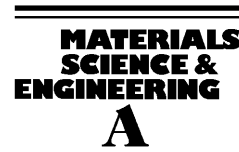




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Multilayered interface in Ti/Macor[®] machinable glass-ceramic joints

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Abstract

Macor[®] machinable glass-ceramic and commercially pure (cp.) titanium were joined by active metal brazing, using a 64Ag–34.5Cu–1.5Ti (wt.%) filler alloy. The influence of the brazing temperature and holding stage on the microstructure and hardness profile of the interface, as well as on the shear strength of the joint, were assessed. Brazing was performed in a high vacuum furnace at 850, 890 and 930°C for 10 and 30 min. The reaction between the braze alloy and both materials led to the formation of a multilayered interface. The interfacial microstructure was analysed in a scanning electronic microscope (SEM) and the composition of each reaction layer was investigated by energy dispersive X-ray scans (EDS). The interfacial hardness profile was determined by a series of microhardness tests on each reaction layer. The mechanical strength of the joint was assessed from shear tests conducted at room temperature. Brazing at 850°C with a 10 min holding stage produced stronger joints, with an average shear strength of more than 85% of the glass-ceramic bulk strength. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Active brazing; Glass-ceramic; Titanium; Microstructure; Mechanical properties

1. Introduction

The industrial and technological developments that occurred over the past decades led to such demanding requirements on structural materials properties that metals could not withstand the challenge by themselves. Engineering ceramics are high performance materials that combine low specific density with the ability of fulfilling severe property requirements such as thermal, corrosive and mechanical resistance. High brittleness and sensibility to flaws are their main drawbacks, both being incompatible with the production of complex shape components [1–5].

Research and development of reliable ceramic-ceramic or ceramic-metal joining techniques has enabled simple-shape ceramic parts to be joined together or to metals producing more complex structures and allowing the combination of material properties in order to

achieve specific requirements. These techniques led to a widespread range of engineering ceramics applications in structural components. Active metal brazing is the most used joining technique for low or moderate temperature applications. In this process, bonding is promoted by the reaction of the braze alloy with both components to be joined. The braze alloy contains small quantities of an active element or elements that react with ceramic anions, enabling the formation of several products, some of which are wetted by braze solvent metals [1,2,6].

Metal/ceramic interfaces are characterised by an abrupt discontinuity of properties (crystallographic, electronic, mechanical, thermodynamic and thermomechanical) [5,7,8]. Successful joining will depend mainly on the interface characteristics, namely its mechanical behaviour, which in turn is highly dependent on the microstructure developed, and on how this discontinuity of properties is accommodated by the interface. Therefore, the knowledge of the reaction product nature and distribution, and its chemical and mechanical characteristics are of fundamental importance.

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The characterisation of the interface formed between Macor[®] and cp. titanium joined by active metal brazing at 930°C has been reported in previous studies [9–12]. However, to the best knowledge of the authors there are no studies reporting the influence of the brazing temperature and holding stage upon the microstructural and chemical features of the interface or on the mechanical strength of the joint.

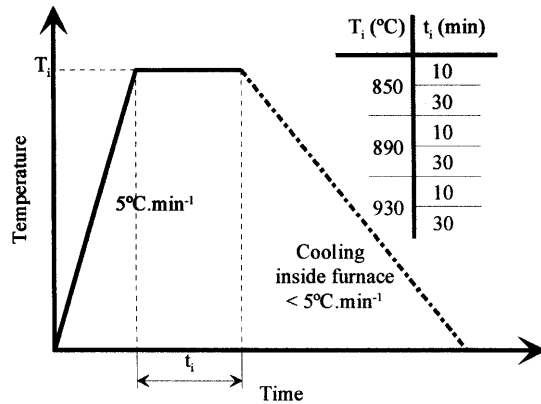


Fig. 1. Brazing thermal cycle.

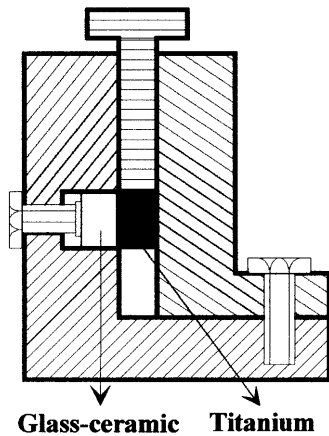


Fig. 2. Shear strength test apparatus.

