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Brazing parameters determine the degradation and mechanical behaviour of alumina/titanium brazed joints

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The main aims of the present study are simultaneously to relate the brazing parameters with the correspondent interfacial microstructure, the resultant mechanical properties and the electrochemical degradation behaviour of commercially pure titanium/alumina brazed joints. A filler metal on the Ag-26.5Cu-3Ti system has been used. Three different brazing temperatures (850, 900 and 950°C) and three holding times (0.3, 1.2, 2.4 ks) were tested, in order to understand the influence of each combination of brazing temperature holding times, over the final microstructure and properties of the joints. The mechanical properties of the M/C joints were assessed on the basis of bond strength tests carried out using a shear solicitation scheme. The fracture surfaces were studied morphologically and structurally using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction analysis (XRD). The degradation behaviour of the M/C joints was assessed by means of electrochemical techniques. It was found that a brazing temperature of 850°C and a holding time of 2.4 ks, produces the best results in terms of bond strength, 130 ± 16 MPa. The mechanical properties obtained could be explained on the basis of the different compounds identified on the fracture surfaces by XRD. On the other hand, a brazing temperature of 950°C produces the best results in terms of corrosion rates (lower corrosion current), $3.44 \pm 0.73\ \mu\mathrm{A\,cm^{-2}}$. However, the joints produced at 850°C using a holding time of 1.2 ks present the best compromise between mechanical properties and degradation behaviour, 122 ± 12 MPa and $7.59 \pm 1.47\ \mu\mathrm{A\,cm^{-2}}$ respectively. The role of Ti diffusion from the metallic Ti to the Al_2O_3 surface is fundamental in terms of the final value achieved for the M/C bond strength. On the contrary, the Ti distribution along the brazed interface does not seem to play any relevant role in the M/C joints electrochemical performance. © *2000 Kluwer Academic Publishers*

1. Introduction

In some engineering applications complex ceramic components can be obtained by assembling simpler components. In other cases, ceramics need to be joined to metals, in order to combine interesting properties of each material. Both problems can be easily addressed if convenient joining techniques are available. Therefore, the study of ceramic/metal joining is not only an appealing research topic but also an essential tool from the technological point of view.

The key to a successful joining technology lies in the ability to modify the interface to accommodate the vastly different types of chemical bonding, from the metallic bonding of the metal to the ionic or covalent bond of the ceramic in order to reduce the electronic discontinuity at the joined surfaces [1]. This is usually achieved by producing a graded interface [1, 2]. This graded interface is also essential in reducing the unfavourable effects due to two kinds of factors: the thermal mismatch and the differences between the two classes of materials, metals and ceramics [1, 3–6]. In fact, metals present higher thermal expansion coefficients than ceramics, while ceramics usually present higher Young's modulus than metals. These differences between metals and ceramics induce very high stresses on the interface during the process, in particular during

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the cooling stage after joining [3–6]. These stresses can also be a problem during the service life of the heterogeneous assemblies [3–6]. The interfacial stresses can lead to ceramic fracture due to the low toughness of the ceramic component [3, 6], or may cause interfacial cracking and reduce the joint strength [7–9]. Graded interfaces that can avoid premature failures may be obtained using interlayers with adapted mechanical and expansion properties [3, 6, 10, 11]. Either soft metals that have low yield strength, such as copper [9, 12, 13], or hard metals that have relatively low thermal expansion coefficient, such as molybdenum and niobium [9, 13], can be used as interlayers. Furthermore, the optimum design of the shape of the bonding zone helps to minimise the magnitude of the residual stress [14]. However, for certain applications, brazing methods using reactive filler metals continue to be an attractive alternative to interfacial layers for obtaining a graded interface. This is due to the fact that brazing is performed in a single step and the contacting substrates require little preparation prior to the joining operation [9, 15]. For instance, the use of a filler alloy in the Ag-Cu system, which is ductile, enables pre-forms to be fabricated readily and confers on the joints some ability to accommodate the thermal mismatch, stresses [16]. Some additions of high reactive transition elements (such as Ti, Zr, Nb) to the Ag-Cu mother alloy have been reported as a way of producing vacuum brazing alloys [17–19], which promote the wettability of the ceramics at a moderate temperature. Of course the new alloys should continue to show a eutectic behaviour [18, 19].

The specific requirements placed on the joint such as strength, corrosion behaviour or functionality will determine that only a few of the many methods that are available for joining dissimilar materials will be technologically possible. Among the diversity of methods, active brazing appears to be one of the most flexible joining techniques in the obtaining of strong interfaces [2, 20]. The evaluation of the quality of a metal/ceramic joint may follow several criteria depending on the specific needs of the application. Special care should be taken in selecting the materials and the joining technique if the M/C joint is not to degrade under a corrosive environment. The available studies on the corrosion of M/C joints are quite limited [2, 21, 22]. Some studies in this field present results emphasising the brazing filler metal and the metallic substrate electrochemical behaviour *per se* [23, 24], or the oxidation of brazing alloys at high temperatures [25]. However, these studies present no data relative to the real M/C brazed joints behaviour.

The present study reports the production of alumina/commercially pure titanium brazed joints by using an active filler metal, Ag-26.5Cu-3Ti. The influence of brazing parameters, such as the brazing temperature and holding time on the M/C joints mechanical and degradation behaviour, was studied. The interfacial microstructures corresponding to each of the brazing temperature/holding time combinations were related to the attained mechanical properties and electrochemical degradation of the joints. It was possible to explain both the mechanical and the degradation behaviour based on the observed interfacial reaction products, and to propose brazing parameters that led to a better compromise between these two types of properties.

2. Materials and methods

Commercially pure titanium (Ti) (Titanium Products Limited, UK), grade 2, and a commercial grade alumina (Al_2O_3) (Degussa, Germany), with a composition and a production method according to DIN 40685 standard, were selected to produce the M/C joints. The brazing of Al_2O_3 to Ti was carried out using Ag-26.5Cu-3Ti (CB4) (Degussa, Germany) filler metal foil, with a thickness of 100 μm. Before being joined, the surfaces of the materials to be brazed were polished with a SiC abrasive paper up to 1200 mesh, and then ultrasonically cleaned in acetone followed by rinsing in distilled water. The M/C joints were produced at three different temperatures, 850, 900 and 950°C. Three different holding times, 0.3, 1.2 and 2.4 ks, were studied for each one of the tested brazing temperatures. The optimised thermal cycles [21] were: heating and cooling rates of 5 $^\circ$C min^{-1} and 1.2 $^\circ$C min^{-1} respectively, and two stages of 1.8 ks at 300°C and 100°C below the brazing temperature, in order to promote the temperature homogenisation inside the furnace. A slight uniaxial force of about 0.5 MPa was applied during the brazing to maintain alignment of the workpieces. A vacuum level of 10^{-3} Pa was used at the brazing temperature.

The bond strength of the M/C joints was evaluated in a shear solicitation fracture test. The samples consisted of one piece of Ti with 10 mm thick and 13.6 mm in diameter and one piece of Al_2O_3 with 5 mm thick and 5 mm in diameter, with a brazing alloy foil in between. The samples were tested at a cross-head speed of 0.5 mm min^{-1}, by applying a load at the ceramic part of the joint, in a universal mechanical testing machine, Lloyd Instruments LR 30 K. For each different combination of brazing parameters at least 10 samples were tested. Further details on the testing methodology have been previously reported and may be found elsewhere [21].

