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The effect of brazing temperature on the titanium/glass-ceramic bonding

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Abstract

The aim of this work is to study the effect of time and brazing temperature on the interfacial microstructure and mechanical properties of the joint obtained by active metal brazing between c.p. titanium and a fluorosilicate machinable ceramic–glass using a 64Ag–34.5Cu–1.5Ti (wt%) brazing alloy. The reaction between the brazing alloy and the two materials leads to the formation of several interfacial reaction layers with different compositions, morphologies and extensions. These layers are constituted by various reaction products that ensure chemical bonding between the two materials, their stability and capability to accommodate the discontinuity of properties across the interface determining the success of the joining. The interfacial microstructure was analysed by SEM and the composition of each reaction layer was investigated by EDS. Microhardness tests were performed across the interfacial zone and the global interfacial mechanical behaviour was evaluated by means of shear tests. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metal/ceramic joining; Active metal brazing; Titanium; Ceramic–glass; Microstructure; Mechanical properties

1. Introduction

Most applications of ceramics in devices and structures require some type of metal–ceramic bonding. The ability of joining ceramics to and with metals is a limiting aspect of many plans for the future use of both structural and functional ceramics. Active metal brazing is one of the most useful techniques employed for joining ceramics to metals. In this process, bonding is promoted by the action of the brazing alloy, which contains small quantities of a reactive element, usually titanium, that reacts with ceramic anions promoting the formation of different products, namely a family of titanium oxides [1], some of which are wetted by solvent brazing metals.

The success of the bonding depends on the characteristics of the reaction products, which must be stable and must be able to accommodate the discontinuity in materials properties at the interface [2]. The nature of interfacial products depends on the reactions taking place between the brazing alloy and the two materials to be joined: these reactions are controlled by the processing conditions. By changing these

conditions it is possible to modify the interface microstructure and consequently the mechanical properties of the metal/ceramic joint. The present work concentrates on the formation of the interfacial microstructure in the brazing of a ceramic–glass and titanium with Ag–Cu–Ti alloys, as well as the mechanical characterisation of the interface.

2. Materials and experimental techniques

Discs of commercially pure titanium and ceramic–glass of 13.5 mm diameter and 5 mm thickness (12 mm for the shear tests) were wet-ground using grid SiC paper to a mean roughness (Ra) of 0.26 and 0.29 μm , respectively. The nominal composition of ceramic–glass is shown in Table 1. The brazing alloy (64Ag–34.5Cu–1.5Ti wt%; 50.8Ag–46.5Cu–2.7Ti at%) was a 0.1 mm thick foil cut to the same diameter as the samples to be joined. Prior to brazing all samples were cleaned in acetone with ultrasonic agitation.

The brazing alloy discs were inserted between the titanium and ceramic–glass samples. A pressure of 2.56×10^{-2} MPa was applied to the assembly in order to ensure intimate contact. Fig. 1 shows the brazing thermal cycle and the processing variables; at brazing temperature the vacuum level was 10^{-4} mbar.

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Table 1
Ceramic–glass nominal composition (wt%)

SiO ₂	MgO	Al ₂ O ₃	K ₂ O	B ₂ O ₃	F
46	17	16	10	7	4

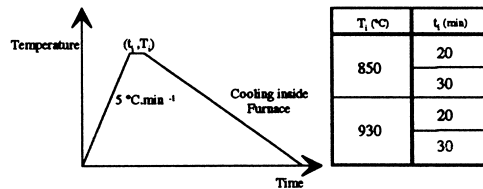


Fig. 1. Brazing thermal cycle.

In order to perform SEM observations, EDS analysis and microhardness tests, the samples were cut perpendicularly to the interface, and after a 1 μm diamond polish, the deformed surface layer was removed by polishing using a solution of 0.04 μm SiC and hydrogen peroxide.

The mechanical behaviour of the interface was characterised by microhardness and shear tests.

The microhardness testing system used is the Fisherscope H100 equipped with a Vickers indenter. The nominal applied load is 100 mN. The load is applied electromagnetically, the resolution being better than 1 μN. A series of indentations have been performed across the interface to evaluate the evolution of the microhardness from the ceramic to the metal.