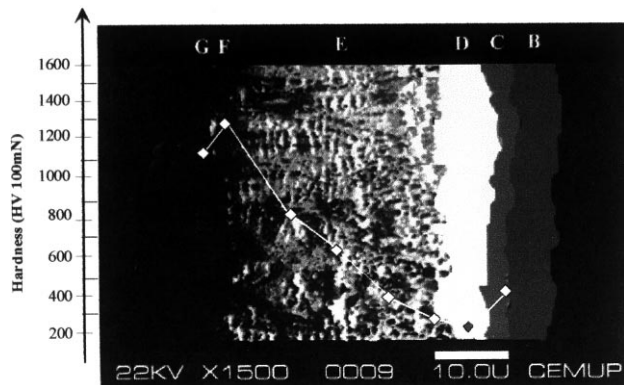


Fig. 3. Interface and hardness profile for brazing at 850°C with a 10 min holding stage.

2. Experimental techniques

Samples of Macor[®] (SiO₂–46, Al₂O₃–16, MgO–17, K₂O–10, B₂O₃–7, wt.%) and cp. titanium (99.6 wt.%), both of 13 mm in diameter, were cut with a diamond saw to a thickness of 5 mm and then wet ground with SiC paper. After grinding the mean roughness (Ra) of the glass-ceramic and the metal samples was 0.29 and 0.26 μm, respectively. A 64Ag–34.5Cu–1.5Ti (wt.%) braze alloy foil (0.1 mm thick) was cut into disks with the same diameter as the samples to be joined. Prior to brazing all materials were degreased in acetone with ultrasonic agitation and dried in air.

The braze alloy foil was inserted between the glass-ceramic and the metal samples. A contact pressure of 2.56×10^{-2} MPa was applied to the assemblage during the brazing thermal cycle by means of a stainless steel mass. Brazing was performed in a vertical furnace, which was evacuated by a combination of rotary and turbomolecular pumps to a vacuum level better than 10^{-4} mbar. The brazing thermal cycle is shown in Fig. 1.

Joints for microstructural and chemical characterisation and microhardness tests were cut perpendicularly to the interface and cold mounted in epoxy resin. Final polishing with a solution of 0.04 μm colloidal silica suspension and hydrogen peroxide ensured the removal of any deformed layer. The interfaces were examined in a SEM and chemically analysed by EDS at an accelerating voltage of 15 keV. Microhardness tests were performed across the interface with a FISHERSCOPE H100 equipped with a Vickers indenter. The nominal load (100 mN) was applied electromagnetically and the load resolution was better than 1 μN.

Samples of Macor[®] and cp. titanium with a diameter of 13 mm and 12 mm length were brazed for shear tests. The shear strength test apparatus, which is presented in Fig. 2, is similar to the one used by Hongky et al. [13]. The strength of the joint was assessed at room temperature by testing a minimum of nine samples for each brazing condition.

3. Results and discussion

The braze alloy reacted with both Macor[®] and cp. titanium promoting the formation of a multilayered interface, which is apparently free of pores and cracks. Figs. 3–6 present the microstructure and the hardness profile at the interface for some representative cases of the processing conditions. Letters from A to G, starting from the titanium side of the interface, identify the reaction layers according to their chemical composition and microstructural features; in Figs. 4–6 only part of layer A is shown. Figs. 7 and 8 present the elemental distribution across the interface for the two limiting

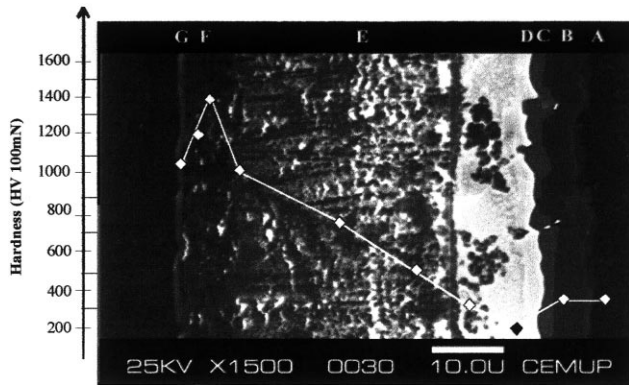


Fig. 4. Interface and hardness profile for brazing at 850°C with a 30 min holding stage.

