ZrO<sub>2</sub> interface regions exhibit rather similar microstructures. However, the mechanical properties of the joints in these two systems are very different. The tensile strength of the joint is significantly lower in the case of TA6V/Al<sub>2</sub>O<sub>3</sub> (3MPa) than for TA6V/ZrO<sub>2</sub> (150MPa).

1 - INTRODUCTION

In many current industrial applications, ceramics must be joined to a metal or to a metallic alloy. Examples include engine components, electronic devices and ceramic/metal composites. The processes developed to form strong and reliable joints have to overcome the largely differing properties of ceramics and metals /1/. There are three major types of joining techniques : (1) mechanical joining, (2) direct joining, or (3) indirect joining /2/. Brazing is one of the commonly employed indirect techniques for which metal braze alloys including active elements (e.g., Ti) were developed in order to modify the chemistry of the ceramic surface and hence, to improve the wetting of the ceramic by the liquid braze /2,3/. The interaction between the metal and the ceramic determines the structure of the interface and hence the properties of the system. It is therefore important to understand and control the chemical reactions which occur at the ceramic/metal interface. Moreover, the mechanical properties of the joint have to be known for a complete characterization of the interface. The work presented here consists in the identification of the microstructure and composition of interfacial compounds formed upon brazing of titanium alloy TA6V and alumina or zirconia. The mechanical behaviour of the joints is also studied and discussed.

2 - EXPERIMENTAL

(a) Materials

The ceramics which were used are made by Céramiques Techniques France. The alumina is 99.8 % Al<sub>2</sub>O<sub>3</sub> (average grain size  $\approx$  4  $\mu$ m) and the zirconia is partially stabilized with 3 mol. % Y<sub>2</sub>O<sub>3</sub> (average grain size  $\approx$  0.35  $\mu$ m). The ceramics were joined by active brazing to a Ti-6Al-4V wt % alloy designated as TA6V. This alloy is made of 6% Ti alloy (33.4% Ti, 66.6% Al at 25 °C).

intergranular phase (78.5Ti-3.7Al-17.8V at %). The brazing filler metal is glassy ribbon of Cu-40Ag-5Ti wt % (about 80 μm thick) and is produced by Vacuumschmelze GmbH-Germany. Thermal expansion curves of the materials use this study are presented in Fig. 1, on which one can see a rather similar behaviour of ZrO<sub>2</sub> and TA6V.

Samples were prepared in disc form, 10 mm in diameter and 5 mm thick. The ceramic surfaces were polished to a mirror finish (2 μm diamond) to increase wetting; the metallic surfaces had a 8 μm diamond polish. Brazing was performed by heating samples for 2 to 10 minutes in a vacuum furnace (≈ 3.10<sup>-5</sup> Torr) in the temperature range 850-890°C, and subsequently cooling them to room temperature in 4 hours.

(b) Microstructural characterization of brazed joints

Cross sections of the TA6V/Al<sub>2</sub>O<sub>3</sub> and TA6V/ZrO<sub>2</sub> interfaces were characterized by scanning electron microscopy (SEM) and electron probe microanalysis. In addition, transmission electron microscopy (TEM) and electron diffraction were used to image the phases at higher resolution and to give crystal structure information.

(c) Mechanical strength measurements of brazed joints

The mechanical strength of the joints was evaluated by tensile tests conducted at room temperature on brazed samples having the configuration represented in Fig. 2. The fracture surfaces were examined by SEM.

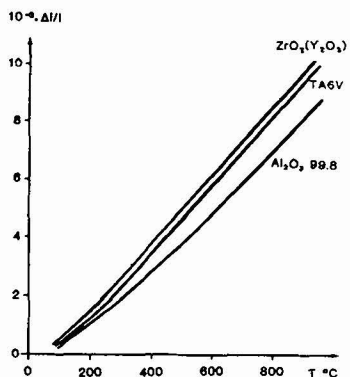


Fig. 1 - Thermal expansion curves of TA6V, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

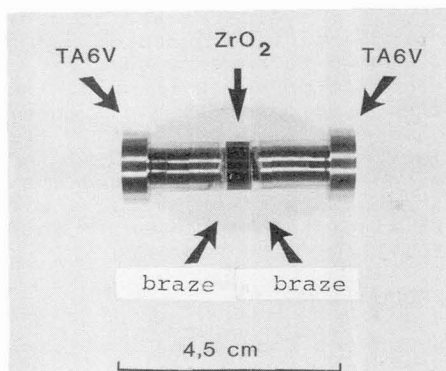


Fig. 2 - Micrograph showing the tensile specimen.