Microstructural characterisation of the interfaces was carried out by scanning electron microscopy (SEM) using a Jeol JMS-630 1F microscope equipped with a Noran Instruments energy dispersive spectroscopy (EDS) device, both on cross-sections and fracture surfaces. X-ray diffraction analysis (XRD) of the fracture surfaces was used to identify the reaction products present on the original joints. The XRD studies were performed in a Siemens D-5000 X-ray diffractometer. Peak search databases and DOS-Diffract-AT® software were also used. Tests were performed with Cu K_α radiation at (40 kV; 30 mA) using a graphite monochromator and a copper anode. The 2θ angles were scanned from 15 to 90°, at a 0.02° min^{-1} scanning rate. All XRD analyses were carried out with a sample rotation of 60 r.p.m in order to eliminate any eventual sample positioning effect.

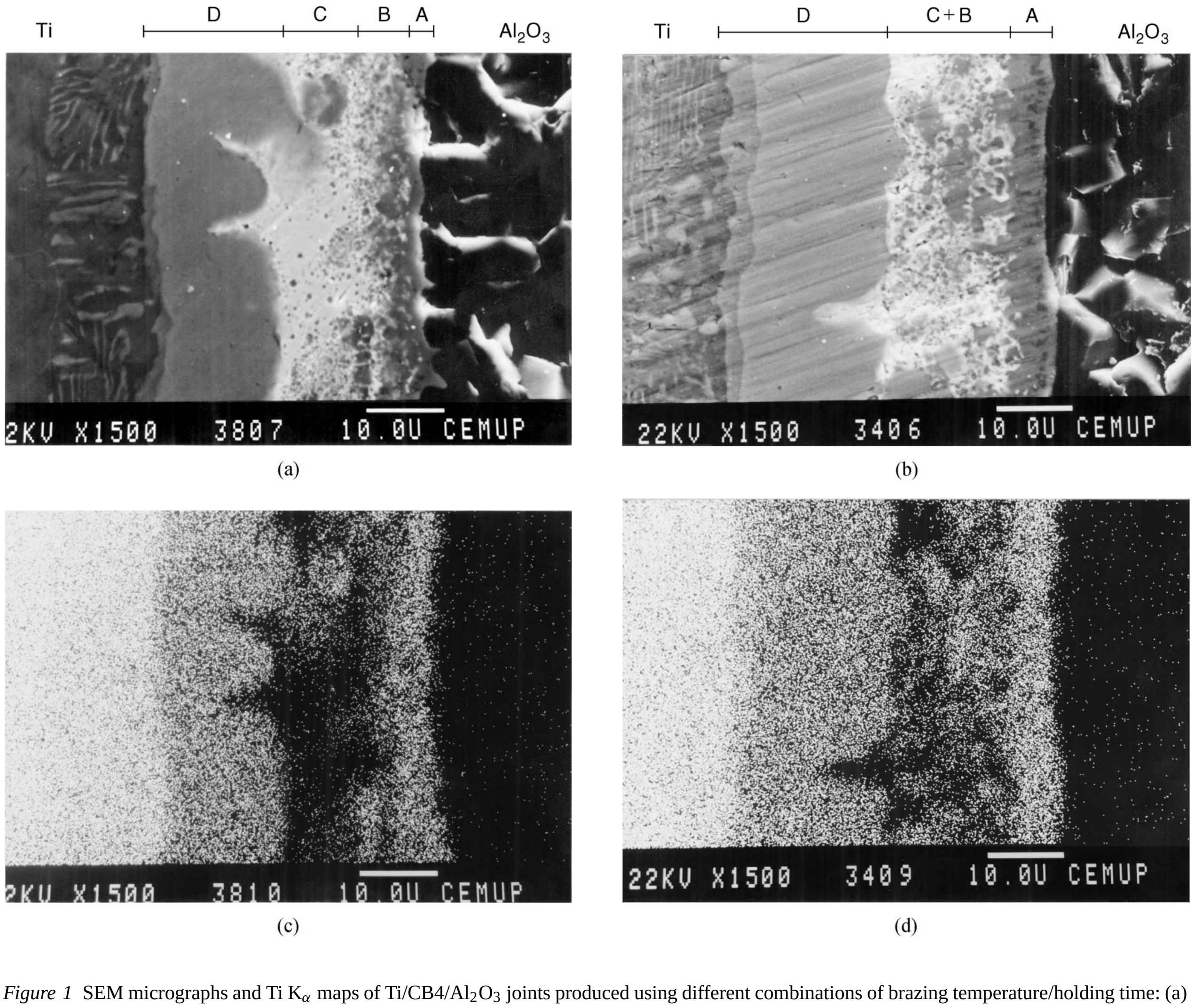
The corrosion behaviour of M/C joints was assessed by electrochemical techniques. These tests were performed on Ti/Al_2O_3 joints (cross-sections), on Ti plates and on the as-received brazing alloy foil. The experimental programme included the measurement of the corrosion potential as a function of time (E_{corr}) and potentiodynamic polarisation experiments. In all experiments, a saline solution (0.15 M NaCl) was used as the testing environment. All tests were conducted at room temperature (20 ± 2°C) and the potentials were measured against the saturated calomel electrode (SCE). Initially, the specimens were immersed in the solution and their corrosion potentials were monitored for at least 24 hours via a potentiostat/galvanostat (EG&G Par, model 273-A). The potentiodynamic polarisations were carried out using the same equipment. The polarisations potential was scanned from −500 mV to 2000 mV relative to the saturated calomel electrode, using a polarisation scanning rate of 2 mV min^{-1}. Several electrochemical parameters were obtained. The corrosion rates and the Tafel coefficients were computed by successive iterations (least square method) of the Stern-Geary equation [26].

3. Results and discussion

3.1. Microstructures of the Ti/Al_2O_3 joints

The previously studied [27] behaviour of the CB4 brazing alloy ensured that brazed joints were formed successfully for all studied combinations of brazing temperatures and holding times. The good alumina wetting behaviour of CB4 was observed, and this brazing alloy also spread over the sides of the ceramic pieces. The microstructures of the joints produced at high temperatures (950°C) using high holding times (2.4 ks) revealed the presence of voids within the brazed joint, and in most cases the CB4/Al_2O_3 interface was cracked. This cracking was presumably due to stresses caused by the mismatch between the thermal expansion coefficients of the joint materials, Ti, brazing alloy and Al_2O_3.