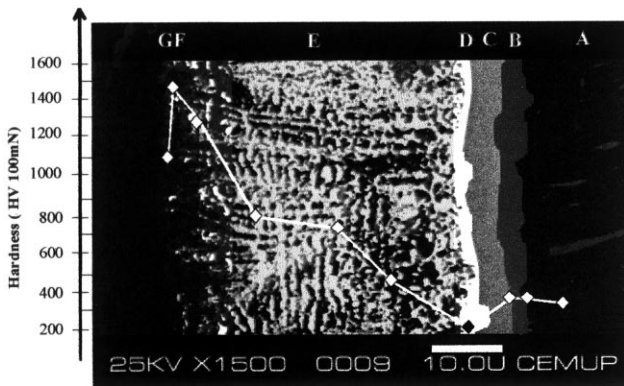


Fig. 5. Interface and hardness profile for brazing at 890°C with a 10 min holding stage.

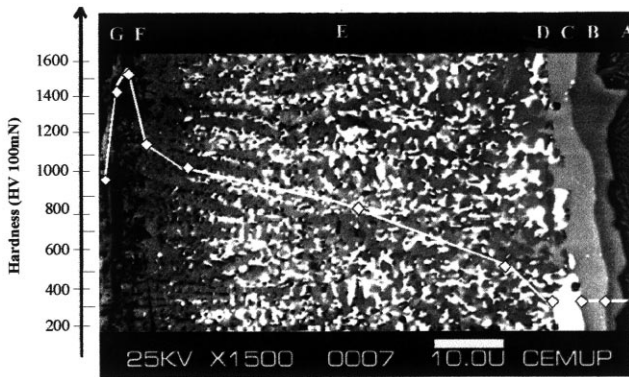


Fig. 6. Interface and hardness profile for brazing at 930°C with a 30 min holding stage.

cases of processing conditions (850°C–10 min and 930°C–30 min).

From an inspection of Figs. 3–6 it can be concluded that the interface is composed of seven reaction layers, except for a brazing temperature of 850°C with a 10 min holding stage where only six layers have been identified (layer A is absent). The interface extension, which ranges from about 50 μm (850°C–10 min) to 150

μm (930°C–30 min) increases mainly with the brazing temperature and only to a lesser extent with the holding time.

Reaction layer A shows a lamellar structure and is primarily responsible for the increase of the interface extension while the thickness of the other layers is almost independent of the brazing temperature and holding time. The thickness of reaction layer A ranges from 0 μm at 850°C–10 min to 80 μm at 930°C–30 min. Layer A is mainly composed by titanium (Ti > 90 at.%) and its Cu content, ranging from about 2–7 at.%, increases with the brazing temperature and holding time. This layer results from Cu diffusion into the titanium sample. The examination of the Ti–Cu phase diagram [14] suggests that at the brazing temperature a β -(Ti) solid solution is formed (Fig. 9). During cooling to room temperature this solid solution undergoes the eutectoid reaction at 790°C resulting in a lamellar microstructure composed of an α -(Ti) solid solution and Ti_2Cu .

Layer A is not detected when brazing is performed at 850°C–10 min suggesting that at this temperature there was not enough time to allow the formation of a β -(Ti) solid solution; instead an α -(Ti) solid solution must have been formed. The α -(Ti) solid solution is not detectable easily due to its low Cu content; the small amounts of Cu (up to 0.9 at.%) detected in the titanium sample near the interface may be due to the proximity of the Cu rich layers B and C. Increasing the holding

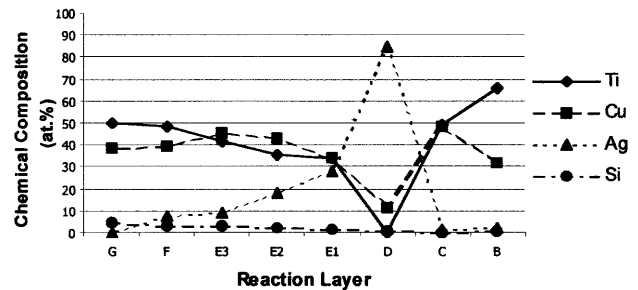


Fig. 7. Elemental distribution for brazing at 850°C with a 10 min holding stage.

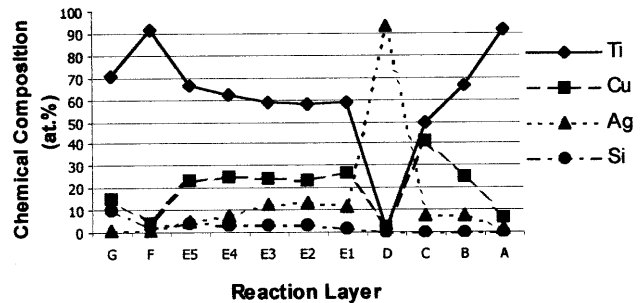


Fig. 8. Elemental distribution for brazing at 930°C with a 30 min holding stage.