Shear tests were made in an apparatus described elsewhere [3]. Four samples (13.5 mm diameter and 24 mm length) for each brazing condition were tested. The ceramic–glass shear strength was also evaluated.

3. Results

The brazing alloy reacted with both the titanium and the ceramic–glass leading to the formation of several interfacial reaction products, disposed in layers across the interface. At the same brazing temperature the interfacial zone does not exhibit relevant differences, either in composition or in the thickness of each reaction layer, for both of the brazing holding times. Each reaction layer is distinguished by a letter, **A**, **B**, . . . , **I**, starting from that closest to the titanium, taking in account their microstructural and chemical analysis.

Interfaces free of pores were obtained for all of the tested processing conditions. The interfacial microstructures resulting from brazing at different temperatures are shown in Figs. 2 and 3. The mean thickness and chemical composition of each reaction layer are listed in Tables 2–4.

The main differences between the interfacial reaction zone of samples brazed at 850°C and 930°C are as follows:

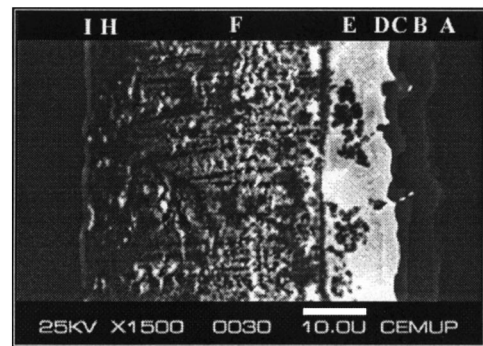


Fig. 2. Interfacial microstructure at 850°C.

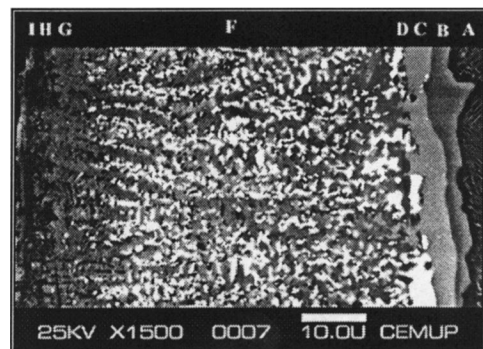


Fig. 3. Interfacial microstructure at 930°C.

Table 2
Mean thickness of the reaction layers

Layer	Thickness (μm)	
	850°C	930°C
A	5	80
B	4	3
C	2	4
D	4	4
E	8	–
F	36	40
G	–	6
H	8	6
I	1	2
Interface	68	145

Table 3
Chemical composition of the reaction layers at 850°C

Layer	Chemical composition (at%)					
	Ti	Cu	Ag	Si	Mg	Al
A	97.8	1.7	0.5	–	–	–
B	67.1	31.1	1.8	–	–	–
C	50.1	47.1	2.8	–	–	–
D	1.4	6.8	89.9	–	1.9	–
E	44.1	30.6	21.2	3.3	0.8	–
F	44.8	33.3	12.7	3.2	0.9	1.1
G	–	–	–	–	–	–
H	58.3	34.9	0.8	3.2	1.0	1.1
I	56.7	36.7	0.1	4.1	0.9	1.5

Table 4
Chemical composition of the reaction layers at 930°C

Layer	Chemical composition (at%)					
	Ti	Cu	Ag	Si	Mg	Al
A	91.4	7.3	1.3	–	–	–
B	66.8	25.7	7.5	–	–	–
C	50.4	41.8	7.8	–	–	–
D	1.4	2.8	93.2	–	2.5	–
E	–	–	–	–	–	–
F	58.4	23.7	13.4	2.9	0.8	0.7
G	67.1	27.2	0.8	3.6	0.2	0.9
H	91.6	4.2	0.5	2.8	0.2	0.6
I	70.4	15.1	0.7	9.7	1.5	2.5

1. The mean interfacial thickness is 68 μm at 850°C and 145 μm at 930°C. This difference is due mainly to reaction layer **A**, which is only 5 μm thick at 850°C, whilst at 850°C, with a thickness of 80 μm , it represents almost 50% of the interface.
2. The formation of reaction layer **E** is only at 850°C and of reaction layer **G** is only at 930°C.