Fig. 1 presents typical microstructures obtained for Ti/CB4/Al_2O_3 joints. This figure shows the influence of the brazing temperature and holding time over the attained microstructures. The influence of the brazing temperature on the obtained microstructures is clear. In fact, comparing the joints produced with the same holding time 0.3 ks, using different brazing temperatures, 850 (Fig. 1a), 900 (Fig. 1e) and 950°C (Fig. 1g), some differences were detected in terms of both the composition profile and the respective microstructure. When the brazing temperature is increased, layer A is richer in Ti (45, 48 and 55 at %, respectively at 850, 900 and 950°C) and Ag disappears from the vicinity of this layer. The other difference observed is related to the composition of the central area (C). At 850°C, a



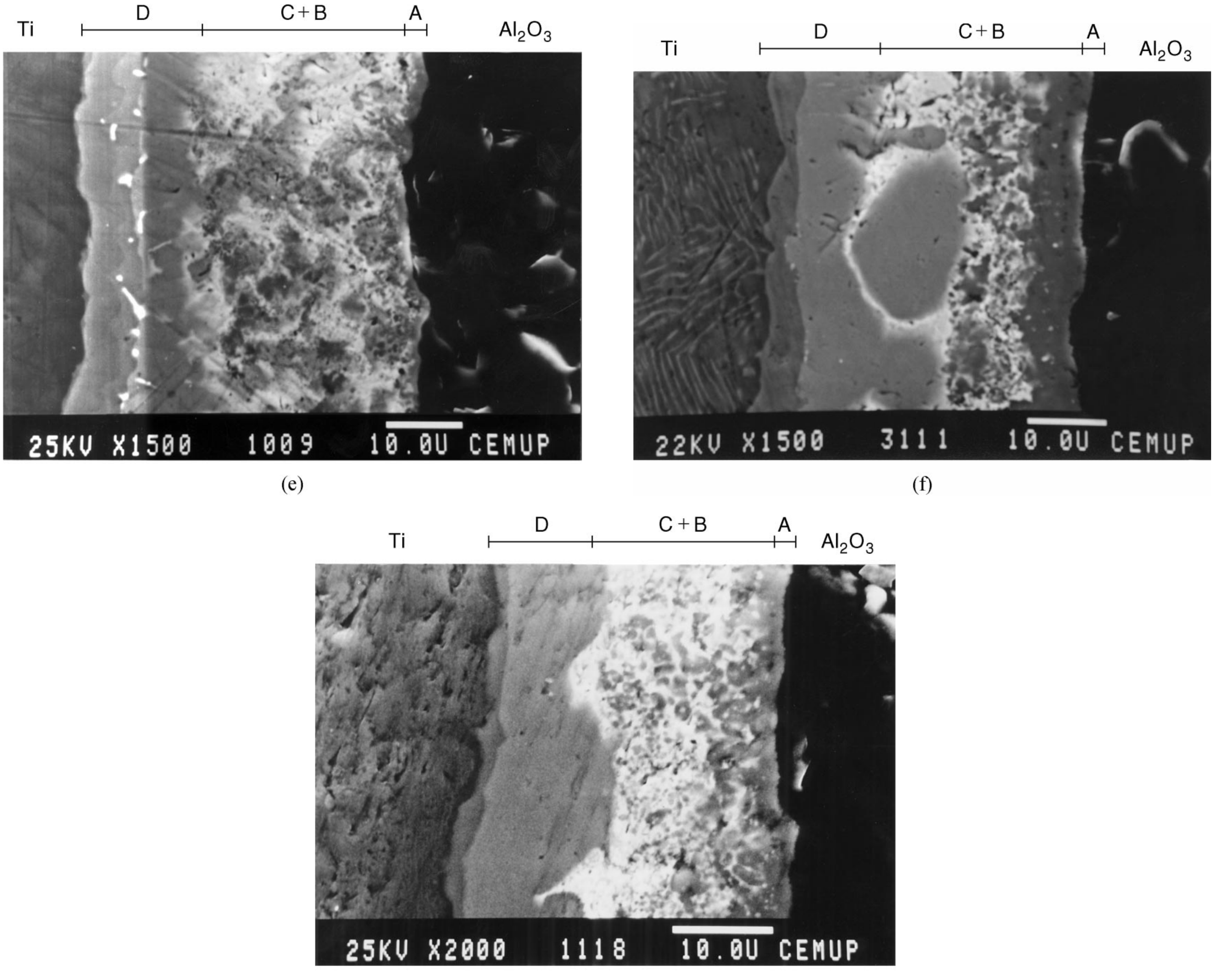
(a)

(b)

(c)

(d)

Figure 1 SEM micrographs and Ti K_α maps of Ti/CB4/Al_2O_3 joints produced using different combinations of brazing temperature/holding time: (a) 850°C/0.3 ks, (b) 850°C/2.4 ks, (c) Ti K_α map relative to the joint presented in a), (d) Ti K_α map relative to the joint presented in b), (e) 900°C/0.3 ks, (f) 900°C/2.4 ks and (g) 950°C/0.3 ks. (*Continued*)



(e) (f)

(g)

Figure 1 (*Continued*).

significant area composed mainly of Ag (white areas) may be observed, and the gradient of composition (region noted as B) from layer A to the central area (C) may be described as an almost continuous increase in Ag and decrease in Cu and Ti until it reaches the area noted as, layer D, which is mainly composed of Cu and Ti. At 900°C layer D appears to be "on formation". This layer D is composed of a mixture of several "semi-layers". At 950°C the microstructure is mostly composed of zones A, B and D. A increase in the holding time to 2.4 ks (Fig. 1b and f) does not result on any noticeable change of the interfacial microstructure. However, as said before, the formation of voids and interfacial cracking was observed for joints produced at 950°C and 2.4 ks. For a low holding time (Fig. 1a, e and g), layer A is richer in Ti for higher temperatures, around 62 at% at 900°C and 52 at% at 850°C. This means that the increase in temperature leads to a faster diffusion of Ti through the brazing alloy to the vicinity of the Al_2O_3 surface.

The holding time influence on the M/C joints microstructure can also be observed on the SEM microstructures. This is clear when comparing Fig. 1a (850°C, 0.3 ks) with 1b (850°C, 2.4 ks) and Fig. 1e (900°C, 0.3 ks) with 1f, (900°C, 2.4 ks). The first observation is that the influence of the holding time at each brazing temperature seems much more evident than the influence of the brazing temperature using a constant holding time. For instance, for the joints produced at 850°C the Ti diffusion path on the respective Ti K_α distribution maps is evident. In fact, the Ti amount has increased gradually from the silver rich layer to just near the Al_2O_3 surface (Cu presents a similar distribution). When the holding time is increased to 2.4 ks, this Ti diffusion effect is even more noticeable, and an extended layer A (thicker) can be observed. The evolution of the M/C joints microstructures produced at 900°C, from 0.3 to 2.4 ks of holding time, as Figs 1e and f show, may be described in terms of the composition of layer D and the thickness of layer A. The microstructures formed at 950°C using 0.3, 1.2 and 2.4 ks are very similar. The main differences are in terms of the final joint thickness and in certain gaps detected in the filler metal/Al_2O_3 interface. As a result of all these differences observed for this Ti distribution as a function of the brazing temperature and holding time, it may be suggested that the Ti detected along the interface is not only coming from the brazing alloy but also from Ti itself.