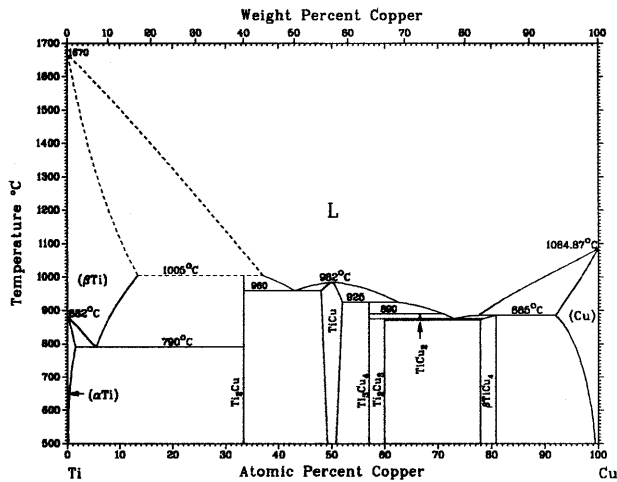


Fig. 9. Ti-Cu phase diagram [14].

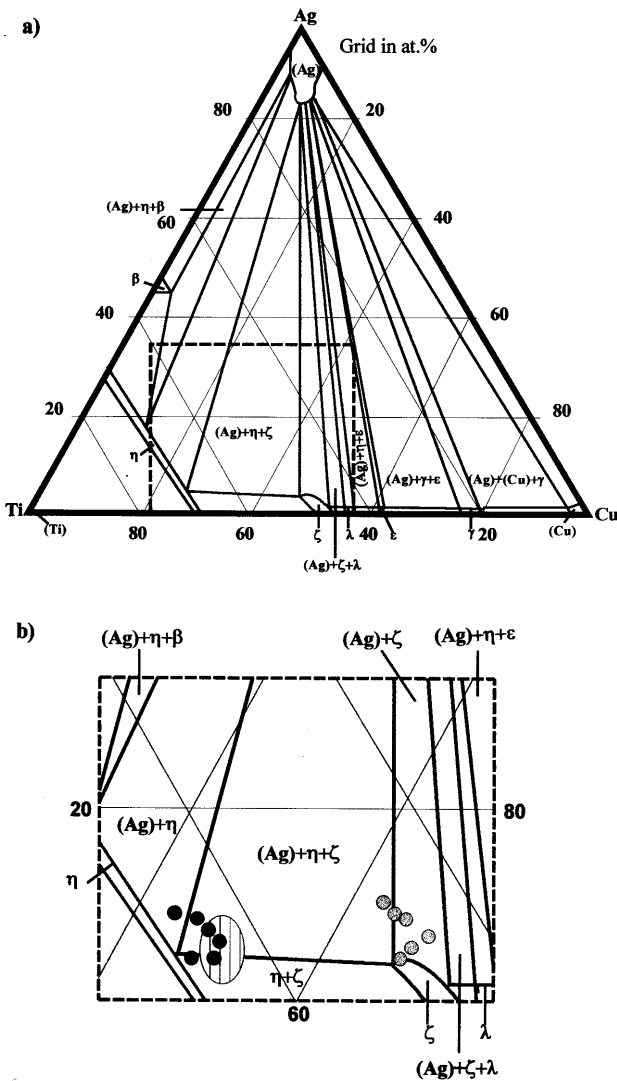


Fig. 10. (a) Isothermal section through the Ti-Cu-Ag phase diagram at 700°C [15]. (b) Magnification of a) in which the compositions of layers B (●), C (⊙) and layer E dark constituent (hatched) are marked.

time up to 30 min enables the formation of the β -(Ti) solid solution, which is transformed into the lamellar constituent (layer A) during cooling.

Layers B and C are composed of Ti and Cu; Ag is also detected but in low amounts (Figs. 7 and 8). For all processing conditions the atomic fraction ratio Ti/Cu is close to 2 for layer B and close to one for layer C, always with a slight excess of Ti. Layers B and C consist of η -Ti₂(Cu,Ag) and ζ -TiCu, according to their chemical composition and the analysis of the isothermal section of the Ti-Cu-Ag system at 700°C (Fig. 10), below which there are no invariant reactions [15]. These layers are of variable thickness and in some zones of the interface one of them or even both are absent.