3 - RESULTS

(a) Microstructure of brazed joints

Figure 3 illustrates the microstructure of a TA6V/Al<sub>2</sub>O<sub>3</sub> brazement. The electron microprobe compositional line scan of this interface (Fig. 3c) indicated that complex chemical reactions occurred between braze alumina and the titanium alloy. In particular, segregation of Ti to the braze/Al<sub>2</sub>O<sub>3</sub> interface was readily seen.

Adjacent to Al<sub>2</sub>O<sub>3</sub>, a continuous and sinuous layer "a" (≈ 2-3 μm thick) whose composition is 50Ti-35Cu-15Al (at %) was observed. TEM observation showed that layer "a" is made of equiaxed grains that are larger farther from Al<sub>2</sub>O<sub>3</sub> (Fig. 4a). Very few dislocations were observed in the different grains which were investigated. Electron diffraction indicated that phase "a" has a CuTi structure with a lattice parameter a = 11.43 ± 0.10 Å (Table 1, Fig. 4b). Crystallographic features of this phase are similar to those reported for ternary oxide Cu<sub>2</sub>Ti<sub>4</sub>O<sub>4,5</sub>. Moreover, the (Ti+Al)/Cu experimental ratio was found equal to 1.9 which is in rather good agreement with the Ti/Cu ratio of the compound Cu<sub>2</sub>Ti<sub>4</sub>O. Therefore, although electron microprobe analysis of oxygen is missing, our data lead to the conclusion that layer "a" is the compound Cu<sub>2</sub>(Ti+Al)<sub>4</sub>O with 3.3 < Ti/Al < 5.6.