Gubbels *et al.* [28], studying the Ti/Ag-4%Ti/Al_2O_3 system, concluded that the reaction does not stop after all Ti is diffused from the filler material to the reaction layer. This is due to the activity of Al, which is not yet

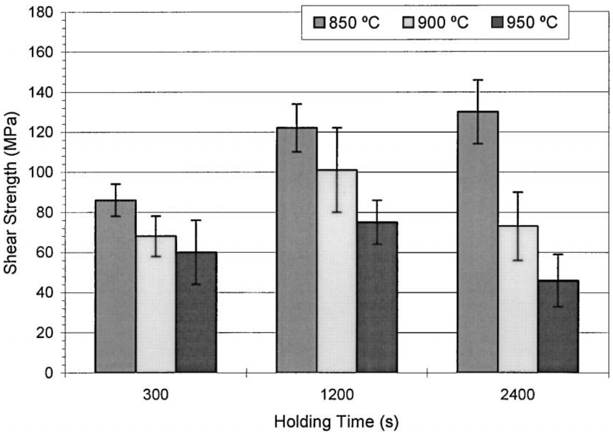


Figure 2 Bond strengths of Ti/CB4/Al_2O_3 joints obtained for each tested combination of brazing temperature/holding time.

the same in the whole couple, contrary to what happens in the $Al_2O_3/Ti/Al_2O_3$ couple. In fact, the layer stops growing when the activities of Al, Ti, and O have come to be almost the same everywhere in the diffusion couple.

3.2. Bond strength measurements of the Ti/Al_2O_3 joints

Fig. 2 presents the obtained shear fracture test results. These tests were aimed at evaluating the bonding strengths of the M/C joints. By analysing the obtained data and emphasising the brazing temperature influence, the best results were obtained at 850°C for all holding times, as compared to the other tested temperatures. However, at 900°C, reasonable strength values can be obtained. Those bond strengths can not only be attributed to the Ti layer already referred to (see Fig. 1), but also to the adjacent ductile (as compared to other intermetallics) Cu-Ti intermetallic compounds [29], formed at the interface with Al_2O_3 at both brazing temperatures, which appears to be a barrier preventing the propagation of cracking propagation. Above 900°C there is a significant decrease in shear strength values. For the brazing temperature of 850°C there is a tendency to obtain higher strength values with an increasing holding time (from 0.3 ks to 2.4 ks). A different evolution was observed for brazing temperatures of 900°C and 950°C. In the first case the ideal holding time was 1.2 ks (101 ± 21 MPa) and above this holding time (2.4 ks) a significant decrease (−27%) in strength was observed. In terms of energy consumption it is recommended that a holding time of 0.3 ks be chosen, instead of a time of 2.4 ks, because the shear strength values obtained are very similar, 68 ± 10 and 73 ± 17 MPa respectively. Relative to the M/C brazings produced at 950°C, the best results were obtained for a holding time of 1.2 ks. However, at this temperature there is a very significant decrease in the strength when compared with the brazings produced with the same time at 850 (−40%) and 900°C (−26%). These results are related to the compounds formed on the interface during the brazing cycle, especially with the higher amounts of titanium oxides near the Al_2O_3 surface. It may also be speculated that the smaller thickness of the joints produced at 950°C could contribute to a weaker interface. Moreover, the stresses caused by the mismatch between the thermal expansion coefficient of the joint materials could be pointed out as a contributor to the lower mechanical properties observed.

It is not so clear whether the bond strength obtained for the M/C joints produced at 850°C using 1.2 ks (122 ± 12 MPa) of holding time is statically different from that produced at the same temperature but using 2.4 ks (130 ± 16 MPa). In order to determine whether the differences between the bond strengths obtained at each holding time were statistically significant a hypothesis test was carried out. A t-Student distribution was selected, and it was assumed that the variances in both ranges of data were unequal (heteroscedastic t-test). The following hypotheses were considered:

$$H_0 \Rightarrow \mu_1 = \mu_2 \tag{1}$$

and

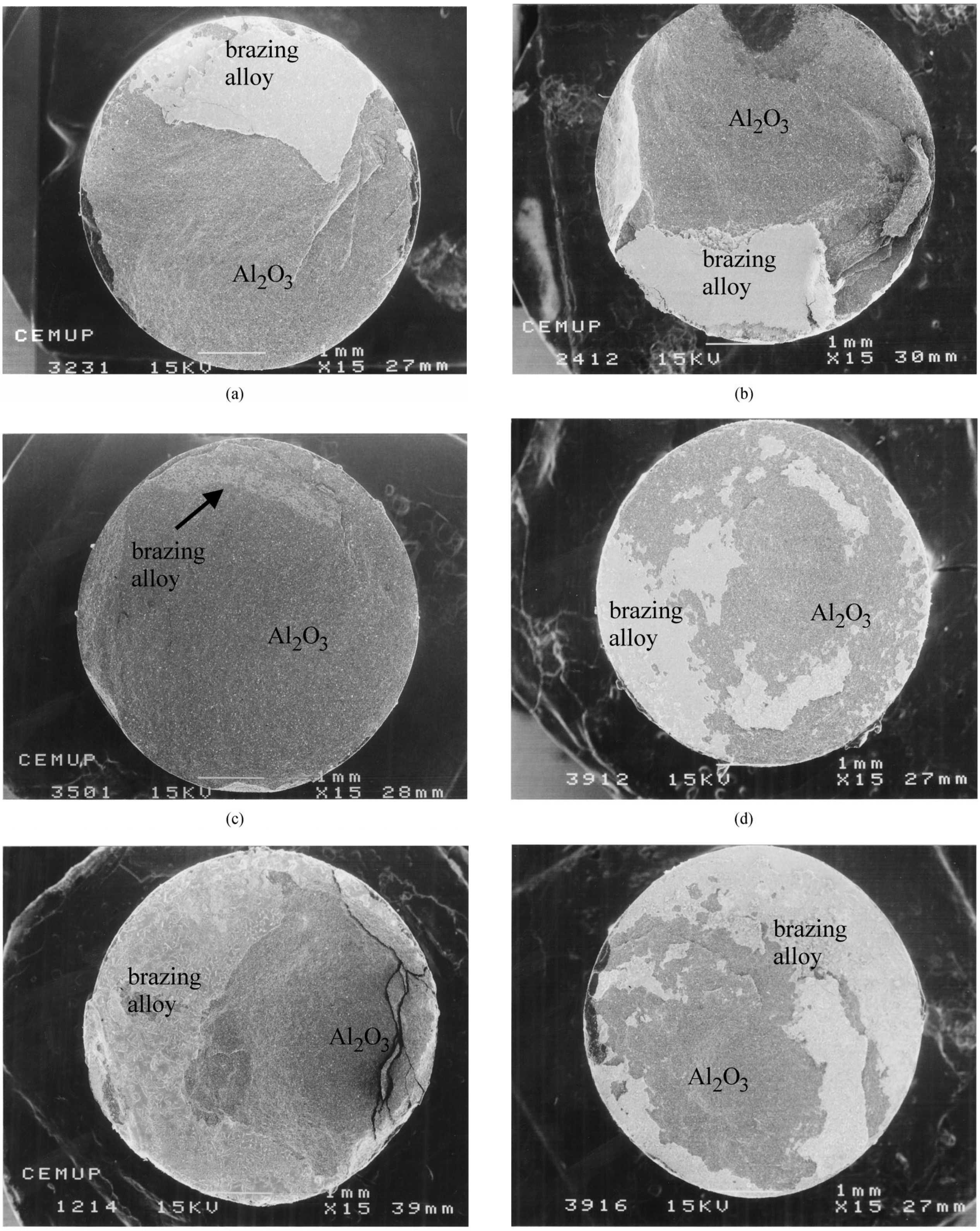
$$H_1 \Rightarrow \mu_1 \neq \mu_2 \tag{2}$$

The tests were carried out for a confidence level of 99.5%. The hypothesis H_0 means that the bond strength obtained for sample 1 (μ_1) produced at one determined holding time is statistically equal to the bond strength obtained for sample 2 (μ_2), which was produced using a different time. It was found that the differences between the average values of the M/C joints bond strength were statistically different (in all cases H_0 was rejected) for joints produced using different holding times.