As shown in Figs. 7 and 8, layer D is an (Ag) solid solution and corresponds to a silver segregation zone that may result from the solidification process¹. Silver is the less active element of the braze alloy and has a weak affinity to copper and titanium. Copper has a strong tendency to form intermetallics with titanium and both titanium and copper have a strong affinity to some of the glass-ceramic elements, namely silicon and oxygen. From Figs. 7 and 8 it is clearly visible that the silver content in other layers is very low, except for layer E where the (Ag) solid solution is also present. A similar segregation process was observed during the elaboration of an identical braze alloy [16]. The braze alloy solidification microstructure showed that a titanium and copper rich phase is generally surrounded by a silver rich phase, in an Ag-Cu eutectic matrix.

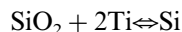
The thickness of layer D is always close to 5 μ m and is almost independent of the brazing conditions. This layer is continuous at low brazing temperatures and short holding times (see Fig. 3), but it becomes less continuous as the brazing temperature or the holding time increase (Fig. 6 presents a zone of the interface where this layer is practically absent).

Layer E is heterogeneous and is composed of two distinct constituents. In order to evaluate correctly the elemental distribution across this layer, EDS analyses were performed sequentially (E₁, E₂, ...), starting from the side layer of E that is closest to the titanium sample. Each analysis corresponds to an area of 10 μ m in length and 40 μ m in height, with E_{n+1} immediately located after E_n. The darker constituent (60.9–65.1Ti; 31.5–36Cu; 0.9–1.6Ag; 1.4–1.8Si; 0.3–0.9Al at.%) consists of η -Ti₂(Cu,Ag) (hatched zone in Fig. 10(b)). The brighter constituent (2.9–4.1Ti; 4.9–6Cu; 87–88.1Ag; 0.9–1.3Si; 0.2–0.5Al; 2.3–2.4Mg at.%) corresponds to an (Ag) solid solution.

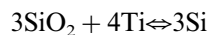
¹ The ternary system Ag-Cu-Ti [15] possesses a miscibility gap. One of the melts is rich in Ag (>60 at.% Ag) and the other one is mainly composed of Cu and Ti.

Layers **F** and **G** are composed of Ti, Cu and Si; Al up to 3 at.% is detected, too. Increasing the brazing temperature and/or the holding time yields an increase of the Ti and Si contents in these layers. Titanium has the ability to react with a wide range of ceramics, forming hypostoichiometric compounds at the interface that, due to their metallic or semi-metallic nature, are compatible with both metal and ceramic parts ensuring chemical bonding [1,5,6,17]. In this study, titanium stemming from the braze alloy and from the base metal causes the dissociation of the glass-ceramic through chemical reactions. Temperature increments will increase the diffusion rate of Ti and consequently its concentration at the interface. The glass-ceramic dissociation also becomes more intense due to the dependent temperature increase in both the reaction kinetics and the Ti concentration near its surface. Consequently, the Si concentration at the interface is raised when the brazing temperature is increased.

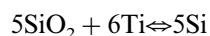
SiO₂ represents almost 50 wt.% of the nominal chemical composition of the glass-ceramic. Of all the elements that compose the glass-ceramic, silicon is the only one that displays a relatively high concentration at the interface, reaching more than 10 at.% in layer **G**. Therefore reactions between silica and titanium should be predominant at the glass-ceramic surface. Some of the possible reactions are:



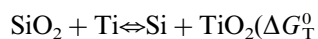
$$+ 2\text{TiO} (\Delta(G)_T^0 = -29000 + 1.1T \text{ cal}\cdot\text{mol}^{-1}),$$



$$+ 2\text{Ti}_2\text{O}_3 (\Delta G_T^0 = -70700 - 1.2T \text{ cal mol}^{-1}),$$



$$+ 2\text{Ti}_3\text{O}_5 (\Delta G_T^0 = -86750 - 2.85T \text{ cal}\cdot\text{mol}^{-1}),$$



$$= -2858 + 0.28T \text{ cal}\cdot\text{mol}^{-1}).$$

Data collected from [18] has been used in order to calculate ΔG_T^0 . These redox reactions are thermodynamically favourable for all processing conditions indicating that, for standard conditions, the formation of all titanium oxides listed is possible. The formation of these oxides, metallic or semi-metallic in nature, should pro-

mote the bridging between the ceramic and the metallic parts.