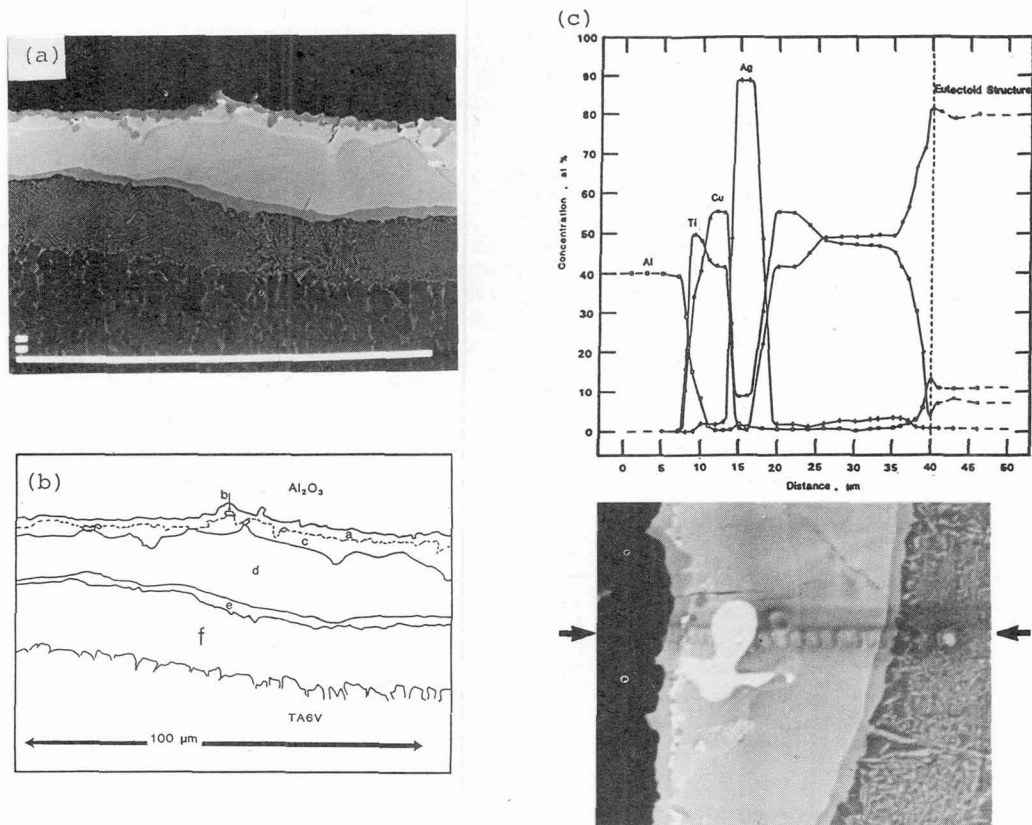


Fig. 3 - Cross-section of the TA6V/Cu-Ag-Ti/Al<sub>2</sub>O<sub>3</sub> interface after brazing : (a) SEM micrograph, (b) Schematic drawing, (c) Microprobe line scans showing the composition variation across the interface.

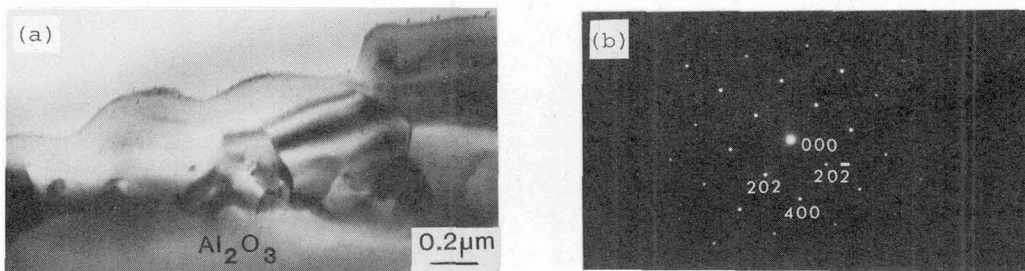


Fig. 4 - (a) TEM micrograph showing the microstructure of the Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O layer adjacent to Al<sub>2</sub>O<sub>3</sub>, (b) Electron diffraction of Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O ; the zone axis is [010].

The reaction of the braze with the base metal gave a series of interfacial phases. Adjacent to TA6V, a lamellar structure ("f") was formed. It consists of an  $\alpha$ -Ti phase (black phase in Fig. 3a) and a phase "e" whose composition is 69.8Ti-24.6Cu-5.6Al at %. Electron diffraction showed that "e" has a hexagonal structure (Table 1). A review of the literature relative to crystal structures of intermetallic phases /6/ indicated that this phase has crystallographic characteristics similar to those of  $Ti_3Sn$  and  $Ni_3Sn$ . Taken into account that the (Ti+Al)/Cu experimental ratio is approximately 3:1, we can propose the formulation  $(Ti,Al)_3Cu$  for phase "e". Further, we find phases "e", "d" and "c" which are essentially made of Cu and Ti (Fig. 3c). Phases "e" and "d" have both a tetragonal structure (Table 1) which is consistent respectively with that of the  $Ti_2Cu$  and  $TiCu$  compounds. Concerning layer "c", it can be deduced from Fig. 3c that this layer is the compound  $Ti_3Cu_4$  (Table 1). However, in some areas of the "c" layer, grains containing up to 12 at % Al were also identified. These grains, which have an orthorhombic structure (Table 1), can be identified with the  $Ti(Cu,Al)_4$  compound. Last, some discrete particles "b" which are an Ag-rich solute are embedded in layer "c".

Table 1

Characteristics of the phases formed in the TA6V/Cu-Ag-Ti/Al<sub>2</sub>O<sub>3</sub> joint.