The fracture surfaces were observed by SEM some of these surfaces being presented in Fig. 3. It was possible to observe that the mode of crack propagation depends on the brazing parameters (temperature and time). The more typically observed type of fracture propagation occurs in two stages. In the first stage, the fracture propagation occurs through the ceramic, close to the filler metal. In the second stage the fracture propagates through the filler metal. The best values for the M/C bond strengths (Fig. 3c, 850°C 2.4 ks) obtained correspond to a different type of fracture propagation. This type of fracture evolution is in accordance with the mode of fracture explained by Moret *et al.* [3]. When the joint is strong enough, mode I crack initiation occurs in the ceramic. This crack initiation mode occurs on the lateral surface of the ceramic, in the maximum tensile stress area, whereas mode II crack propagation follows in the ceramic along the joint. The worst values of bond strengths (Fig. 3f, g and i) correspond to the fracture nucleation near the Al_2O_3 and its propagation along the interface near the Al_2O_3.

3.3. X-Ray diffraction studies of the Ti/Al_2O_3 joints

Fig. 4 presents XRD spectra corresponding to the fracture surfaces, on the Al_2O_3 side, of the joints Ti/CB4/Al_2O_3, produced at 850, 900 and 950°C, using a holding time of 1.2 ks, (only this time being selected for this characterisation because it generated the best

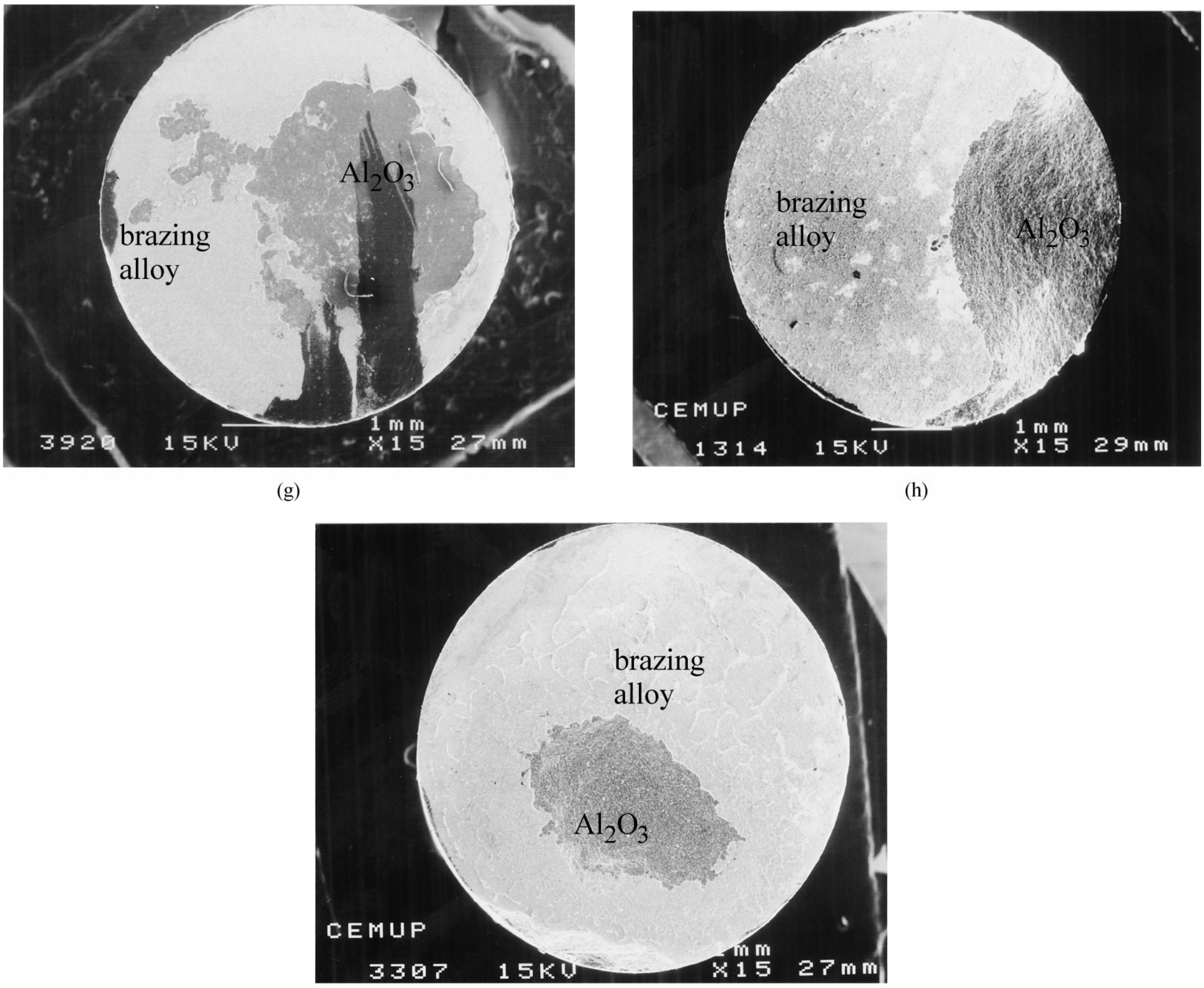


(a) (b) (c) (d) (e) (f)

Figure 3 SEM micrograph of the Ti/CB4/Al_2O_3 joints shear fracture surfaces showing a general view of the Al_2O_3 side of the fracture: (a) 850°C/0.3 ks, (b) 850°C/1.2 ks, (c) 850°C/2.4 ks, (d) 900°C/0.3 ks, (e) 900°C/1.2 ks, (f) 900°C/2.4 ks, (g) 950°C/0.3 ks, (h) 950°C/1.2 ks and (i) 950°C/2.4 ks. (*Continued*)

results in terms of bond strengths). Several new phases were detected in the fracture surfaces of the brazed joints (i.e. in the exposed fracture path).