Reaction layer **A** has a lamellar structure and a high Ti content. Although not continuous, reaction layers **B** and **C** have a fairly homogeneous aspect. Chemical analysis reveals that they are essentially constituted by Ti and Cu. Reaction layer **D** is very rich in Ag (≈ 90 at%): at 930°C, in opposition to 850°C, this layer is not continuous.

Reaction layer **E** is composed of two phases, the lighter phase (4.1Ti–4.6Cu–88.1Ag–0.9Si–2.3Mg at%) being the matrix, the darker one phase (65.1Ti–31.5Cu–1.6Ag–1.8Si at%) being distributed heterogeneously. Reaction layer **F** is composed of the same two phases of **E**. At 850°C it represents more than 50% of the interface thickness and its lighter phase contents decreases as one moves towards the ceramic–glass. At both temperatures black rounded shape particles with less than 1 μm were distributed from layer **E** to the end of layer **H**. These particles are composed of Mg and F and are similar to those found in ceramic–glass. The coarser particles are surrounded by a thin layer of Si or SiO₂. At 850°C they are generally coarser than at 930°C.

Reaction layers **G**, **H**, and **I**, are composed essentially of Ti and Cu. Si, but very low contents of Ag, Mg and Al have also been detected.

The evolution of the microhardness across the interface is plotted in Fig. 4 for 850°C brazing temperature. An identical evolution is exhibited by samples brazed at 930°C. From the analysis of the figure two aspects may be noted:

1. the hardness presents a sharp maximum in reaction layers near to the ceramic (layers **I**, **H** and **G**), and
2. the hardness decreases continuously from those layers until layer **D** (Ag rich phase), where it presents the minimum.

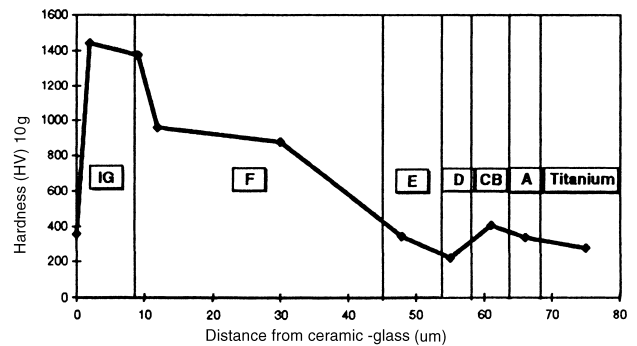


Fig. 4. Microhardness evolution across the interface for a 850°C brazing temperature.

Table 5
Shear strength resistance of metal/ceramic–glass bonding for different brazing conditions

Brazing conditions	Shear strength (MPa)	
	Minimum	Maximum
850°C, 20 min	40	71
850°C, 30 min	33	57
930°C, 20 min	49	63
930°C, 30 min	46	54

The interface shear strength was almost independent of the brazing conditions as can be seen in Table 5. The higher shear stresses of the bonding are similar to the minimum values of the ceramic–glass (60 MPa).

4. Discussion

Taking in account the Cu–Ti equilibrium phase diagram (Fig. 5), and the chemical composition and the microstructure of layer **A**, this layer results from a eutectoid reaction at 798°C. It should be composed of Ti₂Cu and α Ti. The difference between its thickness at 930°C and 850°C is due to two factors: (i) the diffusion-rate decrease of Cu into Ti with temperature, and (ii) the diffusion of Cu into α Ti (close-packed hexagonal) being more difficult than into β Ti (body-centred cubic).

According to the relationship between the atomic fractions of Ti and Cu in layers **B** (Ti/Cu \approx 2) and **C** (Ti/Cu \approx 1), their chemical composition, and the isothermal section of the Ti–Cu–Ag system at 700°C (Fig. 6), layer **B** may be essentially composed of η -Ti₂ (Cu, Ag) and layer **C** by ζ -TiCu. In both of the layers, Ag solid solution may be present.