Furthermore, titanium and copper oxides, titanium silicides, and titanium-copper-silicon intermetallics have been identified near to the ceramic surface in several studies, when joining was accomplished using similar active metal brazes. For instance, Cu₂Ti₄O and TiO have been detected in reaction layers formed between Ti-containing braze alloys and Al₂O₃ [19]. In other studies, Cu₂(Ti,Al)₄O [7,8] and Ti₃Cu₃O phases [20] were also identified. Loehman and Tomsia [5] referred titanium silicides as reaction products resulting from the reaction of an Si₃N₄ substrate and a molten Ti-containing braze alloy. Peytour et al. [8] suggested the formation of Ti₅(Cu,Si)₃ and (Ti,Cu)Si₂ in the reaction layer near Si₃N₄, when joined to a titanium alloy using a Ti-activated alloy. Yano et al. [21] identified Ti₅Si₃ in an SiC/SiC joint brazed by a Ag–Cu–Ti alloy. According to the chemical compositions of layers **F** and **G**, the formation of some of these compounds probably has occurred promoting the bridging between ceramic and metal parts of the joining.

From the analysis of the interfacial hardness profile displayed for each processing condition the following aspects can be emphasised:

- All interfaces present a similar profile.
- The hardness profile presents a sharp maximum located either at layer **F** or at the transition between this layer and layer **G**. This maximum increases with the brazing temperature, reaching hardness values of 1350/1400, 1450 and 1500/1550 HV at brazing temperatures of 850, 890 and 930°C, respectively. The holding stage has little effect on the hardness profile.
- Hardness decreases continuously from these layers up to layer **D**, where it reaches its minimum ($\cong 200$ HV), and then increases to 300/350 HV in layers **C**, **B** and **A**.
- The hardness of layer **E** increases as it approaches the glass-ceramic, being close to 400 HV near layer **D** and close to 900/950 HV near layer **F**.

Typical hardness values of each reaction layer are presented in Table 1. The high hardness values of layers **F** and **G** are in good agreement with the nature of the products (intermetallics and/or oxides) proposed for these layers. The maximum value increases with the brazing temperature, as does the Ti and Si contents of layers **F** and **G**. These compositional and hardness changes may indicate that different reaction products are formed and/or that the proportion between the products that constitute these layers has been altered.

The average shear strength and Weibull modulus for each processing condition are summarised in Table 2. The shear strength, ranging from 68 to 59 MPa, although almost independent of the brazing conditions, has a slight tendency to decrease when the brazing temperature is raised. Joints brazed at 850°C with a 10 min holding stage display the maximum average shear

Table 1
Hardness of reaction layers

Reaction layer(s)	Hardness (HV 100 mN)
A	300
B/C	300–350
D	200
E	400–950
F	1350–1550
G	1100–1350

Table 2
Average shear strength and Weibull modulus of brazed joints and Macor®

Processing conditions (°C, min)	Shear strength ^a (MPa)	Weibull modulus
850, 10	68 (8)	8
850, 30	62 (12)	6
890, 10	62 (8)	10
890, 30	65 (14)	5
930, 10	60 (19)	4
930, 30	59 (9)	8
Macor® machinable glass-ceramic	80 (8)	12

^a Standard deviation in parenthesis.

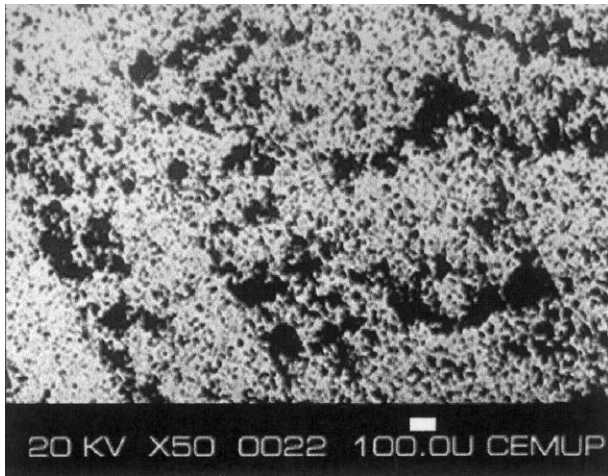


Fig. 11. The glass-ceramic side of the fracture surface. The darker zones are reaction products.