Layers	Crystal structures	Lattice parameters (Å)			Phases
		a	b	c	
a	cubic	11.43			$Cu_2(Ti,Al)_4C$
b	cubic	4.07			Ag (Cu in sol)
c	tetragonal	3.12		19.9	$Ti_3Cu_4$
c	orthorhombic	4.52	4.46	12.08	$Ti(Cu,Al)_4$
d	tetragonal	3.11		5.9	TiCu
e	tetragonal	2.96		10.85	$Ti_2Cu$
f	hexagonal	2.95		4.68	$\alpha$ -Ti
f	hexagonal	5.92		4.73	$(Ti,Al)_3Cu$

The microstructure of the TA6V/ZrO<sub>2</sub> brazements exhibited interfacial characteristics which are very similar to those observed in the system TA6V/Al<sub>2</sub>O<sub>3</sub>, the same interfacial reaction products being formed in the two systems. However, some features are different :

- It is worth noting that the zirconia close to layer "a" is blackened a braze, which indicates oxygen deficiency for the ceramic. Thus, there is a source of oxygen at the braze/ceramic interface because of the oxygen mobility in ZrO<sub>2</sub>. Conversely, no diffusion of zirconium in the braze was observed.
- In both systems, aluminum is detected in interfacial layers close to the ceramic. However, the Al concentration is lower in the case of TA6V/ZrO<sub>2</sub> than for TA6V/Al<sub>2</sub>O<sub>3</sub>. This trend indicates some diffusion of Al from Al<sub>2</sub>O<sub>3</sub> into the braze.

#### (b) Tensile strength of brazed joints

As can be seen in Table 2, the mechanical behaviour of the two types of samples is very different. The fracture surfaces of the samples are also different (Fig. 5). This can be directly related to the difference between thermal expansion coefficients of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TA6V (Fig. 1).

It can be seen that in the case of Al<sub>2</sub>O<sub>3</sub>, fracture has taken place within the ceramic and is mostly intergranular (Fig. 5a). Rupture results from propagation of cracks already formed in the ceramic near the interface upon cooling from the brazing temperature. In the case of ZrO<sub>2</sub>, all samples fractured within the joint area near the ZrO<sub>2</sub> surface and in no case rupture had propagated inside zirconia. Fig. 5b shows a typical fracture surface made of two zones: one predominantly regular, the other puckered as can be seen at a higher magnification in Fig. 5c.

Table 2

Tensile strength of TA6V/Al<sub>2</sub>O<sub>3</sub> and TA6V/ZrO<sub>2</sub>.

Metal/Ceramic	Number of specimens	Brazing temperature (°C)	Tensile strength (MPa)
TA6V/Al <sub>2</sub> O <sub>3</sub>	10	870 ±10	3 ± 1
TA6V/ZrO <sub>2</sub>	7	870 ±10	150 ± 50