Layer **D** may be the result of Ag segregation. A similar segregation process was observed during an identical brazing alloy elaboration. The brazing alloy solidification microstructure shows that a darker phase, rich in Ti and Cu, is generally surrounded by a lighter phase, rich in Ag, which is followed by the Ag–Cu eutectic. This distribution of phases indicate that the high affinity between Ti and Cu leads to the

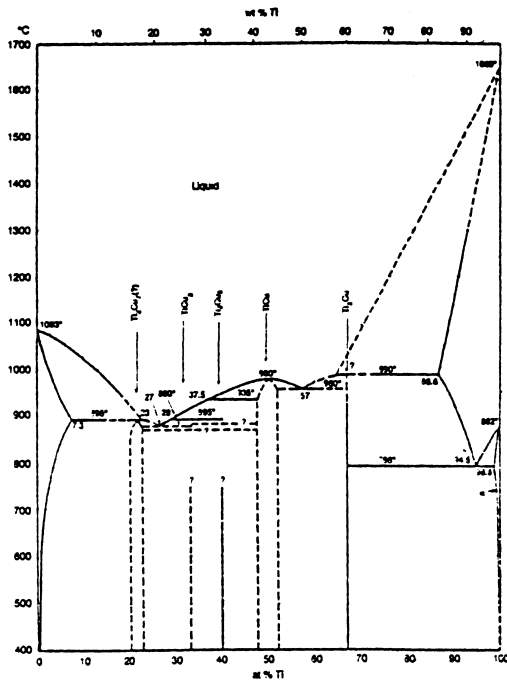


Fig. 5. Cu–Ti equilibrium phase diagram [4].

formation of solid solutions and or intermetallic compounds, that become surrounded by Ag solid solution during solidification and cooling. Ag–Cu eutectic forms when there is no free Ti left.

The lighter phase (4.1Ti–4.6Cu–88.1Ag–0.9Si–2.3Mg at%) from layers E and F may be an Ag solid solution. The darker phase (65.1Ti–31.5Cu–1.6Ag–1.8Si at%) may be mainly composed by of η-Ti₂ (Cu, Ag). The high Ti content of layers G, H and I can be explained by the high affinity of Ti towards oxygen. Ti from the brazing alloy and the titanium sample diffuses towards

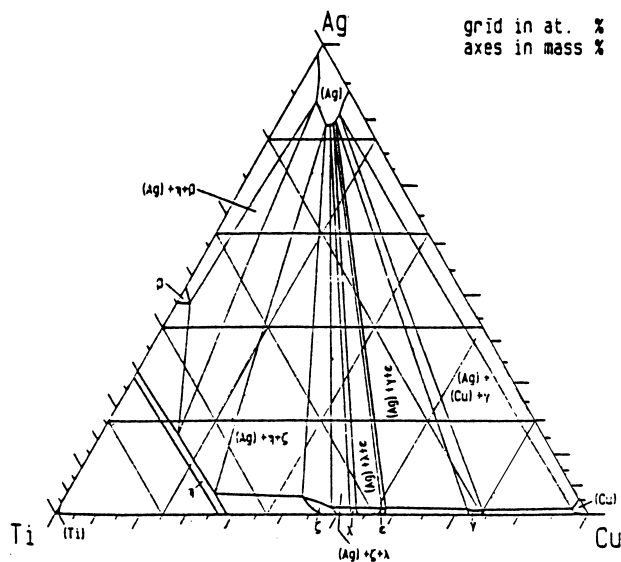


Fig. 6. Isothermal section of the Ti–Cu–Ag system at 700°C.

the ceramic–glass and reacts with its surface, taking part in oxidation–reduction reactions with ceramic–glass oxides, mainly with SiO₂. At 850°C and 930°C the variation of free energy of Eq. (3):

$$\Delta G_T^0 = -121336 + 4.6T \text{ J mol}^{-1},$$

is negative [5], therefore the reduction of SiO₂ by Ti is thermodynamically favourable.