These new peaks, identified in Fig. 4, indicate the presence of Cu_2Ti_4O, $CuTi_2$, $AlTi_3$ and β-Cu_3Ti in the case of the fracture surfaces resulting from the joints produced at 850°C. The formation of apparently smaller amounts of Cu_2Ti_4O, $CuTi_2$ and $AlTi_3$ was observed in the case of the M/C joints produced at 900°C. As far as the joints produced at 950°C are concerned, the following compounds were identified: $CuTi_2$, $AlTi_3$ and Ti_2O. Some difficulties exist regarding the



(g) (h) (i)

Figure 3 (*Continued).*

identification of the $2\theta = 44.540^\circ$ peak, which could be attributed either to Cu_2Ti_4O or to $CuTi_2$ (relative to the M/C joints produced at 850 and 900°C). Probably this peak corresponds to a mixture of Cu_2Ti_4O ($2\theta = 44.903^\circ$, (440) reflection, cubic system) and $CuTi_2$ ($2\theta = 43.473^\circ$, (110) reflection, tetragonal system) due to the miscibility range of Cu_2Ti_4O phase, which also includes $CuTi_2$ [30]. The formation of the Cu-Ti compounds was to be expected, but its stoichiometry is clearly enriched in Ti, confirming that most of the titanium of the brazing alloy is actively contributing to the brazing reactions. In fact, as stated before, Ti is the main component responsible for the wetting of the ceramic surface, and for the interfacial reactions that ensure the attained bondings. This reaction of Ti with Al_2O_3 was further confirmed by the presence of $AlTi_3$, Cu_2Ti_4O and Ti_2O on the interfaces produced using the other studied brazing temperatures. The presence of Ti_2O may be the principal cause of the low shear strength of the joints produced at 950°C (see Fig. 3). Other authors [6, 9] working with similar systems have found TiO instead of Ti_2O. However, in earlier works from our group [27] on which the same M/CB4/C joints were produced at 950°C but using a vacuum level of 10^{-2} Pa instead of the 10^{-3} Pa used in this work, only TiO_2 was detected, and its formation was prescribed as being the main cause of the low M/C bond strength values.

3.4. Degradation behaviour of the Ti/Al_2O_3 joints

The practical application of metal/ceramic joints may cover a variety of devices, or parts of devices, where combinations of adequate mechanical properties and corrosion resistance are required. With the aim of addressing this issue, an evaluation of the M/C joints degradation behaviour was carried out, using electrochemical techniques. M/C joints produced using the three different brazing temperatures and a constant holding time of 1.2 ks (best mechanical results for all temperatures) were tested by this technique. The electrochemical techniques used to characterise the Ti/Al_2O_3 interfaces were the measurement of the open circuit potential (to evaluate the thermodynamic tendency for corrosion) and potentiodynamic polarisations experiments (to evaluate the corrosion kinetics). Table I summarises the data obtained.

As reported in Table I, the Ti/Al_2O_3 bondings produced at 850 and 950°C disclose an open-circuit potential (E_{corr}) value lower than Ti, but similar to the

TABLE I Summary of the electrochemical data obtained for Ti, brazing alloy (CB4) and the respective Ti/CB4/Al_2O_3 joints produced at 850, 900 and 950°C using a holding time of 1.2 ks.

	Open-circuit potential—E_{corr} (mV)	E ($I = 0$) (mV)	Polarisation Resistance—R_{p} (k$\Omega \cdot$cm^2)	Corrosion rate*—i_{corr} (μA cm^{-2})
Titanium	-10 ± 8	-179 ± 26	1205 ± 110	0.108 ± 0.069
Brazing alloy	-190 ± 4	-217 ± 35	234 ± 45	2.30 ± 0.55
M/C—850°C	-170 ± 103	-210 ± 49	74 ± 23	7.59 ± 1.47
M/C—900°C	26 ± 4	-48 ± 23	20.3 ± 5.6	21.4 ± 5.81
M/C—950°C	-177 ± 10	-228 ± 19	245 ± 16	3.44 ± 0.73

* Corrosion current density.

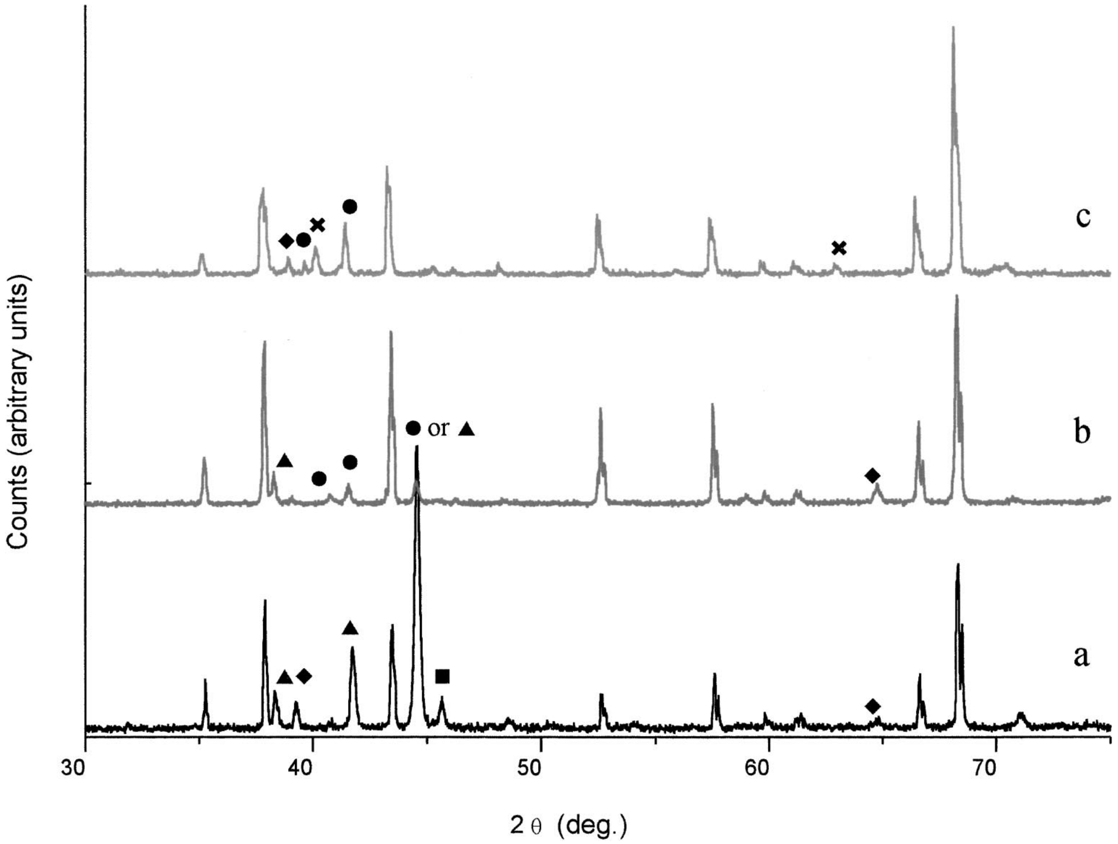


Figure 4 XRD patterns of fracture surfaces of Ti/CB4/Al_2O_3 joints produced at 850 (a), 900 (b) and 950°C (c), using a holding time of 1.2 ks. The new phases observed in the fractured surfaces are identified: ▲—Cu_2Ti_4O, ◆—$AlTi_3$, ●—$CuTi_2$, ■—β-Cu_3Ti and ✖—Ti_2O.

brazing alloy. However, the joints produced at 900°C show less active behaviour ($E_{\mathrm{corr}} = 26 \pm 4$ mV after 24 hours) than the M/C joints produced using other brazing parameters. That means that the film formed on these joints shows higher electrical resistivity than the films formed at the surface of the joints produced at 850 and 950°C, which disclose very similar values to the E_{corr} obtained for Ti. Another very important observation is that the open-circuit potential is affected in a measurable way by each one of the microstructures corresponding to distinct brazing temperatures.