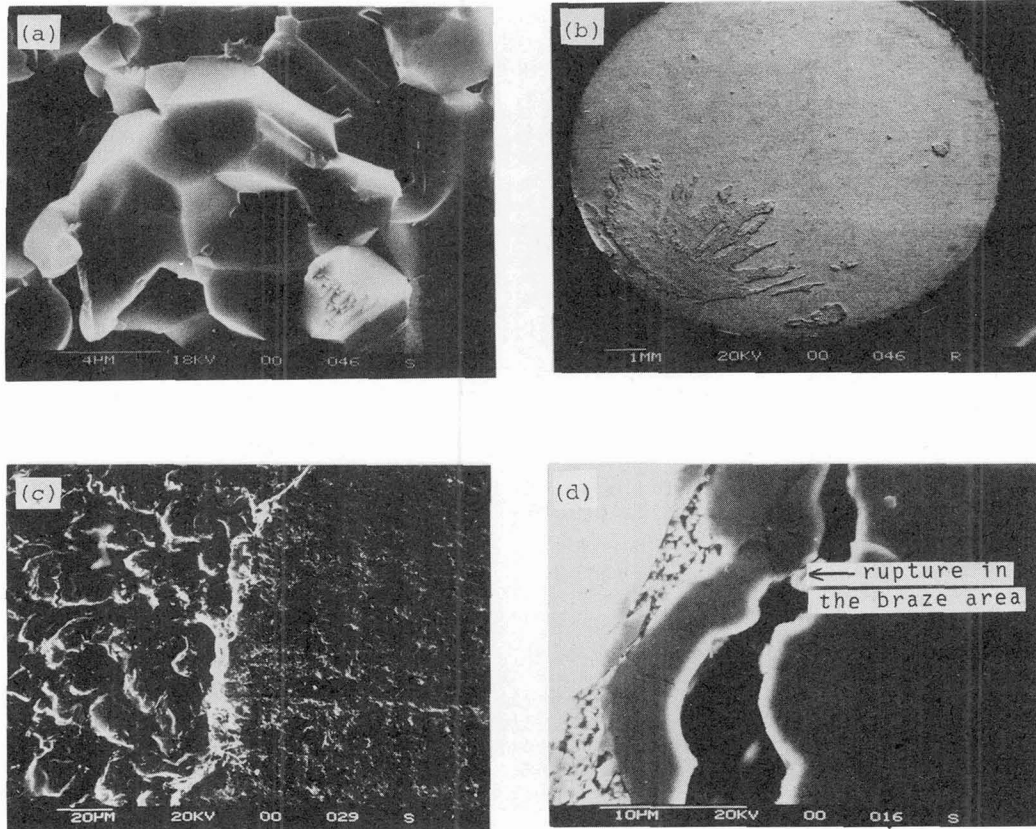


Fig. 5 - (a) Fracture surface of a TA6V/Al<sub>2</sub>O<sub>3</sub> sample, (b) Fracture surface of a TA6V/ZrO<sub>2</sub> sample (ceramic part), (c) Higher magnification of the micrograph shown in (b), (d) Perpendicular section of the surface fracture (metal part) .

Energy dispersive X-ray analysis performed on the surface of the metal part of the ruptured test specimen indicates that the puckered portion of the fracture is made of Cu-Ti phases, as shown in Fig. 5d. As for the predominantly regular part of the fracture, analysis indicates for Ti, Cu and Al compositions similar to those of phase "a". The complementary part of this fracture on the ceramic part of the broken sample was also analysed, and the presence of Ti, Cu, Al was detected. This result indicates that the fracture occurred predominantly within phase "a" in the close vicinity of zirconia.

#### 4 - DISCUSSION

The interface region in the TA6V/Al<sub>2</sub>O<sub>3</sub> and TA6V/ZrO<sub>2</sub> brazements is very complex, and consists of numerous layers of varying composition and thickness. This result indicates a reactivity of the braze alloy with both the ceramic and the titanium alloy.

The reactivity of the Cu-Ag-Ti braze with Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> leads to the formation of the Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O oxide phase. Such a reaction is not yet well defined from a thermodynamical point of view. Nevertheless, it can be assumed that Ti segregates from the molten braze to the ceramic surface because of its affinity for oxygen and that oxygen from alumina or zirconia is dissolved in the braze. Thence, dissolved oxygen may react with titanium to produce Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O //7/. Such a compound may serve as a transition layer and a wettable surface that promotes bonding between the ceramic and the TA6V alloy. The base titanium alloy acts as a source of Ti for the braze, leading to the formation of Cu-Ti intermetallic phases. The existence of Ti<sub>2</sub>Cu, TiCu, Ti(Cu,Al)<sub>4</sub> and Ti<sub>3</sub>Cu<sub>4</sub> and is in good agreement with the stable compounds present in the Ti-Cu phase diagram /8/.

Concerning now the tensile tests, it is also worthwhile to note that zirconia seems to accommodate the stresses introduced by the brazing process, in contrast with what was observed for TA6V/alumina joints prepared with a similar procedure. The better mechanical behaviour observed with zirconia is consistent with the similar thermal expansion coefficients of TA6V and zirconia. We also noted a partial transformation of the initial tetragonal form of zirconia into a monoclinic structure, and it is well known that this transformation increases the resistance to crack propagation in ZrO<sub>2</sub>/9/.

#### 5 - CONCLUSION

The different interfacial phases formed upon brazing of TA6V to ZrO<sub>2</sub> and to Al<sub>2</sub>O<sub>3</sub> were characterized. The chemical interaction of the braze with the ceramic results in a Cu<sub>2</sub>(Ti,Al)<sub>4</sub>O layer. Adjacent to the base metal, a sequence of Cu-Ti intermetallic phases is observed. The mechanical properties of the joints in these two systems are very different. In the case of the TA6V/ZrO<sub>2</sub> joints, a tensile strength of 150 MPa was measured. This value is high enough for considering application of the brazing procedure to real systems.

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