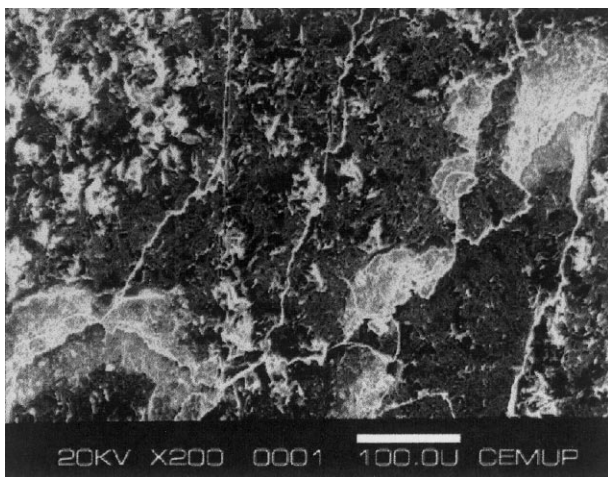


Fig. 12. The titanium side of the fracture surface, where cracks can be observed.

strength corresponding to more than 85% of the glass-ceramic strength. This decrease seems to be related to the increase of the Ti and Si contents of the reaction

layers (F and G) closest to the glass-ceramic and to the intensification of the glass-ceramic dissociation.

To further analyze the strength of the joints, the fracture surfaces were observed in a SEM and analysed by EDS. Joints always fractured partially along the interface and partially through the glass-ceramic breaking the glass-ceramic into several pieces. Both sides of the fracture surface were observed. The glass-ceramic side was partially covered by a thin black layer (or layers) of reaction products (Fig. 11), while the metal side was covered completely by a thicker layer (or layers) with small pieces of glass-ceramic attached (Fig. 12).

The X-ray spectrum of the fracture surface at the glass-ceramic side indicates the presence of Si, Mg, Al and K, but also of Ti and Cu; Si displays the highest peak intensity (Fig. 13). The spectrum corresponding to the titanium side of the fracture surface indicates the presence of all the elements stated above and also of

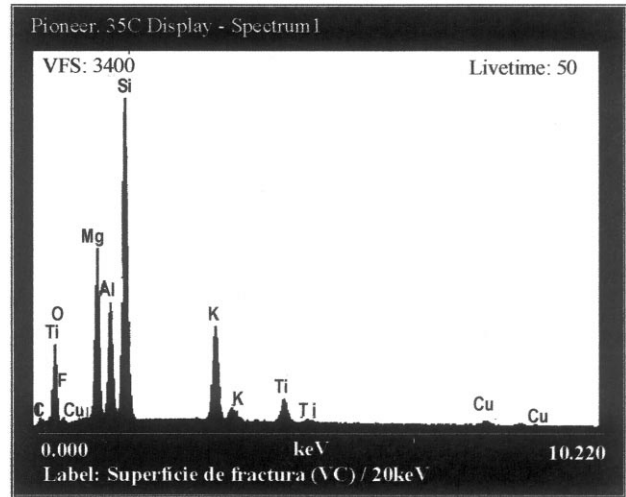


Fig. 13. X-ray spectrum of the fracture surface on the glass-ceramic side.

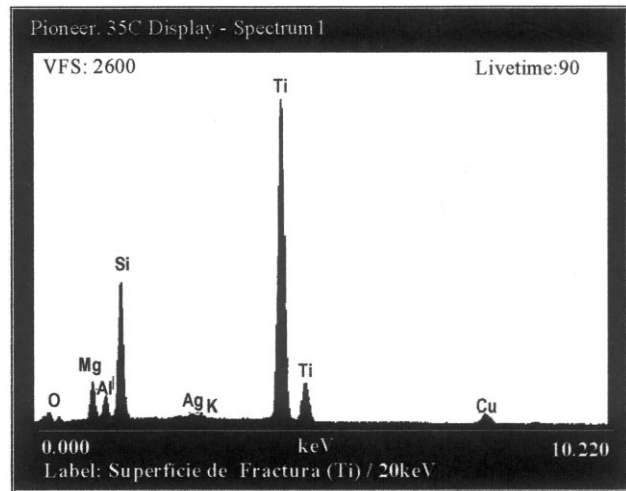


Fig. 14. X-ray spectrum of the fracture surface on the titanium side.

Ag; Ti displays the highest peak intensity (Fig. 14). Of all elements detected at the interface, Ag is the only one that is not detected in the X-ray spectrum of the fracture surface on the glass-ceramic side. On the basis of the X-ray spectra and the elemental distribution, it is clear that the fracture surface on the glass-ceramic side can only include, besides the glass-ceramic itself, layer **G** or layers **G** and **F**. The X-ray spectrum of the fracture surface of the titanium side can, in turn, include the entire interface as well as the glass-ceramic. From these results it is assumed that the nucleation and growth of cracks occur preferentially at the reaction layers **F** and **G**. At these extremely hard (1350/1500 HV) and fragile layers, probably composed of oxides and/or intermetallic compounds, crack propagation is enabled. Cracks grow along these layers in the direction of the glass-ceramic sample; some of them might eventually penetrate into the glass-ceramic to cause premature catastrophic fracture of the sample.