The results of the polarisation experiments (carried out after 24 hours immersion of the samples to stabilise the resting potential), presented in Fig. 5, attest the well-known behaviour of the Ti, in a near neutral (pH = 6.37) chloride-containing solution [31, 32]. In this type of media the potential for the breakdown (pitting) of Ti oxide film is often higher than 3000 mV [32]. In addition a very low i_{corr} (0.108 ± 0.069 μA cm^{-2}) and a low current density of passivation were obtained for Ti when compared with the values attained for the brazing alloy and the M/C joints (see Fig. 5). Up to 2000 mV the nucleation of pits was not detected when the surface was observed by SEM.

For all polarisation curves, the potential for which $I = 0$, E ($I = 0$) is more active than the E_{corr}, due to the cathodic polarisation of the sample prior to the anodic potential sweep. Analysis of the values given in Table I, with the exception of those corresponding to the M/C joints produced at 900°C, shows that the brazing temperature, which means the M/C joint microstructure, does not significantly modify the E_{corr} and E ($I = 0$) values. These results indicate that the corrosion thermodynamics are not significantly affected by the joint microstructure. As regards corrosion kinetics, evaluated by the polarisation resistance (R_{p}) and corrosion current density (i_{corr}), the brazing temperature significantly influences the results obtained. The best results

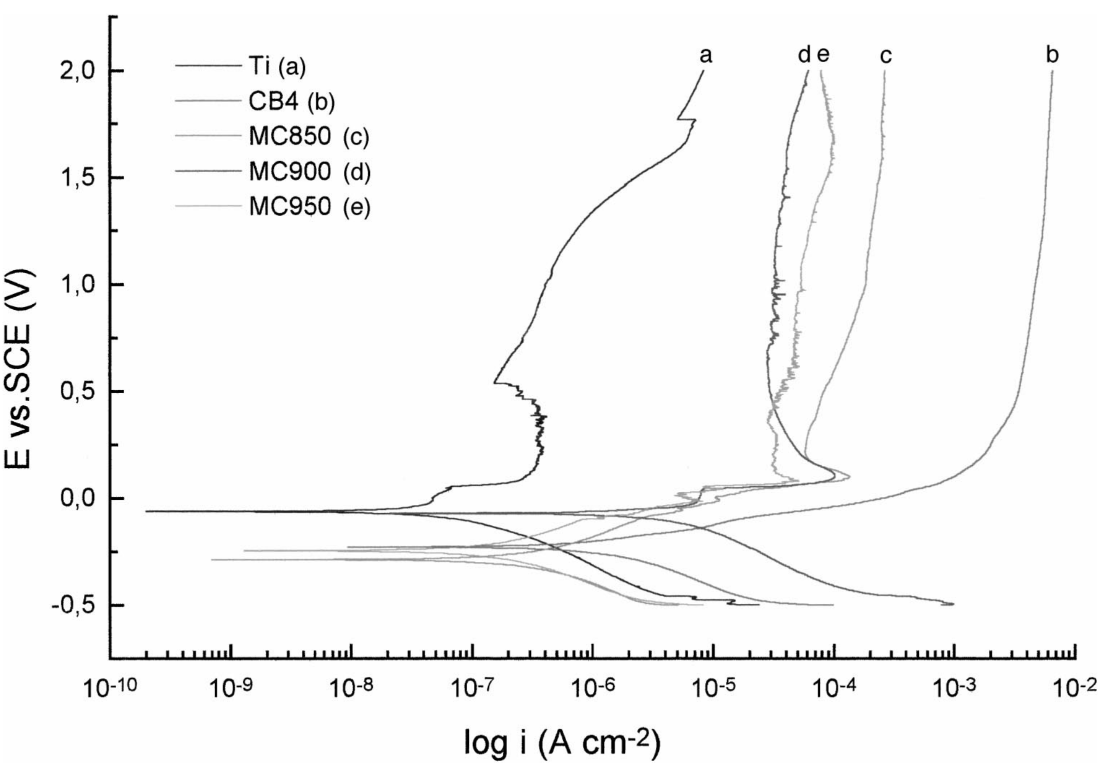


Figure 5 Potentiodynamic polarisation curves for the Ti, the brazing alloy CB4 and the M/C joints produced at 850, 900 and 950°C.

in terms of lower corrosion rate were attained for M/C joints produced at 950°C ($3.44 \pm 0.73\ \mu\text{A cm}^{-2}$), corresponding to an increase of around 1.5 times of i_{corr} instead of the 3.3 and 9.3 times obtained for M/C joints produced respectively at 850 and 900°C, when compared to brazing alloy alone.

The increase of i_{corr} and the respective decrease of R_{p} presented for M/C joints relative to the brazing alloy may be due to the combined effect of the developed microstructures and the particular behaviour of the brazing alloy elements (Ag, Cu and Ti) in solutions rich in Cl^- ions. Cu in solutions with high concentrations of Cl^- ions forms soluble complexes and corrodes actively [33]. The other brazing alloy elements, Ag and Ti, behave quite differently from Cu. The Ti performance has already been discussed above. Ag is "per se" noble, and furthermore, due to the low solubility product constant (Kps) of AgCl, tends to passivate in Cl^- containing solutions [34]. This means that in a microstructure composed of a mixture of well-defined compounds rich either in Cu or in Ag, tested in chloride solutions, each element behaves in a distinct way, acting respectively as anodic and cathodic areas, (Cu-rich zones being less noble than Ag based regions). The role of Ti in the brazing alloy seems secondary relative to Ag and Cu. As a result, the M/C joints produced at 900°C corrode faster relative to the other M/C joints, due to the lower anodic/cathodic area ratio. Similar results in terms of brazing temperature influence on i_{corr}, were obtained by Paiva *et al.* [21] using the same brazing temperatures and holding times for another system, Ti/Ag-28Cu/Al_2O_3. The comparison of the present with the previous [21] results seems to confirm the small influence of Ti in determining the corrosion kinetics of these systems.