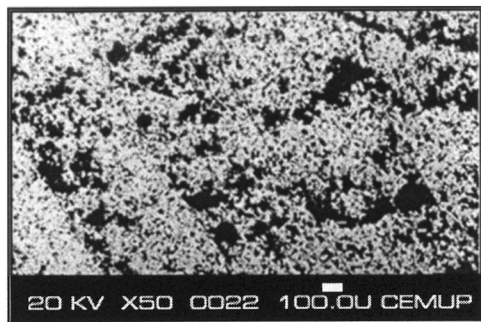
Cu₂Ti₄O and TiO have been detected in reaction layers formed between Ti-containing brazing alloys and Al₂O₃ [6]. In other works Cu₂(Ti, Al)₄O [7,8] and Ti₃Cu₃O phases [9] were also identified. Loehman and Tomsia [2] indicate titanium silicides as possible reaction products between a Si₃N₄ substrate and a molten Ti-containing braze alloy. Peytour et al. [8] suggest the formation of Ti₅(Cu, Si)₃ and (Ti, Cu)Si₂ in the reaction layer near Si₃N₄, when joined to a titanium alloy using an active Ti-containing braze. Yano et al. [10] identified Ti₅Si₃ in a SiC/SiC joint brazed by an Ag–Cu–Ti alloy. Some of these compounds may exist in layers G, H and I. The microhardness results agrees with this microstructural feature, as the higher values (≈1500 HV) should be related with the oxides and intermetallic compounds that may constitute these reaction layers.

Mg–F particles may be released from ceramic–glass when it reacts with the brazing alloy. Since these particles do not react with the brazing alloy and are composed of lighter elements, they are “driven” across the interface. The layer detected around the coarser layers is probably composed of SiO₂: at 930°C this layer is harder to find because its reaction kinetics with titanium are higher than at 850°C.

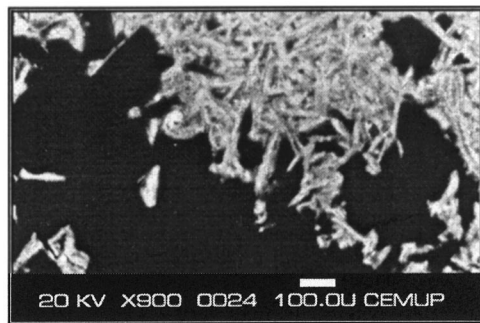
Considering Ti, Cu and Ag distributions across the interface some conclusions can be made.

1. Ti from the brazing alloy and the titanium sample diffuses “in the direction” of the ceramic–glass reacting with it, forming probably several oxides (and other compounds) that ensure chemical bonding between the ceramic and metal parts.
2. Cu also diffuses “in the direction” of the ceramic–glass. It is probably included in oxides formed in reaction layers near to the ceramic surface and in intermetallics from layers E to I. Reaction layers A, B and C result mainly from Cu diffusion towards the titanium sample.
3. Ag seems to segregate mainly to layer D and apparently is a passive agent in the bonding reaction, as it is almost undetected in the layers close to the ceramic.

To go further into the analysis of the interface strength, the fracture surface was observed by SEM. Fig. 7 presents one side (the titanium side) of the surface fracture. It can be seen that a complex fracture occurred and that the crack propagated partially along the ceramic–glass and partially along



(a)



(b)

Fig. 7. Presenting: (a) one of the fracture surfaces of a titanium/ceramic-glass bonding, and (b) a high magnification view of (a).

the hardest interface layers. This is a typical fracture behaviour for all the brazing conditions tested. This behaviour agrees with the shear strength of the interface, which approaches that of the ceramic.

5. Conclusions

The microstructural and mechanical characterisation of the titanium/ceramic-glass bonded by active metal brazing allows the following conclusions to be drawn.

1. Interfaces free of pores were obtained for all of the processing conditions explored.
2. Changes in the tested processing conditions seem to have no significant effect upon the nature of the interfacial reaction products.
3. The brazing temperature mainly affects the extension of the reaction layer adjacent to titanium and the Ag solid solution phase distribution across the interface.
4. The mechanical properties of the joint are not influenced by the tested processing conditions.
5. From a mechanical point of view, the joint is successful once it has a shear strength that approaches that of the ceramic-glass.
6. Fracture always occurs partially along the hardest interfacial layer and partially along the ceramic-glass.

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