4. Concluding remarks

(1) The experiments performed in this study showed that Macor[®] machinable glass-ceramic and cp. titanium can be successfully joined by active metal brazing in a temperature range of 850–930°C for 10–30 min using a 64Ag–34.5Cu–1.5Ti (wt.%) filler alloy. All processing conditions produced multilayered interfaces free of pores.

(2) The chemical composition and the extension of the interface, as well as the interfacial hardness profile and the joint shear strength, are primarily affected by the processing temperature. The interface extension increases with the brazing temperature and its size ranges from about 50 to 150 µm.

(3) The hardness profile of the interface presents the peak near the glass-ceramic surface (1350–1500 HV). This maximum is due to the formation of intermetallics and/or oxides as a result of reactions between titanium and the glass-ceramic constituents (mainly SiO₂).

(4) A higher shear strength of 68 MPa is displayed by joints processed at 850°C with a 10 min holding stage, which is more than 85% of the glass-ceramics bulk strength. Increasing the brazing temperature produces a slight decrease of the joint shear strength. Fracture of joints always occurs partially along the hardest layers of the interface and partially through the glass-ceramic.

Acknowledgements

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References

- [1] E. Lugscheider, W. Tillman, *Materials and Manufacturing Processes* 8 (1993) 219.
- [2] E. Lugscheider, M. Boretius, W. Tillman, *Welding and Cutting* 7 (1991) 146.
- [3] M. Santela, *Ceramic Bulletin* 71 (1992) 947.
- [4] S. Kang, J. Selverian, *Journal of Materials Science* 28 (1993) 5514.
- [5] R. Loehman, A. Tomsia, *Ceramic Bulletin* 67 (1988) 275.
- [6] M. Nicholas, S. Peteves, *Scripta Metallurgica et Materialia* 30 (1994) 1091.
- [7] R. Barbier, C. Peytour, A. Revcolevschi, *Journal of the American Ceramic Society* 73 (1990) 1582.
- [8] C. Peytour, R. Barbier, A. Revcolevschi, *Journal of Materials Research* 5 (1990) 127.
- [9] L.A. Rocha, M.A. Barbosa, R. Puers, *Reviewed Proceedings of the 1st International Conference on High Temperature Capillarity, Bratislava, Slovakia, May 8–11, 1994*, N. Eustathopoulos (Ed.), 1994, p. 359.
- [10] L.A. Rocha, M.A. Barbosa, R. Puers, *Journal of Materials Science: Materials in Medicine* 6 (1995) 835.
- [11] L.A. Rocha, *Development of a Hermetic Metal/Ceramic Encapsulation System for Injectable Telemetric Electronic Devices*, Ph.D. thesis, Universidade do Minho, Guimarães, Portugal, 1996.
- [12] L.A. Rocha, M. A. Barbosa, R. Puers, *Proceedings of Advances in Materials and Processing Technologies — AMPT '97, Guimarães, Portugal, July 22–26, 1997*, Instituto de Materiais — Universidade do Minho, Guimarães, 1997, p. 319.
- [13] O. Hongqi, J. Zhihao, W. Xiaotian, *Journal of Materials Science* 29 (1994) 5041.
- [14] *Binary Alloy Phase Diagrams CD-ROM*, 2nd Edition plus updates, ASM International.
- [15] *Handbook of Ternary Alloy Phase Diagrams*, P. Villars, A. Price, H. Okamoto (Eds.), Vol. 3, ASM-International, 1994, p. 2358.
- [16] A. Guedes, A.M.P. Pinto, *Proceedings of the 8th National Meeting of the Portuguese Materials Society, Marinha Grande, Portugal, June 11–13, 1997*, Sociedade Portuguesa de Materiais, 1997, p. 167.
- [17] M. Nicholas, *Active Metal Brazing*, in: M. Nicholas (Ed.), *Joining of Ceramics*, Chapman and Hall, London, 1990, pp. 73–93.
- [18] *Metallurgical Thermochemistry*, 5th Edition, O. Kubaschewski, C. Alcock (Eds.), Pergamon Press, Oxford, 1979.
- [19] W. Lee, O. Kwon, C. Kang, *Journal of Materials Science* 30 (1995) 1679.
- [20] M. Santela, J. Horton, J. Pak, *Journal of the American Ceramic Society* 73 (1990) 1785.
- [21] T. Yano, H. Suematsu, T. Iseki, *Journal of Materials Science* 23 (1988) 3362.