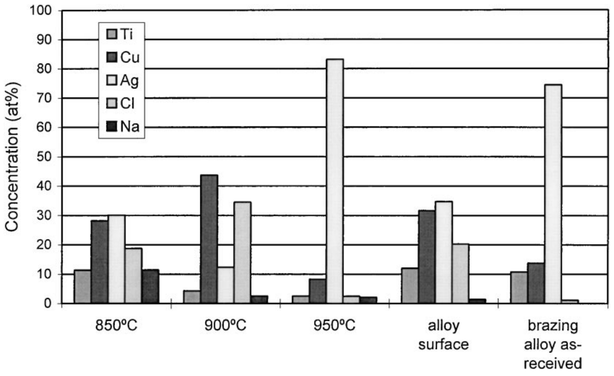
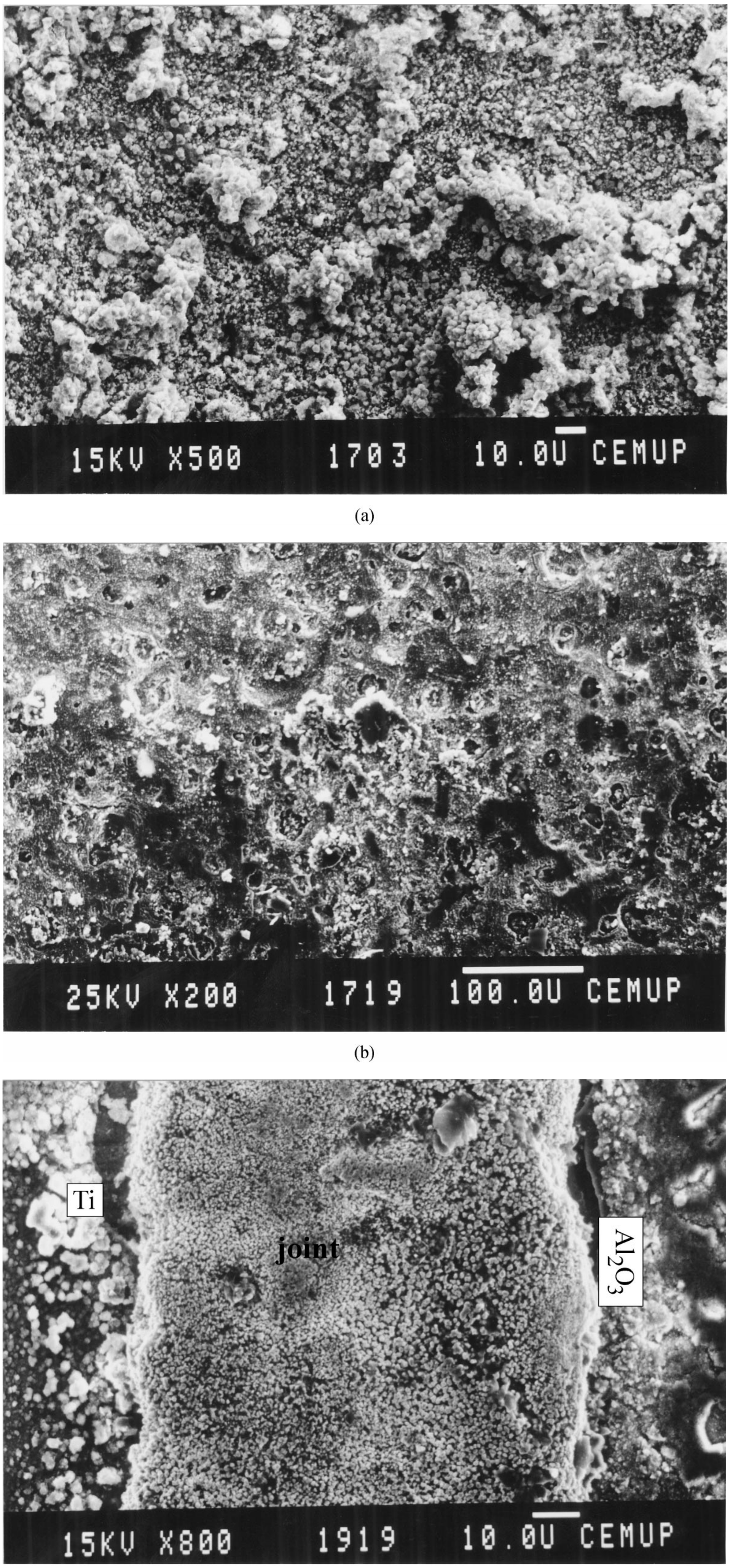


Figure 6 Chemical composition determined by EDS, of the degradation products formed on the brazing alloy (brazing alloy as-received and alloy surface after removing the degradation products) and on the M/C joints during the electrochemical experiments.

In order to try better to understand the effect of Cl^-, the degradation products formed at the brazing alloy and M/C joints surfaces were analysed by EDS (after being ultrasonically cleaned in distilled water). The film formed was detached by bending the brazing alloy foil. The surface in contact with the original brazing alloy, and the original brazing alloy surface itself, were exposed and analysed by EDS. The summary of this EDS analysis is presented in Fig. 6. Fig. 7 presents some SEM micrographs showing the aspect of the brazing alloy CB4 (Fig. 7a and b) and the M/C joint produced at 950°C (Fig. 7c), after the electrochemical experiments.

The EDS analysis of the exposed original brazing alloy surface (after release of the corrosion products) (Fig. 6 and 7b) shows quite a different composition, a high amount of Ag (75 at%) and low amount of Cu (14 at%), relative to the amount present in the brazing



(a)

(b)

(c)

Figure 7 SEM micrographs showing: (a) the degradation products formed on the CB4 brazing alloy surface, (b) a view of the CB4 surface after removing the corrosion products and (c) the aspect of an M/C joint produced at 950°C after an electrochemical polarisation experiment.

alloy CB4. On the surface of the products of corrosion (Fig. 6 and 7a), the last surface in contact with the test solution, a similar concentrations of Cu and Ag, around 32–35 at%, Ti (12 at%) and a high amount of Cl (20 at%) were detected. The explanation for this chemical composition gradient should be that the kinetics of Cu in forming soluble complexes is more important than the formation of compounds between the Ag and Cl. That film has been low i_{corr} ($2.30 \pm 0.55\ \mu\text{A cm}^{-2}$), and during the anodic polarisation the film created was compact and isolating.

It is easy to create a correlation between the chemical composition of degradation products and the corrosion rate obtained for M/C joints. A high amount of Cu and Cl and a relatively low amount of Ag corresponds to an increase in the corrosion rate. Comparing the corrosion rates presented in Table I with those in Fig. 6, the same ranking for the corrosion rates was obtained in terms of amounts of Cu and Cl detected. This means that the degradation products formed at the M/C joints surface produced at 950°C are more stable and create a film that is more compact, as can be seen in Fig. 7c. This result should be due to the fact that the amount of Cu free to react with Cl and form soluble complexes is very low, while the principal element, the Ag, forms stable AgCl compounds. An Ag-rich phase was also obtained by Rocha *et al.* [22] in glass ceramic/Ag-27Cu-2Ti/Ti joints, and by Paiva *et al.* [35] in Al_2O_3/Ag-34.5-1.5Ti/Ti joints tested in Hank's balanced solution (chloride-containing solution).

4. Conclusions

It was found that the brazing temperature has a strong influence over the bond strength and the electrochemical behaviour, particularly over the corrosion rates (i_{corr}) of Ti/CB4/Al_2O_3 brazed joints. This is mainly due to the different interfacial morphologies and reaction products corresponding to a particular brazing condition.

The role of Ti diffusion, from the metallic Ti to the Al_2O_3 surface and its distribution on the interface, is fundamental in determining of the M/C bond strength values. By contrast, in terms of the electrochemical results, the role of Ti seems secondary, as compared to Ag and Cu.

A brazing temperature of 850°C gives the best results in terms of bond strength, while a brazing temperature of 950°C gives the best results in terms of corrosion rates. However, the Ti/CB4/Al_2O_3 joints produced at 850°C using a holding time of 1.2 ks afford the best compromise between mechanical properties and degradation behaviour, 122 ± 12 MPa and $7.59 \pm 1.47\ \mu\text{A cm}^{-2}$ respectively.

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